FUNDAMENTAL INSIGHTS INTO THE CHARGE TRANSFER PROCESSES IN DYE-SENSITIZED SOLAR CELLS: HOLE TRANSFER, REGENERATION, CHARGE RECOMBINATION, AND ELECTRON INJECTION

by

Ke Hu

A dissertation submitted to Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy

Baltimore, Maryland

September, 2014

© 2014 Ke Hu

All Rights Reserved
Abstract

There has been an increasing demand for clean and renewable energy worldwide in the 21st century because of foreseeable shortage of fossil fuels and the environmental concerns of using them. Converting solar energy into electricity or chemical bonds for energy storage has been demonstrated to be a viable way to a sustainable energy future. The scope of this thesis involves understanding fundamental aspects of dye-sensitized solar cells (DSSCs) that use molecular visible light chromophores chemically anchored on mesoporous nanocrystalline anatase TiO$_2$ thin films to harvest the sun light and convert to electrical energy. Challenges and solutions are discussed for designing DSSCs with higher solar energy conversion efficiencies.

Chapter 2 describes the characterization of the redox properties of TiO$_2$ interfaces sensitized to visible light by a series of cyclometalated ruthenium polypyridyl compounds bis-ligated to a terpyridyl ligand, with three carboxylic acid/carboxylate or methyl ester groups for surface binding, and a tridentate cyclometalated ligand with a conjugated triarylamine (NAr$_3$) donor group. These unique molecules with two coupled redox active centers showed non-Nerstian redox behavior at TiO$_2$ interfaces. They also created disparate dipole moments and open circuit photovoltage with different quantum yield of intramolecular hole transfer upon illumination. A special intermolecular hole transfer event was observed spectroscopically and modeled by Monte Carlo simulation that rendered an average hole hopping frequency on TiO$_2$ surface.

Chapter 3 presents two donor-acceptor organic dyes differing only by a two-heteroatom change from oxygen to sulfur within the donor unit. Despite similar optical and redox properties for the two dyes, a consistently higher open-circuit voltage ($V_{oc}$) was measured for the sulfur containing dye relative to the oxygen containing one in both I$^-$/I$_3^-$ or Co$^{III}$/II electrolytes. The improved efficiency observed with the sulfur containing dye in an iodide redox mediator is against the commonly held view that sulfur atoms promote charge recombination attributed to inner-sphere
interactions. Detailed mechanistic studies revealed that this was a consequence of a 25-fold enhancement of the regeneration rate constant that increased the regeneration yield under open circuit conditions. The study showed that a high short circuit photocurrent does not imply optimal regeneration efficiency as was often assumed.

The two organic dyes described in Chapter 3 were further investigated in regards to their aggregation effect on charge recombination to cobalt redox mediators, Chapter 4. Chenodeoxycholic acid was found to reduce aggregation effectively and help slow down charge recombination to the oxidized cobalt redox mediator.

Chapter 5 provides the first spectroscopic evidence for heavy heteroatom, selenium, enhancing charge recombination between TiO$_2$ electrons and oxidized iodide species in DSSCs. This led to a deleterious lower $V_{oc}$ value for the ruthenium sensitizer with a selenium heteroatom in an iodide/triiodide electrolyte. This implies that the design of sensitizer molecules must take into account the position of heteroatoms that may interact with the iodide species in the electrolyte and facilitate faster charge recombination pathway.

Finally, in chapter 6, three panchromatic ruthenium dipyrrinate coordination compounds were tested in DSSCs. Excitation wavelength dependent electron injection yields were observed for higher energy dipyrrin ligand localized excited state than the lower energy MLCT state. These ruthenium sensitizers were found to have MLCT excited states at lower energy with respect to the TiO$_2$ acceptor states. Dye molecules with higher MLCT excited state energy were synthesized to achieve higher electron injection yield without sacrificing $V_{oc}$.

**Thesis Committee:** Gerald J. Meyer (Advisor), Paul J. Dagdigian, and Arthur E. Bragg.
Acknowledgements

The accomplishments in this dissertation are not what one person can achieve. I gratefully thank all that made these possible.

First, I want to thank my parents who have been cultivating me for the past twenty six years. You are always open to hear anything from me and help me go through any difficulties in my life.

Second, I want to express my great appreciation to my research advisor Dr. Jerry Meyer. Jerry not only gave advices to my research projects but also provide me with freedom and encouragement to let me try my own ideas and follow my own nose. As an international student whose first language is not English, I am particularly grateful to my advisor for cultivating me to be both a good presenter and a good writer using English. I cannot thank enough for all the help and support that my advisor gave me during my graduate study.

Third, I would like to thank my research collaborators. Our Canadian friends, Dr. Kiyoshi Robson and Dr. Curtis Berlinguette, provided me with awesome cyclometalated ruthenium samples and organic dyes for solar cell research. Our Chilean friends, Eduardo Schott and Dr. Ramiro Arratia-Perez helped me with DFT calculations. Our Florida friends, Dr. Guocan Li and Dr. Mike Shatruk provided me with great dipyrrinated ruthenium samples for solar cell research as well. I truly enjoyed and appreciate our collaborations that resulted in multiple great publications.

Fourth, I want to thank my oral exam committee members Drs. Jerry Meyer, Kit Bowen, and Art Bragg and my thesis committee members Drs. Jerry Meyer, Paul Dagdigian, and Art Bragg. You provided me with different perspectives towards my research and your support for my thesis research is invaluable.

Fifth, I am thankful to the extended academic family in the Meyer group. I want to thank Dr. Shane Ardo who is giving me research advices by email or skype from time to time even we
did not have time overlap in the lab. I would like to thank particularly Dr. Patrik Johansson who helped me start in the lab. I also want to thank other group members including Dr. John Rowley, Dr. Byron Farnum, Dr. Darren Achey, Dr. Atefeh Taheri, Dr. Will Ward, Dr. Guocan Li, Dr. Cassie Ward, Dr. Renato Sampaio, Ryan O’Donnell, Erinn Brigham, Evan Beauvilliers, Tim Barr, Brian DiMarco, Wesley Swords, and Tyler Motley for all our scientific discussions and individual assistance.

Sixth, I want to thank my best Chinese friends at Hopkins, Wenjian Yu, Jiawang Zhou, Liang Dai, Guilin Liu, and Hong-Fu Ting who helped me and had fun together during the spare time.

Seventh, I would like to thank my extended Hopkins family members Jean Goodwin, Boris Steinburg, and Dennis Kidd who made my graduate study other than research easier.

Last but not least, I am grateful to my aunt and uncle who live about one hour away from where I was living and working. Your care for my graduate life was like the care that my parents gave me when I was in college. I truly appreciate your kindness.
# Table of Contents

Abstract .................................................................................................................................................. ii  
Acknowledgements .............................................................................................................................. iv  
List of Figures ........................................................................................................................................ ix  
List of Schemes ..................................................................................................................................... xix  
List of Tables ......................................................................................................................................... xxi

**Chapter 1: Introduction to Molecular Dye Sensitized TiO$_2$ Interfaces and the Application to Solar Energy Conversion Devices** ........................................... 1
  1.1 Solar Energy Prospects ......................................................................................................................... 1
  1.2 Dye-Sensitized Solar Cells ....................................................................................................................... 5
    1.2.1 Operation Principle of Dye-Sensitized Solar Cells ........................................................................... 5
    1.2.2 Light Harvesting ................................................................................................................................. 11
    1.2.3 Electron Injection to TiO$_2$ ............................................................................................................... 14
    1.2.4 Sensitizer Regeneration ..................................................................................................................... 16
    1.2.5 Interfacial Charge Recombination ..................................................................................................... 19
  1.3 charge Hopping between Immobilized Molecules and the Chemical Applications .............................. 22
    1.3.1 Percolation Threshold for Charge Hopping ....................................................................................... 22
    1.3.2 Molecular Structure Influence on Charge Hopping ........................................................................ 26
    1.3.3 Charge Hopping Mediation .............................................................................................................. 34
    1.3.4 Kinetic Modeling for Charge Hopping ............................................................................................. 38
    1.3.5 Influence of Charge Hopping on DSSC Performance .................................................................. 43
    1.3.6 Molecular Wiring of Insulators for Lithium-Ion Battery Application ............................................ 45
    1.3.7 Multi-electron Redox Catalysis Using Cross-Surface Electron/Hole Transfer ........................... 49
  1.4 Summary ............................................................................................................................................... 55

**Chapter 2: Intramolecular and Lateral Intermolecular Hole Transfer at the Sensitized TiO$_2$ Interface** .......................................................................................................................... 63
  2.1 Introduction ......................................................................................................................................... 63
  2.2 Experimental ....................................................................................................................................... 70
  2.3 Results ............................................................................................................................................... 73
  2.4 Discussion .......................................................................................................................................... 90
    2.4.1 Non-Nernstian Redox Chemistry .................................................................................................... 90
    2.4.2 Intramolecular Hole Transfer ......................................................................................................... 92
    2.4.3 The Role of Dipole Moments ....................................................................................................... 98
    2.4.4 Intermolecular Hole Hopping ...................................................................................................... 101
  2.5 Conclusions ....................................................................................................................................... 108
Chapter 3: Atomic Level Resolution of Dye Regeneration in the Dye Sensitized Solar Cell ................................................................. 128
  3.1 Introduction .................................................................................. 128
  3.2 Experimental ................................................................................ 132
  3.3 Results ......................................................................................... 136
    3.3.1 Synthesis and Characterization ............................................. 136
    3.3.2 Interfacial Charge Recombination ....................................... 143
    3.3.3 Sensitizer Regeneration ...................................................... 149
    3.3.4 Light-to-Electrical Energy Conversion ................................ 151
  3.4 Discussion .................................................................................... 156
    3.4.1 Interfacial Energetics ............................................................ 156
    3.4.2 Interfacial Kinetics ............................................................... 159
  3.5 Conclusions .................................................................................. 166
  3.6 Appendix ...................................................................................... 167
  3.7 Reference ...................................................................................... 186

Chapter 4: Donor-π-Acceptor Organic Hybrid TiO₂ Interfaces for Solar Energy Conversion ................................................................. 190
  4.1 Introduction .................................................................................. 190
  4.2 Experimental ................................................................................ 194
  4.3 Results and Discussion ................................................................ 197
    4.3.1 Surface coverage effect of Dye-O and Dye-S on UV-vis absorption spectra ........................................................................ 197
    4.3.2 Effect of CDCA coadsorption on UV-vis absorption spectra ............................................................................................. 200
    4.3.3 Surface coverage effect on charge recombination between TiO₂(e⁺) and [Co⇌(bpy)]³⁺ ........................................................................... 205
  4.4 Conclusions .................................................................................. 211
  4.5 References .................................................................................... 212

Chapter 5: Direct Spectroscopic Evidence for Constituent Heteroatoms Enhancing Charge Recombination at a TiO₂–Ruthenium Dye Interface ................................................................. 214
  5.1 Introduction .................................................................................. 214
  5.2 Experimental ................................................................................ 218
  5.3 Results ......................................................................................... 231
    5.3.1 Synthesis and Characterization ............................................. 231
    5.3.2 Interfacial Charge Recombination in the Absence of Iodide. ................................................................. 237
    5.3.3 Sensitizer Regeneration by Iodide ........................................ 241
Chapter 5: Interfacial Charge Recombination in the Presence of Iodide

5.3.4 Interfacial Charge Recombination in the Presence of Iodide ........................................... 244

5.4 Discussion .......................................................................................................................... 249

5.5 Conclusions ....................................................................................................................... 253

5.6 Appendix ............................................................................................................................ 254

5.7 References ......................................................................................................................... 262

Chapter 6: Panchromatic Light Harvesting and Hot Electron Injection by Ru(II) Dipyrrinates on TiO₂ Surface ................................................................. 266

6.1 Introduction ......................................................................................................................... 266

6.2 Experimental ...................................................................................................................... 270

6.3 Results and Discussion ...................................................................................................... 279

6.3.1 Synthesis ....................................................................................................................... 279

6.3.2 Electronic Structure ....................................................................................................... 279

6.3.3 Optical Spectroscopy ..................................................................................................... 282

6.3.4 Electrochemistry ............................................................................................................ 285

6.3.5 Solution-Phase Transient Absorption Spectroscopy .................................................... 289

6.3.6 Behavior on TiO₂ Surface .............................................................................................. 294

6.4 Conclusions ....................................................................................................................... 304

6.5 Appendix ............................................................................................................................ 305

6.6 References ......................................................................................................................... 313

Curriculum Vitae ..................................................................................................................... 317
List of Figures

Figure 1.1  Air mass 1.5 solar irradiance spectrum (black). The solid blue curve represents the theoretical maximum solar cell efficiency with a certain band gap semiconductor based on the integration of the solar irradiance spectrum. Adapted from reference 9.................................3

Figure 1.2  Best Research-Cell Efficiencies. Obtained from reference 10. .................................4

Figure 1.3  A typical Current-Voltage (i-V) curve (black) for a dye-sensitized solar cell. The rectangular box in dashed green is the theoretical maximum power output from this solar cell. The rectangular box in shaded blue is the practical maximum power output. The solid curve in red is the power output as a function of the potential. Taken from reference 13. .................................8

Figure 1.4  Champion sensitizer molecules in DSSCs..........................................................13

Figure 1.5  Simplified Jablonski diagram and possible pathways for excited state electron injection to TiO$_2$ acceptor states. Taken from reference 34......................................................15

Figure 1.6  Relevant redox potentials of I$_3^-$/I$^-_-$ and [Co$^{III/II}$(bpy)$_3$]$^{3+/2+}$ employed in DSSCs as redox mediators. Adapted from reference 42.................................................................18

Figure 1.7  Optical Anson plot for nanocrystalline TiO$_2$ electrodes derivatized with the phosphonated triarylamine in EtMeIm$^+$/TF$_2$N$^-$. Potential step was from 0.2 to 1.0 V. Taken from reference 67.................................................................24

Figure 1.8  Proposed mechanism for lateral charge transport through a monolayer of a phosphonated triaryl amine on porous metal oxide on conductive substrate: (a) cross section of a half pore; (b) top view of a monolayer with possibilities of electron hopping in a square (left) and in a triangular (right) lattice; (c) scheme of a metal oxide surface bearing various submonolayer surface concentrations of the aforementioned compound in a square lattice, with charge paths opening above the percolation threshold ($\Gamma \geq 0.5 \Gamma^0$). Taken from reference 67.................................25

Figure 1.9  The calculated reorganization energies including the inner sphere and outer sphere reorganization energies can the measured values for the ruthenium polypyridyl series, organic indoline dye series, and metal phthalocyanine series compounds. Taken from reference 70......28

Figure 1.10 Schematic model showing the configuration of Ru(dmb)(dcb)(NCS)$_2$ on the (101) surface of anatase TiO$_2$. ‘dmb’ is 4,4’-dimethyl-bipyridine and ‘dcb’ is 4,4’-dicarboxy-bipyridine. Taken and modified from reference 71.................................................................30

Figure 1.11 Structures of the phosphonate-derivatized polypyrindyl complexes. Taken from reference 75.................................................................33

Figure 1.12 Transient absorption difference magic-angle (left axis) and anisotropy (right axis) changes for cis-Ru(dnb)(dcb)(NCS)$_2$/TiO$_2$ (black, solid) and cis-Ru(dcb)$_2$(NCS)$_2$/TiO$_2$ thin films immersed in neat acetonitrile monitored at 465 nm after pulsed laser excitation. Overlaid in green, on the anisotropy kinetics, are fits to a stretched exponential function. Taken from reference 85. .................................40
Figure 1.13  Absorption change monitored at 570 nm following 417 nm laser light excitation of \([\text{Os}({\text{bpy}})_2(\text{dcqb})]/\text{TiO}_2\) (\(F = 6.5 \times 10^8 \text{ mol/cm}^2\)). Overlaid on the data is a best fit (while line) to Equation 1.6. Residuals for the fit are shown below. Taken from reference 78..............................42

Figure 1.14  Band and density of states (DOS) diagrams showing the working principle of charging and discharging of an insulating battery material by a surface-confined molecular charge transport layer. The shaded and unshaded Gaussian functions represent the occupied and unoccupied electronic states of the redox relay, their intersection defining the Fermi level of the molecular hole transporter. (a) Structure of LiFePO$_4$ and surface anchored BMABP. (b) Band diagram and density of electronic states (DOS) curves of the integrated electrode system at equilibrium. (c) Charging the cathode by hole propagation through the molecular monolayer; hole injection from BMABP$^+$ into LiFePO$_4$ and Li$^+$ release from LiFePO$_4$. (d) Discharging the electrode by reversing these three processes. Taken from reference 87..................................................47

Figure 1.15  Cyclic voltammograms (CV) of BMABP-derivatized LiFePO$_4$ (red, blue) and mesoscopic Al$_2$O$_3$ (green) electrodes. The black line shows the curve of a bare LiFePO$_4$ electrode. The scan rate is 0.1 V/s. The current of BMABP$^+$ was used. Taken from reference 87..........................................................48

Figure 1.16  Dye sensitized photoelectrosynthesis cell (DSPEC) for water oxidation to molecular oxygen at the photoanode and CO$_2$ reduction to methane at the cathode. Taken from reference 92. ........................................................................................................50

Figure 1.17  Transient absorption difference signals after 683 nm pulsed laser excitation of a TiO$_2$ thin film electrode cofunctionalized with Z907 and CoTCPP in an \(\sim 100:1\) molar ratio and immersed in 100 mM TBAClO$_4$/CH$_3$CN (absorbed fluence \(\approx 2.65 \text{ mJ/cm}^2\)). (A) Spectra at the indicated delay times; the 85 \(\mu\)s data are modeled by spectral addition of Co$^{II}$, Co$^{III}$, TiO$_2$(e$^{-}$), and Ru$^{III}$ in a \(\sim 1:1:9:8\) molar ratio (orange). (B) Kinetics monitored at 436 nm that correspond to (i) Z907$^+$ + Co$^{II}$ followed by (ii) Co$^{III}$ + TiO$_2$(e$^{-}$) to yield the initial state, Ru$^{II}$/TiO$_2$/Co$^{III}$. Taken from reference 84..........................................................53

Figure 1.18  Spectral changes of \(5.1 \times 10^{-8} \text{ mol cm}^2\) Ru$^{II}$P$^{2+}$ and \(8.0 \times 10^{-9} \text{ mol cm}^2\) Ru$^{II}$OH$_2$$^+$ coloaded on TiO$_2$ photoanodes with 0.2 V applied bias upon 445 nm (8.3 mW) irradiation for \(\sim 200–300\) s (to approach photoequilibrium). Taken from reference 95. .................................54

Figure 2.1  The visible absorption spectra of the indicated sensitized thin films immersed in 0.5 M LiClO$_4$ CH$_3$CN solutions. ........................................................................................................74

Figure 2.2  The UV-vis-NIR absorption spectra of C1/TiO$_2$ (a) and C5/TiO$_2$ (b) measured at variable applied potentials in 0.5 M LiClO$_4$ CH$_3$CN solutions. The arrows indicate the direction of absorption changes with increased positive applied potential. The insets show the fraction (x) of dye molecules present in C1/TiO$_2$, C5/TiO$_2$ (black solid squares), C1$^+$/TiO$_2$, C5$^+$/TiO$_2$ (red solid squares) and C1$^{2+}$/TiO$_2$, C5$^{2+}$/TiO$_2$ (green solid squares) states. Overlaid on the data are fits to a modified Nernst equation. ..............................75
Figure 2.3  Calculated dipole moment vectors for a) C2; b) C4; c) C5; d) C2⁺; e) C4⁺; f) C5⁺. The table in each image is the percentage contribution of the ruthenium (Ru), Terpyridine’ (Tp) and the triarylamine (NAr,) to the HOMO and LUMO orbitals. ..............................................................77

Figure 2.4  Absorption difference spectra measured at 100 ns delay time after pulsed 532 nm excitation of (a) C1/TiO₂–C5/TiO₂ and (b) E1/TiO₂–E5/TiO₂ immersed in 0.5 M LiClO₄/CH₃CN solution. Highlighted regions in pink are where NAr⁺ absorbs light strongly. ..............................79

Figure 2.5  The UV-vis absorption spectra of C4/TiO₂ immersed in 0.5 M LiClO₄ CH₃CN (black) and immersed in 0.5 M LiClO₄/1.0 × 10⁻⁴ M H₂SO₄ CH₃CN (red). The upper inset shows the absorption difference spectra measured 45 ns after pulsed 532 nm excitation of C4/TiO₂ and the lower inset shows the same data for an H₂SO₄ treated C4/TiO₂ thin film; overlaid in solid curves are simulations; highlighted regions in pink are where NAr⁺ absorbs strongly. ..............................81

Figure 2.6  The data shown in panels (a), (c), and (e) are absorption difference spectra measured after pulsed laser excitation (λex = 532 nm) of C1/TiO₂ biased to 890 mV vs. NHE (C1/TiO₂ : C1⁺/TiO₂ = 50 : 50), 960 mV vs. NHE (C1/TiO₂ : C1⁺/TiO₂ = 15 : 85) and 1035 mV vs. NHE (C1/TiO₂ : C1⁺/TiO₂ = 0 : 100) at the indicated delay times. Overlaid in solid lines are simulations based on the the absorption profiles of C1/TiO₂, C1⁺/TiO₂, C1²⁺/TiO₂ shown in Figure A2.8 and the 1st derivative spectrum of C1⁺/TiO₂, the fractional concentrations of which (black square is C1/TiO₂, red circle is C1⁺/TiO₂, and green triangle is C1²⁺/TiO₂) were shown in (b), (d) and (f) as a function of time. ..............................................................83

Figure 2.7  Absorption changes monitored at 507 nm after pulsed light excitation at the indicated applied potentials (λex = 532 nm, 1.4 mJ/cm²). Overlaid in yellow are the fits to the KWW model (βKWW=0.17). ...................................................................................85

Figure 2.8  Absorption changes monitored at 540 nm after pulsed light excitation with five irradiances (λex = 532 nm 0.3-1.5 mJ/cm²) of C1/TiO₂ immersed in 0.5 M LiClO₄ CH₃CN and biased at 1035 mV versus NHE. Overlaid as solid lines are absorption profiles abstracted from Monte Carlo simulations of 1 (a) and 27 (b) nanoparticles. ..............................................................87

Figure 3.1  Molecular structures of the organic dyes Dye-O and Dye-S. The heteroatoms that have an effect on the regeneration reaction with redox mediators are indicated. The β-LUSO (lowest-unoccupied spin orbital) for the oxidized forms of each dye, Dye-O⁺ and Dye-S⁺, are provided below each structure to highlight the delocalization of the wavefunction onto the heteroatoms of interest (the terminal hexyl substituents were replaced with methyl substituents for the calculations). ....................................................................................131

Figure 3.2  UV-vis absorption spectra of Dye-O (red) and Dye-S (blue) in a) fluid CH₃CN solution and b) anchored to TiO₂ immersed in CH₃CN solution at 298 °K. ..............................................................138

Figure 3.3  Visible absorption spectra of (a) Dye-O/TiO₂ (dye surface coverage Γ =1.0×10⁻⁷ mol·cm⁻²) and (b) Dye-S/TiO₂ (Γ =5.3×10⁻⁷ mol·cm⁻²) measured at the indicated applied potentials in 0.5 M LiClO₄ CH₃CN solution. The insets show the fraction (x) of dye molecules present in the reduced (black squares, ■) and the oxidized state (red circles, ●). Overlaid on this data is a sigmoidal fit, x = 1/(1+10expt(Eapp-E°/a×59 mV)), where a is the ideality factor determined to be 1.27 for Dye-O/TiO₂ and 1.05 for Dye-S/TiO₂. ..............................................................140
Figure 3.4 Absorption difference spectra measured at the indicated delay times after pulsed 532 nm excitation of a) Dye-O/TiO2 and b) Dye-S/TiO2 immersed in 0.5 M LiClO4 CH3CN solution. Overlaid in purple are simulated spectra. ......................................................... 142

Figure 3.5 Absorption change monitored at 635 nm after pulsed light excitation (532 nm; laser fluence: 0.3 mJ/cm2) of Dye-O/TiO2 (left) and Dye-S/TiO2 (right) immersed in 0.5 M LiClO4/CH3CN at the indicated applied potentials. Overlaid in yellow are best fits to the KWW kinetic model. ......................................................... 144

Figure 3.6 Absorption changes measured after pulsed laser excitation of the sensitized film in the presence of the indicated concentration of [Co(bpy)3](ClO4)2; (a) Dye-O/TiO2 and (b) Dye-S/TiO2 or Lii (c) Dye-O/TiO2 and (d) Dye-S/TiO2 in 0.5 M LiClO4 CH3CN. Absorbance changes were monitored at a probe wavelength of 635 nm (excitation wavelength: 532 nm; laser fluence: 0.1 mJ/cm2). Overlaid in yellow are the best fits to bi-exponential kinetic model. ................. 147

Figure 3.7 Plots of observed regeneration rate constants (kobs) of Dye-O/TiO2 (solid squares, ■) and Dye-S/TiO2 (solid circles, ●) obtained from the kinetics fits versus titrated a) [Co(bpy)3]2+ and b) iodide concentrations. .............................................................. 148

Figure 3.8 Current-voltage curves for DSSCs fabricated with Dye-O and Dye-S at AM1.5 illumination using (A) I/I3− and (B) CoIII/II redox mediators. .............................................................. 154

Figure 3.9 Incident-photon-to-current efficiency for DSSCs fabricated using a) I/I3− and b) CoIII/II redox mediators. .............................................................. 155

Figure 3.10 Interfacial energetics of Dye-O/TiO2 and Dye-S/TiO2 in 0.5 M LiClO4/CH3CN solution. .............................................................. 158

Figure 3.11 Molecular structures of two ruthenium(II)-based dyes studies by O’Regan and coworkers11 indicating the site where the heteroatoms have been changed. The β-LUSO (lowest-occupied spin orbital) for the oxidized form of the ruthenium dye where X = S is shown to the left of the β-LUSO for Dye-S+ (also shown in Figure 3.1) to highlight that there is no orbital character over the S atoms in the metal dye and significant orbital character over the S atoms in the organic dye. The portions of the respective dyes that ostensibly interact with the redox mediator are illustrated. The equivalent spin-density plots are found in Figure A3.15. ......................... 163

Figure 4.1 Structure of deoxycholic acid (DCA) and chenodeoxycholic acid (CDCA). ........... 191

Figure 4.2 Molecular structure of the two organic dyes Dye-O and Dye-S. ......................... 196

Figure 4.3 (a) Ground state absorption spectra of Dye-O/TiO2 immersed in neat CH3CN at different surface coverages (5.1 × 10−9 ~ 7.2 × 10−8 mol·cm−2). (b) Normalized absorption spectra for all surface coverages of Dye-O/TiO2. Overlaid in thick red is the Dye-O solution spectrum in neat CH3CN. The arrow shows the direction for increasing surface coverages. ....................... 198

Figure 4.4 (a) Ground state absorption spectra of Dye-S/TiO2 immersed in neat CH3CN at different surface coverages (4.9 × 10−9 ~ 6.7 × 10−8 mol·cm−2). (b) Normalized absorption spectra for all surface coverages of Dye-S/TiO2. Overlaid in thick blue is the Dye-S solution spectrum in neat CH3CN. The arrow shows the direction for increasing surface coverages. ....................... 199
Figure 4.5  (a) Ground state absorption spectra of Dye-O/TiO₂ in neat CH₂CN without chenodeoxycholic acid at different surface coverages (8.8 × 10⁻⁹ ~ 6.9 × 10⁻⁸ mol·cm⁻²) and (b) their normalized spectra. Overlaid in thick red is the Dye-O solution spectrum in neat CH₂CN. The arrow shows the direction for increasing surface coverages..................................................202

Figure 4.6  (a) Ground state absorption spectra of Dye-S/TiO₂ in neat CH₂CN without chenodeoxycholic acid at different surface coverages (5.1 × 10⁻⁹ ~ 6.4 × 10⁻⁸ mol·cm⁻²) and (b) their normalized spectra. Overlaid in thick blue is the Dye-S solution spectrum in neat CH₂CN. The arrow shows the direction for increasing surface coverages..................................................203

Figure 4.7  Plot of the absorption maximum in wavenumbers and wavelength for Dye-O/TiO₂ (solid red squares: with CDCA coadsorption; open red squares: without CDCA coadsorption) and Dye-S/TiO₂ (solid blue circles: with CDCA coadsorption; open blue circles: without CDCA coadsorption) versus the surface coverages. .................................................................204

Figure 4.8  Absorption changes monitored at 740 nm after pulsed 532 nm light excitation of Dye-S/TiO₂ in 0.5 M LiClO₄ and 0.2 M [Co(bpy)]²⁺ CH₂CN solution. Data were recorded for surface coverages of 7× 10⁻⁹ mol·cm⁻² (black) and 3.5× 10⁻⁸ mol·cm⁻² (red). Data is also shown for a 5.0× 10⁻⁹ mol·cm⁻² Dye-S/TiO₂ with chenodeoxycholic acid as coadsorbent (blue). Overlaid in yellow are fits to the KWW function as is described in the text..................................................207

Figure 5.1  (a) Series of ruthenium chromophores Ru-X (X = O, S, Se) used in this study. (b) Previously documented dyes used to probe interfacial electron transfer (X = O, S). ..........................216

Figure 5.2  Labelling scheme for ¹H NMR signal assignments........................................219

Figure 5.3  Experimental UV-vis absorption spectrum overlaid with calculated transitions represented by vertical bars (only the transitions with contributions >30% are shown). Details of calculated transitions (theoretical wavelength in nm, oscillator strength, % contribution to transition): a) Ru-O₅Me; 1, HOMO → LUMO (714, 0.024, 93%); 2, HOMO → LUMO+1 (587, 0.009, 64%); 3, HOMO-1 → LUMO and HOMO → LUMO+1 (513, 0.172, 51% and 31%); 4, HOMO → LUMO+5 and HOMO-2 → LUMO+2 (416, 0.199, 46% and 30%). b) Ru-S₅Me; 1, HOMO → LUMO (690, 0.026, 94%); 2, HOMO → LUMO+1 (575, 0.019, 53%); 3, HOMO-1 → LUMO and HOMO → LUMO+1 (502, 0.179, 39% and 38%); 4, HOMO-1 → LUMO+3 and HOMO → LUMO+5 (420, 0.216, 42% and 41%). c) Ru-Se₅Me; 1, HOMO → LUMO (691, 0.026, 94%); 2, HOMO → LUMO+1 (575, 0.019, 54%); 3, HOMO-1 → LUMO and HOMO → LUMO+1 (503, 0.193, 41% and 39%); 4, HOMO → LUMO+3 and HOMO → LUMO+5 (421, 0.248, 50% and 40%). ..................................................236

Figure 5.4  Absorption difference spectra measured at the indicated delay times after pulsed 532 nm excitation (laser fluence, 0.5 mJ/cm²) of (a) Ru-O/TiO₂ thin film; (b) Ru-S/TiO₂ thin film; and (c) Ru-Se/TiO₂ thin film immersed in 0.5 M LiClO₄/CH₂CN. (black squares: 45 ns; red circles: 100 ns; blue triangles: 500 ns; magenta reverse triangles: 5 μs; green diamonds: 50 μs; blue solid traces: ground state absorption spectra with y-axis on the right; orange solid curves: simulations based on the difference spectra of RuIII-X/TiO₂ and RuII-X/TiO₂ by spectroelectrochemistry).................238

xiii
Figure 5.5 Absorption changes measured after pulsed laser excitation of the sensitized film in 0.5 M LiClO₄/CH₃CN. (λₑₓc, 532 nm; probe, 583 nm; laser fluence, 0.5 mJ/cm²; ground state absorption at 532 nm, ≈ 0.22). Overlaid in yellow are the best fits to KWW kinetic model. ........................................ 240

Figure 5.6 Plot of observed regeneration rate constants (kobs) of Ru-O/TiO₂ (black squares), Ru-S/TiO₂ (red circles), and Ru-Se/TiO₂ (green triangles) versus titrated iodide (I⁻) concentrations. .................................................................................................................................................................................................................. 242

Figure 5.7 Plot of open circuit voltage as a function of incident steady state monochromatic light (λₑₓc, 514.5 nm) for Ru-O/TiO₂, Ru-S/TiO₂, and Ru-Se/TiO₂ measured in solar cells containing 0.5 M LiI and 0.05 M I₂ dissolved in CH₃CN. The inset shows the ground state absorption spectra of the three sensitizers anchored on TiO₂/FTO substrate for the measurement. ........................................................................................................... 245

Figure 5.8 Absorption changes measured after pulsed laser excitation of the sensitized films in 0.4 M LiI + 0.1 M LiClO₄/CH₃CN. (λₑₓc, 532 nm; probe, 375 nm; laser fluence, 2.8 mJ/cm²; ground state absorptions at 532 nm, ≈ 0.26). The sensitized films were electrochemically biased to -240 mV vs NHE. Overlaid in yellow are the best fits to KWW kinetic model. .......................................................... 247

Figure 6.1 Selected frontier molecular orbitals of 1, 2, and 3. Isosurface contour values are 0.05 a.u. H atoms are omitted for clarity except for the ones on carboxylic acid groups. Color scheme: Ru = green, S = yellow, O = pink, N = blue, C = gray, H = cyan................................................................. 281

Figure 6.2 Optical absorption spectra of 1 in MeCN and of 2 and 3 in MeOH at room temperature. .............................................................................................................................. 283

Figure 6.3 Experimental (solid line) and simulated (dashed line) absorption spectra of 1 (blue), 2 (red), and 3 (purple). The gray bars indicate the energy and oscillator strength of electronic excitations. The asterisk marks the excitation in the simulated spectrum that corresponds to the 400-nm absorption in the experimental spectrum (see the “Transient Absorption” section for further details).................................................................................................................................................................................................. 284

Figure 6.4 Cyclic voltammograms of 1 (black), 2a (red), and 3a (blue) recorded in 0.100 M solutions of (Bu₄N)PF₆ in MeCN, CH₂Cl₂, and MeCN, respectively .............................................................. 287

Figure 6.5 Transient absorption spectra (a, b) and kinetic traces monitored at two different wavelengths (c, d) for MeCN solutions of 1 (a, c) and 3a (b, d), under 400 nm pulsed laser excitation. Overlaid in red on the experimental data are the best fits to the function described by equation 6.1. .................................................................................................................................................................................................. 291

Figure 6.6 Ground-state optical absorption spectra of 2 (a) and 3 (b) on TiO₂ surface immersed in a 0.5 M MeCN solution of LiClO₄ at variable TBP concentrations. .......................................................... 295

Figure 6.7 The incident photon-to-current efficiency of 2 (a) and 3 (b) in dye sensitized solar cells with 0.5 M LiI/0.05 M I₂ acetonitrile and the 0 M (black), 0.1 M (red), and 0.5 M (blue) TBP. Also shown in olive green is the absorbance spectrum of the sensitized thin film. ............................................. 297

Figure 6.8 Absorption changes monitored at 542 nm for 2 and 3 anchored to TiO₂ surface after pulsed-laser excitations with 532 nm (a and b) and 416 nm (c and d) light. Overlaid on this data are the best fits to the KWW function. The inset displays the first 0.5 microseconds of data, with dashed
lines showing the amplitudes assigned to charge-separated states, which were used to measure the relative injection yield.

**Figure 6.9** (a) Absorption of dye-free TiO₂ thin-film electrode measured at 800 nm as a function of applied potential (vs. NHE) at variable concentrations of TBP. (b) The data from (a) recast as chemical capacitance. Superimposed on these data are the ground- and excited-state redox potentials of dye 3.

**Figure A2.1** UV-vis absorption spectra of (a) C2/TiO₂ (b) C3/TiO₂ (c) C4/TiO₂ measured at different applied potentials in 0.5 M LiClO₄ CH₃CN solutions. The insets show the fraction (x) of dye molecules present in the fully reduced state (black squares), singly oxidized state (red squares) and doubly oxidized state (green squares). Overlaid are sigmoidal fits, x=1/(1+10exp((E_{app}-E_{1/2})/a×59mV)), where a is the non-ideality factor.

**Figure A2.2** Frontier Molecular Orbitals for the three studied complexes in their ground state.

**Figure A2.3** Frontier Molecular Orbitals for the three studied complexes in their oxidized state with one carboxylic acid group deprotonated.

**Figure A2.4** Absorption change monitored at 640 nm after 532 nm light excitation for C5/TiO₂ immersed in 50 mM LiClO₄ CH₃CN at -45 °C. The data correspond to intra-molecular RuIII → NAr₃ hole transfer with an overlaid fit to a first-order kinetic model.

**Figure A2.5** Absorption change monitored at 550 nm after pulsed light excitation (532 nm) of C1-C5/TiO₂ immersed in 0.5 M LiClO₄ CH₃CN. Overlaid in yellow is the best fit to the KWW kinetic model.

**Figure A2.6** Absorption change monitored at 740 nm after pulsed light excitation (532 nm) of C5/TiO₂ immersed in 0.5 M LiClO₄ CH₃CN at 1/5 saturation surface coverage (black) and saturation surface coverage (red).

**Figure A2.7** The ATR-FTIR spectra of C4/TiO₂ (blue), H₂SO₄ treated C4/TiO₂ (red) and C4 powder (black). The green dashed line serves as a guide line for the peaks appearing at 1712 cm⁻¹.

**Figure A2.8** The UV-vis absorption of C1/TiO₂, C1⁺/TiO₂ and C1²⁺/TiO₂.

**Figure A2.9** Absorption change monitored at 442 nm after pulsed 532 nm light excitation of C5/TiO₂ at the indicated applied potentials. Overlaid in yellow are the fits to the KWW model. Inset: a τ₁/2 analysis of this data plotted against the fraction of oxidized triarylamines.

**Figure A2.10** Plot of open circuit voltages of C2/TiO₂, C4/TiO₂ and C5/TiO₂ in 0.5 M LiClO₄ CH₃CN non-regenerative electrolyte versus steady state irradiances.

**Figure A2.11** Absorption changes monitored at 540 nm after pulsed light excitation with five irradiances (ϕex = 532 nm 0.3-1.5 mJ/cm²) of C1/TiO₂ immersed in 0.5 M LiClO₄ CH₃CN and
biased at 1035 mV versus NHE. Overlaid as solid lines are absorption profiles abstracted from Monte Carlo simulations of 8 TiO₂ nanoparticles (2×2×2 array).

**Figure A2.12** Chi-Squared analysis (a) and residuals for the highest S/N data (b) of Monte Carlo simulations for lateral hole transfer reactions occurring on a single nanocrystal (black), an 8 nanocrystal array (red) and a 27 nanocrystal array (blue). Chi-squared values were calculated using 1000 points evenly spaced on a logarithmic scale. Experimental values were a 21-point moving average of the raw data.

**Figure A2.13** The interfacial density of states for C2/TiO₂, C4/TiO₂, and C5/TiO₂ measured by spectroelectrochemistry in 0.5 M LiClO₄/CH₃CN electrolyte.

**Figure A3.1** Labelling scheme for ¹H NMR signal assignments.

**Figure A3.2** The calculated HOMO and LUMO for Dye-O.

**Figure A3.3** The calculated HOMO and LUMO for Dye-S.

**Figure A3.4** Normalized absorption spectra of Dye-O (solid red line) and Dye-S (solid blue line) and normalized fluorescence spectra of Dye-O (dashed red line) and Dye-S (dashed blue line) in CH₃CN solutions at 298 °K.

**Figure A3.5** Ground state UV-visible absorption spectra of Dye-O (red) and Dye-S (blue) anchored to nanocrystalline TiO₂ films in neat CH₃CN. The corresponding dash-dot lines are for the same films immersed in 0.5 M LiClO₄/CH₃CN solutions.

**Figure A3.6** Cyclic voltammograms of Dye-O (red trace) and Dye-S (blue trace) in 0.1 M NBu₄BF₄ CH₃CN solutions at 298 °K using a Pt working electrode, 100 mV/s scan rate. Dashed line indicates E/2 value.

**Figure A3.7** Cyclic voltammery of Dye-O/TiO₂ (A) (Eₚa = 1190 mV, Eₚc = 860 mV, dye surface coverage Γ = 1.0×10⁻⁷ mol·cm⁻²) and Dye-S/TiO₂ (B) (Eₚa = 1183 mV, Eₚc = 996 mV, Γ = 5.3×10⁻⁸ mol·cm⁻²) immersed in 0.5 M LiClO₄ CH₃CN solution at r.t. (scan rate: 100 mV/s).

**Figure A3.8** Density of TiO₂ acceptor states measured by spectroelectrochemistry. The extinction coefficient of TiO₂(e²) was assumed to be 1000 M⁻¹ cm⁻¹ at 800 nm. The solid and dashed lines were single exponential fits for Dye-O/TiO₂ and Dye-S/TiO₂ in 0.5 M LiClO₄ CH₃CN.

**Figure A3.9** Charge recombination kinetics of Dye-O/TiO₂ (black) and Dye-S/TiO₂ (red) immersed in 0.5 M LiClO₄ CH₃CN monitored at 635 nm (excitation wavelength: 532 nm; laser fluence: 0.3 mJ/cm²). Overlaid in yellow (Solid: Dye-O/TiO₂, Dashed: Dye-S/TiO₂) are the fits using KWW function (β = 0.19).

**Figure A3.10** Plot of Log (kₚ) abstracted from KWW fits shown in Figure 3.5 through equation 2, plotted as a function of the applied bias for the indicated sensitized thin films.

**Figure A3.11** Open circuit photovoltage of Dye-O/TiO₂ (triangle) and Dye-S/TiO₂ (cross) measured in 0.5 M LiClO₄ without redox mediators (steady state excitation wavelength: 514.5 nm).
Figure A3.12 Absorption difference spectra measured at the indicated delay times after pulsed 532 nm laser excitation of a) Dye-O/TiO₂ and b) Dye-S/TiO₂ immersed in 0.2 M LiI /0.3 M LiClO₄ CH₃CN solution. .......................................................................................................................... 182

Figure A3.13 Absorption changes monitored at 720 nm after pulsed 532 nm laser excitation of the sensitized films in 0.5 M LiI CH₃CN (laser fluence: 2 mJ/cm²). Overlaid in yellow are fits to the KWW model (β = 0.8). ............................................................................................................................................. 183

Figure A3.14 a) Absorption changes monitored at 396 nm at 5 different irradiances after pulsed 532 nm laser excitation of Dye-S/TiO₂ in 0.5 M LiI CH₃CN (Correction has been made for absorption changes of Dye-S⁺/TiO₂); b) Absorption changes monitored at 635 nm under the same conditions as a). ............................................................................................................................................. 184

Figure A3.15 Spin-density plots for dyes oxidized dyes TG6⁺, Dye-O⁺ and Dye-S⁺. Note that there is no orbital character over the S atom comprising the terminal substituent of the modified bipyridine ligand in TG6⁺, while there is significant orbital character over the terminal O and S atoms in Dye-O⁺ and Dye-S⁺............................................................................................................................................. 185

Figure A5.1 Absorption changes measured after pulsed laser excitation of the sensitized film in the presence of the indicated concentrations of LiI, (a) Ru-O/TiO₂, (b) Ru-S/TiO₂, and (c) Ru-Se/TiO₂. (λexc, 532 nm; probe, 583 nm; laser fluence, 0.5 mJ/cm²). Overlaid in yellow are the best fits to triexponential kinetic model. ............................................................................................................................................... 254

Figure A5.2 Difference absorption spectra of (a) Ru-O/TiO₂, (b) Ru-S/TiO₂, and (c) Ru-Se/TiO₂ measured at the indicated applied potentials in 0.5 M LiClO₄/CH₃CN solution. ........................................................................................................................................ 255

Figure A5.3 Absorbance change measured at 900 nm as a function of applied potential. .......... 256

Figure A5.4 Absorption changes measured after pulsed laser excitation of a) Ru-O/TiO₂, b) Ru-S/TiO₂, and c) Ru-Se/TiO₂ sensitized films in 0.4 M LiI + 0.1 M LiClO₄/CH₃CN. (λexc, 532 nm; probe, 375 nm; laser fluence, 2.8 mJ/cm²; ground state absorptions at 532 nm, ≃ 0.26). The sensitized films were electrochemically biased to the indicated potentials vs NHE. Overlaid in yellow are the best fits to KWW kinetic model. Panel d shows the average rate constants measured at each of the three bias conditions. ....................................................................................................................... 257

Figure A5.5 DFT-calculated HOMO molecular orbitals for complexes Ru³⁺-X₃Me and HOMO molecular orbitals for complexes Ru³⁺-X₃Fe. .............................................................................................................................................. 258

Figure A5.6 Lithium cation effect shown by LiClO₄ titration; (a) Ru-O/TiO₂, (b) Ru-S/TiO₂, and (c) Ru-Se/TiO₂ are the ground state UV-vis absorption change. (d), (e), and (f) are the corresponding delta absorption change using the ground state absorption of the slides immersed in neat CH₃CN as the baseline. ................................................................................................................................................. 259

Figure A5.7 UV-vis absorption spectra of (a) Ru-O/TiO₂ (b) Ru-S/TiO₂ (c) Ru-Se/TiO₂ slides in 0.5 M LiClO₄/CH₃CN with the indicated tetrabutylammonium iodide (TBAI) concentrations. All the absorption spectra have been corrected for the occurrence of triiodide absorption in the titration solutions. .............................................................................................................................................. 260
Figure A5.8  UV-vis absorption spectra of (a) Ru-O/TiO$_2$ (b) Ru-S/TiO$_2$ (c) Ru-Se/TiO$_2$ slides in 0.3 M LiClO$_4$/CH$_3$CN with the indicated tetrabutylammonium triiodide (TBAI$_3$) concentrations. All the absorption spectra have been corrected for triiodide absorption in the titration solutions.

Figure A6.1  Photoluminescence spectrum of 3 in EtOH/MeOH (4:1 v/v) solution at 77 K.

Figure A6.2  Cyclic voltammogram of 3b recorded in 0.100 M solutions of (Bu$_4$N)PF$_6$ in MeCN.

Figure A6.3  Difference absorption spectrum of 3 dissolved in neat EtOH under –30°C at the indicated delay time after 532 nm laser excitation. (Absorbance of 3 at 532 nm is 0.1). Inset: the absorbance change monitored at 460 nm.

Figure A6.4  Ground-state absorption spectra of 2 (a) and 3 (b) on TiO$_2$ surface immersed in neat MeCN (green curve) or in a 0.5 M solution of LiClO$_4$ in MeCN (black curve).

Figure A6.5  Absorbance of a TiO$_2$ thin film at the indicated applied potentials (vs. NHE) in 0.5 M LiClO$_4$/MeCN.
List of Schemes

Scheme 1.1  Simplified mechanism for a regenerative dye-sensitized solar cell ......................... 6

Scheme 1.2  Kinetic processes at an illuminated dye-sensitized electrode in a dye-sensitized solar cell. The subscripts ‘inj’, ‘cr’, ‘reg’, and ‘dispr’ mean injection, charge recombination, regeneration, and disproportionation respectively ................................ 10

Scheme 1.3  Gerischer-type model representing the overlap of donor and acceptor state of [Ru(bpy)$_2$(dcbq)]$^{0/-}$ (a) and hemin/heme (b) with TiO$_2$ conduction band edge. Taken from reference 83 .......................... 37

Scheme 1.4  A cartoon showing how hole hopping at high surface coverage of N3 dye was able to help facilitate regeneration by iodide while isolated N3 at low surface coverage did not. Taken from reference 86 .................................................. 44

Scheme 2.1  Excited state electron injection and intramolecular hole transfer for a Sensitizer-linker-Donor compound anchored on TiO$_2$ surface .................................................................. 65

Scheme 2.2  The interfacial redox equilibrium under study .......................................................... 67

Scheme 2.3  Molecular structures of the compounds with the indicated Ru$_{III/II}$ (blue) and NAr$_3$$^{+/-0}$ (red) reduction potentials ......................................................................................... 69

Scheme 2.4  The chemical capacitance of C3/TiO$_2$ (a) and C5/TiO$_2$ (b) as a function of applied potential. The solid curves represent best fits to the experimental data with the indicated non-ideality factors. The dashed curves represent ideal Nernstian behavior. The overlap of the chemical capacitance represents potentials where both triaryl amine and ruthenium redox chemistry occurs. ........................................................................ 95

Scheme 2.5  Electron transfer and hole hopping processes observed after 532 nm laser excitation of C1$^-$/TiO$_2$: excited state electron injection (a); interfacial charge recombination (b); lateral intermolecular hole hopping (c) ........................................................................... 102

Scheme 2.6  Monte Carlo simulation of lateral intermolecular hole hopping on spherical TiO$_2$ nanocrystallites. Black dots represent the C1$^+$ sites that are evenly distributed on the surface. Red spheres are C1$^{2+}$ and blue spheres are C1. Thirty steps of random walks are shown .................. 106

Scheme 5.1  Synthesis of Ligands L1H-L3H.$^a$ ........................................................................ 232

Scheme 5.2  Synthesis of Metal Complexes Ru-X.$^a$ and Ru-X$_2$. ........................................ 233

Scheme 6.1  Molecular structures of Ru(II) dipyrrinates studied in this work .......................... 269

Scheme 6.2  Synthesis of complexes 1–3: (a) [(p-cymene)RuCl$_2$]$_2$, Et$_3$N, MeCN, reflux, 12 h; (b) bpy, AgNO$_3$, NH$_4$PF$_6$, MeOH, reflux, 16 h; (c) dmb, AgNO$_3$, NH$_4$PF$_6$, MeOH, reflux, 16 h; (d) Et$_3$N:H$_2$O:DMF = 1:1:3 (v/v/v), reflux, 18 h. ......................................................................................... 278

Scheme 6.3  An energy level diagram illustrating excited state dynamics of 3a. ..................... 293
Scheme A3.1  Synthesis of Dye-S.\textsuperscript{a}
List of Tables

Table 2.1  Electrochemical and photophysical data for the sensitized thin films .................................. 97

Table 3.1  Summary of Spectroscopic and Electrochemical Properties for Dye-O and Dye-S in solution and anchored to TiO$_2$. ......................................................................................................................... 141

Table 3.2  Second-order regeneration rate constants ($k_{reg}$) abstracted for Dye-O/TiO$_2$ and Dye-S/TiO$_2$ in 0.5 M LiClO$_4$/CH$_3$CN containing cobalt- and iodide-based redox mediators. ........ 148

Table 3.3  Regeneration efficiencies calculated by 5 at the indicated forward bias conditions. .150

Table 3.4  Solar Cell Performance Parameters Obtained Under Simulated AM 1.5 Illumination (1 Sun) for Dye-O and Dye-S. ......................................................................................................................... 153

Table 4.1  Charge recombination rate constants abstracted from KWW modeling at different surface coverages of Dye-S/TiO$_2$. ......................................................................................................................... 208

Table 5.1  Reduction Potentials of Ru-X (X = O, S, Se) in Solution and on Mesoporous TiO$_2$. 235

Table 5.2  Second-Order Regeneration Rate Constants ($k_{reg}$) for Ru-X/TiO$_2$ by I$^-$ in CH$_3$CN. .243

Table 5.3  Rate constants for charge recombination between TiO$_2$(e$^-$) and I$_3^-$ for Ru-X/TiO$_2$. 248

Table 6.1  Electrochemical properties of complexes 1-3, 2a, and 3a (the potentials are referenced to NHE). ................................................................................................................................. 288

Table 6.2  IPCE and comparative actinometry of dyes 2 and 3 on TiO$_2$ surface. ......................... 298

Table A2.1  Calculated Dipole Moments vector components, orientation with respect to the TiO$_2$ surface normal and electrostatic potential drop for C$_2$, C$_4$ and C$_5$ in their two protonation studied states (a. triprotonated and b. diprotonated) and in their two oxidation state (Ru(II) and Ru(III)). ........................................................................................................................................... 110

Table A6.1  Energies$^a$ and compositions$^b$ of selected frontier MOs of 1, 2, and 3. .................. 305

Table A6.2  Assignment of electronic transitions for 1, 2, and 3 from TD-DFT calculations in solvent. ........................................................................................................................................ 306
Chapter 1: Introduction to Molecular Dye Sensitized TiO$_2$ Interfaces and the Application to Solar Energy Conversion Devices

1.1 Solar Energy Prospects

The U.S. Energy Information Administration reported in the “International Energy Outlook 2013” that the total world energy use had risen to 524 quadrillion British thermal units (Btu) in 2010.\(^1\) That was an average energy consumption rate of 17.6 TW (TW=10\(^{12}\) W). Over 80% of the total energy consumption was from fossil fuels and over 87% from non-renewable energy sources (including nuclear energy). The world energy consumption is still expected to rise to 630 Btu (21.2 TW) in 2020.\(^1\) However, the fossil fuel production is not expected to keep up the pace of the increasing global energy demand especially in the developing world in which higher energy demand is requested for growing population and faster civil modernization.\(^1\) Furthermore, the vast use of fossil fuels after the first industrial revolution has caused the atmospheric CO$_2$ level to soar. The average global CO$_2$ level in June, 2014 has broken a record of 400 ppm where it had never exceeded 300 ppm over the past 800 thousand years.\(^3,3\) Meanwhile, the consequent global warming and rising sea level urged governments and associated world agencies to set regulations on CO$_2$ emission worldwide.\(^4\)

In order to achieve a sustainable development, clean and renewable energy sources are in call. Current renewable energy sources in use include a large percentage of biomass followed by hydropower, wind power, geothermal heat, and solar power that represents less than 0.3%.\(^5\) The insignificant amount of energy production from solar power is a result of the disadvantage with
respect to the cost over other energy sources. The majority of the solar panels installed are based on crystalline silicon.\(^6\) In order to achieve high efficiency in standard silicon photovoltaics, the silicon needs to be rigorously purified to a high level, and this is too energy consuming to be inexpensive. Nevertheless, due to rapid increases in crude oil prices, dramatic decreases in silicon panel costs, and large governmental subsidies, solar capacity installations have been booming for the past few years.\(^5\) A 36.8% increase of solar power was achieved in 2013 over 2012.\(^5\)

The practical use of electrical power from solar energy on a large scale requires optimization of three key photovoltaic parameters: efficiency, cost, and stability.\(^7\) The theoretical highest efficiency that can be achieved by a single junction solar cell is the so called “Shockley Queisser Limit”, 33.7%. The other 66.3% loss is comprised of light absorption, thermal relaxation, and extraction losses.\(^8\) Figure 1.1 shows the standard Air Mass (AM) 1.5 solar irradiance spectrum.\(^9\) Smaller band gap semiconductor material can harness more solar photons and hence higher current densities but may create less voltage. The net result is that there is an optimal band gap for harvesting solar energy. Currently, single junction monocrystalline Si or Group III-V semiconductor like GaAs approach the Shockley Queisser limit, Figure 1.2.\(^10\) However, as mentioned before a high cost for the massive production has been a bottle neck for high efficiency photovoltaic materials. Chemists are searching for “third generation photovoltaics” that meet the aforementioned three key characteristics of successful photovoltaic materials. Dye-sensitized solar cells represent one of them. The easy and low energy consumption fabrication process makes it a potentially new type of low cost solar cell to help feed our energy demand in the future.\(^11\)
Figure 1.1 Air mass 1.5 solar irradiance spectrum (black). The solid blue curve represents the theoretical maximum solar cell efficiency with a certain band gap semiconductor based on the integration of the solar irradiance spectrum. Adapted from reference 9.
Figure 1.2 Best Research-Cell Efficiencies. Obtained from reference 10.
1.2 Dye-Sensitized Solar Cells

1.2.1 Operation Principle of Dye-Sensitized Solar Cells

The use of a mesoporous nanocrystalline anatase TiO$_2$ thin films as the semiconductor in DSSCs opened a wide door for research twenty three years ago. O’Regan and Grätzel in 1991 first achieved a solar cell efficiency over 7% by attaching molecular ruthenium coordination compounds to such a high surface area thin film as the light absorber.$^{11}$ The operation principle of the type of solar cell is demonstrated in Scheme 1.1. The thin film is composed of $\sim$20 nm diameter TiO$_2$ nanoparticles interconnected and sintered on a transparent conducting oxide (TCO) surface, typically fluorine doped tin oxide (FTO). The mesoporous TiO$_2$ film is roughly 10 $\mu$m thick. Dye molecules that have strong visible light absorptions are anchored on the TiO$_2$ surface through carboxylic acid groups. Upon light irradiation through the FTO/TiO$_2$, dye molecules absorb light and reach the metal-to-ligand charge transfer (MLCT) excited states. With proper alignment to the TiO$_2$ conduction band, the MLCT excited states will inject electrons into the TiO$_2$ acceptor states and the dye molecules are formally oxidized. The oxidized sensitizer molecules are subsequently reduced back to the ground states by electron donors of the redox mediator in the electrolyte. Meanwhile, the injected electrons inside the TiO$_2$ nanoparticles migrate to the back contact of FTO producing a photocurrent in the external circuit. The oxidized redox mediators are reduced at the counter electrode, typically platinized FTO to complete the circuit. In this cycle, no net chemistry occurs and the cell is termed ‘regenerative’. The open circuit voltage is determined by the quasi-Fermi level of TiO$_2$ with respect to the reduction potential of the redox mediator couple at the counter electrode.$^{12}$
Scheme 1.1 Simplified mechanism for a regenerative dye-sensitized solar cell.
Figure 1.3 shows a typical Current-Voltage (i-V) curve for a DSSC under AM1.5 and 100 mW/cm$^2$ (1 Sun) illumination condition. With no work load or applied potential, all the injected electron collected into the external circuit form the so called short circuit current ($i_{sc}$). As the work load is added to the external circuit or with an applied potential, the current will start to drop. At very large resistance, the circuit current will drop to zero. This represents the largest voltage output the cell can produce and is called open circuit voltage ($V_{oc}$). To generate electrical power, the solar cell optimally operates at condition where the product of the current and the voltage is the largest. This condition is called the power point (PP). Now we can define another important factor of a DSSC, the fill factor (FF). The FF is the ratio of the measured maximum power output and the theoretical maximum power output. It can be described as Equation 1.1:

$$FF = \frac{i_{pp}V_{pp}}{i_{sc}V_{oc}}$$

A FF of one can never be obtained due to various loss mechanisms like charge recombination, insufficient regeneration, non-unity charge collection, etc. Some of these loss mechanisms will be discussed in the later chapters for some particular systems in detail. A solar cell efficiency characterization includes measuring $i_{sc}$, $V_{oc}$ and FF from i-V measurements. The efficiency ($\eta$) of a solar cell can be calculated through Equation 1.2:

$$\eta = \frac{i_{sc}V_{oc}FF}{P_0 A_{cell}}$$

where $P_0$ is the AM 1.5, 1 Sun condition (100 mW/cm$^2$) and $A_{cell}$ is the cell area illuminated.
Figure 1.3 A typical Current-Voltage (i-V) curve (black) for a dye-sensitized solar cell. The rectangular box in dashed green is the theoretical maximum power output from this solar cell. The rectangular box in shaded blue is the practical maximum power output. The solid curve in red is the power output as a function of the potential. Taken from reference 13.\textsuperscript{13}
More than two decades of efforts have been dedicated to optimizing DSSC efficiencies. Knowing the time scales for each elementary step is very useful. Scheme 1.2 shows some main kinetic processes with approximate time scales employing the most commonly used I$_3^-$/I$^-$ as the redox mediator.$^{13,14}$ Most of the time scales for each process can be obtained from transient absorption measurements. After light excitation of the sensitizer molecules, the excited state electron injection is generally considered as an ultrafast process.$^{13}$ The majority of the electron injection process is completed in most, if not all, cases within 10 ns. Charge recombination of the injected electron with the oxidized dye, on the other hand, is orders of magnitude slower than the injection process and typically occurs on the microsecond to millisecond time scale. This “rectifying effect” makes quantitative light to current conversion in DSSCs possible. The sensitizer regeneration by iodide is governed by the driving force between the formal S$^{+0}$ reduction potential of the sensitizer and the one electron reduction potential of the iodide species. For champion sensitizers employed in DSSCs, this process usually occurs on the nanoseconds to microseconds time scales. An intermediate oxidized iodide species, I$_2$•$^-$ was found to undergo disproportionation to form I$_3^-$. The kinetic rate constant of disproportionation in operational DSSCs is under debate in the literature but was reported to be around $3 \times 10^9$ M$^{-1}$ s$^{-1},^{15}$ the same as was measured in fluid solution.$^{16}$ The back electron transfer from TiO$_2$(e$^-$) to I$_3^-$ is found to be extremely slow, requiring milliseconds to seconds. This has been attributed to a more negative potential of one electron reduction potential of I$_3^-$ to I$_2$•$^-$+I$^-$. The feature of an unfavorable one electron acceptor of I$_3^-$ renders the redox mediator to be successful in making champion DSSCs.
Scheme 1.2 Kinetic processes at an illuminated dye-sensitized electrode in a dye-sensitized solar cell. The subscripts ‘inj’, ‘cr’, ‘reg’, and ‘dispr’ mean injection, charge recombination, regeneration, and disproportionation respectively.
In order to achieve optimal performance, one needs to consider both kinetics and energetics of sensitizer molecules and redox mediators. The excited state of the sensitizer molecule needs to be a strong enough reductant to inject an electron into TiO$_2$ acceptor states efficiently and rapidly. The oxidized state of the sensitizer molecule needs to be a strong enough oxidant to be reduced by the electron donor in the electrolyte. The sensitizer regeneration process needs to be fast enough to prevent TiO$_2$(e$^-$) from leaking out to the oxidized dye. This point will be explained in a great detail in chapter 3. On the other hand, the Gibbs free energy stored in the excited state needs to be small enough to allow long wavelength absorption so that a greater portion of the solar spectrum can be harvested. As the optimal band gap is 1.34 eV proposed by the Shockley-Queisser limit,$^8$ the optimal absorption onset would be ~920 nm. The interplay between kinetics and energetics is a paramount consideration for optimizing DSSC efficiencies.

1.2.2 Light Harvesting

Unlike silicon or GaAs based semiconductors that acts as both light harvester and charge collector, anatase TiO$_2$ as an n-type wide band gap semiconductor acts only as the charge collector but not light harvester. In fact, with a band gap of 3.2 eV, TiO$_2$ only absorbs light in the UV region.$^{13}$ Surface anchored molecules that absorb light in the visible region are the light harvester in DSSCs. Ruthenium polypyridyl coordination compounds are the most widely used and successful molecular sensitizers. The visible light absorption region is mainly composed of Metal-to-Ligand Charge Transfer (MLCT) transitions. With visible light excitation into an MLCT band, Ru$^{II} \rightarrow$ bpy (bpy stands for bipyridine) for example, the ruthenium metal center is formally oxidized to Ru$^{III}$ and the bpy ligand is formally reduced. This charge transfer excited state can be depicted as [LL'Ru$^{III}$bpy$^{-2+}*$, where L and L’ are the other two bidentate ligands.$^{17}$ This relatively intense (extinction coefficient $\varepsilon \approx 10^4 \sim 5\times10^4$) and broad absorption band along with proper energetic alignment with the TiO$_2$ conduction band level makes ruthenium polypyridyl coordination compounds ideal for sensitizing TiO$_2$ in DSSC application.
Currently, the certified DSSC efficiency record holder is [Ru(Htctpy)(NCS)](TBA)$_3$. where ‘Htctpy’ is mono-protonated 4,4',4’’-tricarboxy-2,2',6',2’’-terpyridine and ‘TBA’ is n-tetrabutylammonium, Figure 1.4.\textsuperscript{18} This dye was termed the ‘black dye’ as the absorption onset is in the near infrared region ~900 nm. Other former champion sensitizers include the widely studied N3 dye, which is Ru(H$_4$dcbpy)(NCS)$_2$ where ‘H$_4$dcbpy’ is 4,4’-dicarboxy-2,2’-bipyridine, and the form of N3 with two unprotonate carboxylic acids is called N719, Figure 1.4.\textsuperscript{19} A common motif in these champion sensitizer molecules is that they all bear monodentate isothiocyanate as ligands. This structural motif seems to tune the interfacial energetics most optimally as well as facilitating rapid regeneration. On the other hand, the monodentate nature is prone to ligand loss photochemistry under prolonged illumination.\textsuperscript{20} Many efforts have been undertaken to solve this challenge by replacing isothiocyanate ligand with motifs like cyclometalated structures. The structural design introduced a strong Ru-C organometallic σ-bond as well as multi-dentate chelating effect, making them robust sensitizers.\textsuperscript{21-25}

Ruthenium as a post-second row transition metal is still a rare element on the earth. The natural abundance is even lower than gold.\textsuperscript{26} Furthermore, the MLCT extinction coefficient of N3 or the black dye is not large enough to enable the use of TiO$_2$ films with thickness below 10 μm. Indeed, in order to achieve unity light harvesting efficiency in the blue to green visible region, a new class of organic dye molecules have recently come into play that have common high extinction coefficients. The general design follows donor-π-acceptor motif so that the transition dipole moment is directed towards the carboxylic acid anchoring group.\textsuperscript{27} This helps promote excited state electron injection to TiO$_2$ nanoparticles. The most studied electron donor part of organic dyes is coumarin and triarylamine moieties.\textsuperscript{27} In fact, the highest efficiency that has been achieved with an organic dye, RK1 is shown in Figure 1.4.\textsuperscript{28}
Figure 1.4 Champion sensitizer molecules in DSSCs.
1.2.3 Electron Injection to TiO₂

Electron injection is the first step of charge separation processes at the TiO₂ interface. A large body of data showed ultrafast multiphasic electron injection to TiO₂.¹³ One nanosecond after photon absorption, the excited state absorption signature was absent, indicating complete electron injection, in < 1 ns. However, most of the data were obtained using the so called ‘model system’, which used inert electrolytes and non-regenerative cells.²⁹-³² Recently, data acquired under operational solar cell conditions has shown evidence for slower electron injection processes in some cases.³³ Nevertheless, electron injection process was acknowledged to have multi-phasic behavior that extended from less than 100 fs to nanoseconds dependent upon the experimental conditions. The origin of such behavior was mainly attributed to different excited states that injected electrons and the exponential rise of the number of TiO₂ acceptor states as a function of potential.¹³

Figure 1.5 shows a simplified picture of different pathways that could result in electron injection into the TiO₂ acceptor states.³⁴ It was found that the singlet MLCT could result in ultrafast electron injection within the instrument response time (< 50 fs), Process A in Figure 1.5. This kind of electron injection before vibrational cooling and intersystem crossing (ISC) is termed ‘hot injection’. ¹MLCT to ³MLCT inter-system crossing was also found to be ultrafast ~70 fs, Process B in Figure 1.5. About 30% slower electron injection on the picosecond time scale was found to occur from the thermally equilibrated triplet excited state (THEXI state), Process D in Figure 1.5. The slower electron injection might result from the nature of low energy levels of the triplet MLCT state or to a lower density of TiO₂ acceptor states available to the THEXI state. This reasoning is in line with non-adiabatic Marcus electron transfer theory that charge transfer rates increase with the overlap of the excited state and TiO₂ acceptor states in the TiO₂ nanocrystal.
Figure 1.5 Simplified Jablonski diagram and possible pathways for excited state electron injection to TiO$_2$ acceptor states. Taken from reference 34.
1.2.4 Sensitizer Regeneration

Sensitizer regeneration is an essential step that enables sensitizers to absorb subsequent photons and generate current. There are two types of regeneration, intramolecular regeneration and intermolecular regeneration.\textsuperscript{13} For intramolecular regeneration, an electron donor is covalently linked with one of the ligands that coordinates to the metal center, typically ruthenium. Ideally, intramolecular regeneration translates the hole created after electron injection away from the TiO\textsubscript{2} surface. A few such electron donors were developed including phenothiazine (PTZ) derivatives, triarylamine derivatives, tetrathiafulvalene derivative, etc.\textsuperscript{25,35-39} Eventually, the hole needs to migrate to the counter electron to be reduced and this requires intermolecular electron transfer to complete this step. The I\textsubscript{3}⁻/I⁻ redox mediator is by far the most successful redox mediator used in most champion solar cells. As mentioned before, fast regeneration is important in order to compete kinetically with charge recombination. There are two proposed and possible pathways for sensitizer regeneration by I\textsubscript{3}⁻/I⁻ redox mediator as shown in Equation 1.3-a,b and 1.4-a,b.\textsuperscript{40,41}

\[
\begin{align*}
S^+ + I^- & \rightarrow S^+ + I^- \quad (1.3-a) \\
I^- + I^- & \rightarrow I_2^- \quad (1.3-b) \\
S^+ + I^- & \leftrightarrow [S^+ \cdots I^-] \quad (1.4-a) \\
[S^+ \cdots I^-] + I^- & \rightarrow S^0 + I_2^- \quad (1.4-b) \\
I_2^- + I_2^+ & \rightarrow I_3^- + I^- \quad (1.5)
\end{align*}
\]

The first mechanism involves the iodine atom formation pathway. The as formed iodine atom quickly reacts with one equivalent of iodide in the electrolyte to form diiodide (I\textsubscript{2}⁻). The one electron reduction potential for I\textsuperscript{-}/I\textsuperscript{-} is 1.23 V vs. NHE as shown in Figure 1.6.\textsuperscript{42} This is higher than that of all the champion sensitizers. It means that if the iodine atom formation pathway is operative in DSSCs, then the regeneration process is an uphill reaction. Although strong evidence has shown...
that uphill reactions for iodide oxidation to the iodine atom can be fast, the DSSC community believes that direct formation of diiodide without iodine atom as the intermediate is the plausible reason for fast regeneration by iodide. This regeneration mechanism is described as Equation 1.4. First, one iodide ion approaches the oxidized sensitizer and form a closely related ion pair. Then, a second iodide ion approaches the ion pair. The one electron transfer to reduce the oxidized dye back to the ground state and the formation of an I-I bond takes place in one concerted step. The second regeneration mechanism is about 300 mV more favorable than the iodine atom pathway, making regeneration a downhill reaction for some champion sensitizers. Nevertheless, diiodide is the intermediate for both proposed mechanisms. Diiodide itself is subject to disproportionation and eventually forms triiodide as shown in Equation 1.5. The disproportionation process is energetically favored by 1.28 eV and consequently a loss of ~600 mV of the $V_{oc}$ as shown in the energetic diagram in Figure 1.6.

The huge free energy loss due to I$_3^-$ disproportionation lowers the maximum DSSC efficiency and researchers have been actively searching for alternative redox mediators. The second most studied redox mediator is based on cobalt coordination compounds such as [Co$^{III/II}$-(bpy)$_3$]$^{3+/2+}$, and its derivatives. This one electron redox shuttle has Co$^{III/II}$ redox potential that can be easily tuned by substitution of different groups on the bipyridine rings. The energetics is shown in Figure 1.6 along with the two electron reduction potential of I$_3^-$/$I^-$. Around 200 mV free energy could be potentially saved by this redox mediator substitution. Indeed, several research articles have reported the $V_{oc}$ values to be approaching 1 V by using cobalt based redox mediators, which I$_3^-$/$I^-$ couple is not able to achieve.
Figure 1.6 Relevant redox potentials of $I_3^-/(I_2^{\cdot-}, I^-)$, $0.0 \: I_2/I_2^{\cdot-}$, $+0.35 \: I^-/3I^-$, $+0.56 \: [Co^{III/II}(bpy)_3]^{3+/2+}$, $+0.93 \: I_2^{\cdot-}/(2I^-)$, $+1.23 \: I^{\cdot}/I^-$ employed in DSSCs as redox mediators. Adapted from reference 42.42
1.2.5 Interfacial Charge Recombination

When an injected electron reacts with an oxidized equivalent either on the surface or in the electrolyte, the electron transfer reaction is termed interfacial charge recombination or simply charge recombination (CR). This is an unwanted electron transfer process as the energy derived from the absorbed photon is not converted to electrical power and is wasted as heat. A great amount of work has been done to study the nature of charge recombination as well as methods to retard it.

Charge recombination kinetics do not usually follow a simple kinetic rate law. Although in some cases, a second-order equal concentration kinetic model satisfactorily described charge recombination data, a greater body of data showed skewed kinetics that extended over time scales from tens of nanoseconds to hundreds of milliseconds. The most commonly used kinetic model is the Kohlrausch–Williams–Watts (KWW) function which is written as Equation 1.6:

$$\Delta Abs = A \exp\left[\frac{k}{\beta}(kt)^\beta\right]\quad (1.6)$$

$$k_{cr} = \left[\frac{1}{k\beta} \times \Gamma\left(\frac{1}{\beta}\right)\right]^{-1}\quad (1.7)$$

The parameter $\beta$ has values between 0 and 1 and is inversely related to an underlying Lévy distribution of rate constants. In other words, the larger the $\beta$ value is, the narrower the distribution. Note that when the $\beta$ value is equal to 1, the KWW function collapses to a first-order kinetic model. The KWW function is popular for modeling charge recombination data because it adequately models a large body of experimental CR data, and is very simple. With normalized data, there are only two free floating parameters, $k$ and $\beta$. However, these abstracted fitting parameters do not necessarily give insightful kinetic information. Due to the interplay of $k$ and $\beta$, one often calculates an average rate constant in order to compare different data sets. Equation 1.7 shows one way of calculating the KWW derived average charge recombination rate constant, $k_{cr}$, by taking the first
moment. For a more rigorous comparison of kinetic rate constants, β values are sometimes fixed throughout the data set.

Several theories have been proposed to explain the stretched exponential nature of charge recombination kinetics. Notable ones include Continuous-Time Random-Walk (CTRW) model first derived by Scher and Montroll and later extended to TiO$_2$ by Nelson from UK$^{51}$ and a Random-Flight model proposed by Tachiya from Japan.$^{52}$ At sensitized TiO$_2$ interfaces, both the CTRW and random flight model suggest that charge recombination is limited by trapping and detrapping of TiO$_2$(e$^-$)s and electrons only move when they populate the TiO$_2$ conduction band. The difference is that CTRW only allows re-capture of electrons to the nearest trap whereas Random-Flight model allows re-capture to any empty traps. Using Monte Carlo simulations, both models fit experimental data with reasonable agreement and provide quite different trapping-detrapping rates.

Charge recombination studies to oxidized dye molecules have been quantified in respect to the change of the surface anchored sensitizers where the formal reduction potential was systematically altered and the TiO$_2$-sensitizer distance was controlled.$^{38,53-58}$ Charge recombination was believed to take place in the Marcus inverted region as driving force being larger than 1 V for most of the common ruthenium sensitizers. However, several articles reported a weak or no dependence on the free energy change that accompanies CR.$^{53,54}$ Tuning distance between the oxidized dye center and the TiO$_2$ surface has been proven to be effective in retarding charge recombination in many cases.$^{37,38,56}$ Larger distance will decrease the electronic coupling between TiO$_2$(e$^-$) and the oxidized dye molecule, resulting in an exponential decrease of charge recombination rate constants. There are two common ways to increase the distance for charge recombination. One is to use a rigid spacer like phenylenethynylene.$^{56}$ The second way is to covalently link an electron donor with the chromophore.$^{37,38,59}$ However, care needs to be taken for the second method as a highly conjugated linker between the chromophore and the electron donor will make the electronic communication between the injected electron and both the chromophore
and the donor possible. Rapid intramolecular hole transfer through a conjugated linker is likely to provide charge recombination pathway to the closer chromophore center. This point will be elaborated in chapter 2 in detail.\textsuperscript{25,60}

Charge recombination from TiO\textsubscript{2}(e\textsuperscript{−}) to oxidized iodide species is known to be slow. It was believed that the slow charge recombination was due to the nature of two electron reduction of triiodide.\textsuperscript{13} One electron reduction of triiodide is energetically unfavorable to access by TiO\textsubscript{2}(e\textsuperscript{−}) as can be understood from Figure 1.6. Besides, triiodide is anionic and coulombic repulsion from a negatively charged TiO\textsubscript{2} surface is expected. Recently, some experimental data has shown that molecular iodine, I\textsubscript{2}, may be the most important electron acceptor in DSSCs. Iodine is a better one electron transfer acceptor than is I\textsuperscript{3−}.\textsuperscript{61} Some unpublished data showed that the charge recombination kinetics is cation dependent, suggesting electric field influence. My own dissertation research in collaboration with the Berlinguette group in Canada, found heteroatom change on sensitizer molecules profoundly influenced charge recombination to I\textsuperscript{3−}. The V\textsubscript{oc} values were directly correlated with the charge recombination kinetics.\textsuperscript{62}

Charge recombination to [Co\textsuperscript{III}(bpy)\textsubscript{3}]\textsuperscript{3+} is believed to be inhibited for very different reasons than that described for the I\textsubscript{3−}/I\textsuperscript{−} redox mediator. A spin change accompanies the reduction of [Co\textsuperscript{III}(bpy)\textsubscript{3}]\textsuperscript{3+} to [Co\textsuperscript{II}(bpy)\textsubscript{3}]\textsuperscript{2+}. The Co\textsuperscript{III} center is low spin with a (t\textsubscript{2g}\textsuperscript{6}) electronic configuration and upon reduction the Co\textsuperscript{II} production is high spin with a (t\textsubscript{2g}\textsuperscript{5}, eg\textsuperscript{*2}) configuration.\textsuperscript{63,64} This spin change apparently hinders recombination relative to other outer-sphere redox mediators such as ferrocenium/ferrocene or organic electron shuttles.\textsuperscript{36,65} However, high efficiency solar cells employing cobalt based redox mediators are often achieved with certain blocking layer deposited to prevent this unwanted charge recombination process.\textsuperscript{47,48}
1.3 Charge Hopping between Immobilized Molecules and the Chemical Applications

1.3.1 Percolation Threshold for Charge Hopping

Anatase TiO$_2$ has a conduction band edge at around -0.76 V versus the normal hydrogen electrode (NHE) in 0.1 M LiClO$_4$ acetonitrile electrolyte and a corresponding valence band edge at around +2.44 V.$^{13}$ In between lies the band gap that in principle does not allow charges to move. However, in the mid-1990s, experimental evidence were found that the mesoporous nanocrystalline TiO$_2$ surface bound ruthenium coordination compounds were electrochemically redox active even though their reduction potentials were within the band gap of TiO$_2$. Large reversible anodic and cathodic currents were observed from cyclic voltammetry experiments that were beyond what could be attributed to the redox reactions at the planar FTO substrate. This somewhat surprising observation led to the postulation that self-exchange electron transfer between adjacent molecules was responsible for the electro-active thin films.$^{66}$

Bonhôte and coworkers first postulated a detailed mechanism for the conductivity of a monolayer of aromatic amines anchored to nanocrystalline metal oxide thin films.$^{67}$ The method employed was chronoabsorptometry. Upon application of a positive potential jump, the surface anchored triaryl amine compounds were electrochemically oxidized and an absorption feature of the oxidized species was monitored by UV-Vis absorption. The data were plotted as the absorption change as a function of the square root of time, called Anson plot, which showed a linear response at the early absorption rise time, Figure 1.7. An apparent diffusion rate constant, $D_{app}$, was calculated from a modified equation from the classical chronocoulometric method, Equation 1.8, also known as the Cottrell equation:

$$\Delta A = 2 \Delta A_f D_{app}^{0.5} t^{0.5} / (d n^{0.5})$$

(1.8)
where $\Delta A$ is the absorbance change; $\Delta A_f$ is the final absorbance change; and $d$ is the film thickness. By measuring $D_{app}$ of the phosphonated triaryl amine compound anchored on different metal oxide surfaces, TiO$_2$ or Al$_2$O$_3$, in solvents with different dielectric constants, and at different surface coverages, it was found that $D_{app}$ was dependent on both the rate of electron transfer and the density of conducting paths. Ion motions in the electrolyte accompanying hole hopping were required to achieve fast electrochemical oxidation. A vital discovery was that the surface coverage needs to be around 50% to turn on the oxidation process. A graphical depiction of the so-called ‘percolation threshold’ is illustrated in Figure 1.8c. As the density of adjacent electro-active molecules exceeded half of the maximum surface coverage, pathways for oxidizing the whole film could be realized.

Anion insertion accompanying hole hopping upon positive electrochemical polarizations was later observed by Wang and coworkers with a PMI-T2-TPA organic dye, where PMI is perylenemonoimide electron acceptor, T2 is a bithiophene bridge, and TPA is triphenylamine electron donor. Cyclic voltammetry showed that the return wave for the second oxidation of this organic dye was absent unless the voltage reached -0.6 V where the TiO$_2$ conduction band was accessed. It was asserted that anion insertion during the second oxidation hampered electron transfer when the voltage was returned to the initial conditions. One novel feature of this organic dye was that it showed either p-type or n-type conduction when grafted on insulating Al$_2$O$_3$ with similar $D_{app}$. 
Figure 1.7 Optical Anson plot for nanocrystalline TiO$_2$ electrodes derivatized with the phosphonated triarylamino in EtMeIm$^+\text{Tf}_2\text{N}^-$. Potential step was from 0.2 to 1.0 V. Taken from reference 67.67
Figure 1.8 Proposed mechanism for lateral charge transport through a monolayer of a phosphonated triaryl amine on porous metal oxide on conductive substrate: (a) cross section of a half pore; (b) top view of a monolayer with possibilities of electron hopping in a square (left) and in a triangular (right) lattice; (c) scheme of a metal oxide surface bearing various submonolayer surface concentrations of the aforementioned compound in a square lattice, with charge paths opening above the percolation threshold ($\Gamma \geq 0.5 \Gamma^0$). Taken from reference 67.
1.3.2 Molecular Structure Influence on Charge Hopping

Intermolecular electron transfer reactions with surface anchored redox active molecules are generally thought to occur through space. The separation between adjacent molecules is generally larger than 10 Å, providing weak electronic coupling and non-adiabatic electron transfer. Non-adiabatic Marcus theory was used to treat isoenergetic electron transfer on the surface. The rate, $r$, can be described by Equation 1.9:

$$r = \frac{2\pi}{\hbar} |J|^2 \frac{1}{\sqrt{4\pi \lambda_{tot} k_B T}} \exp\left(-\frac{\lambda_{tot}}{4 k_B T}ight)$$ (1.9)

where $J$ is the electronic coupling parameter; $\lambda_{tot}$ is the total reorganization energy; $k_B$ is the Boltzmann constant; $\hbar$ is Planck’s constant divided by $2\pi$; and $T$ is the temperature. The $D_{app}$ measured by electrochemistry can be related to the rate constant described by non-adiabatic Marcus theory by introducing a geometry factor, Equation 1.10:

$$D_{app} = \frac{r R^2}{6}$$ (1.10)

where $R$ is the intermolecular distance between adjacent molecules. Note that due to the nature of interconnected TiO$_2$ nanoparticles and possible inhomogeneous distribution of molecules and orientations, the calculation of $r$ based on non-adiabatic Marcus theory represents an upper limit for $D_{app}$. Barnes, Nelson and coworkers from Imperial College London did careful studies on the comparison of a series of ruthenium coordination compounds and organic dyes (Figure 1.9) based on DFT calculations and temperature dependent CV measurements. They observed an increase in the current response with increasing temperature during CV experiments on a ruthenium–phthalocyanine dye on TiO$_2$/FTO in 0.1 M TBAP (TBA = n-tetrabutylammonium, P = hexafluorophosphate) acetonitrile electrolyte, consistent with a thermal activation process. Arrhenius analysis of $D_{app}$ plotted as a function of $1/T$ combined with non-adiabatic Marcus theory allowed for experimental determination of the reorganization energies for the series of compounds.
They were compared with the theoretical value as shown in Figure 1.9. It was found that the outer sphere reorganization energy ($\lambda_o$) for most compounds accounts for over 80% of the total reorganization energy ($\lambda_{tot}$). The outer sphere reorganization energy is governed by the surface surroundings and electrolyte interactions with the surface anchored molecules whereas the rigidity of the molecules determines the inner sphere reorganization energy ($\lambda_i$). Molecules like phthalocyanine based compounds have a larger $\pi$ system, hence having a smaller inner sphere reorganization energy. However, outer sphere reorganization energy dominates the total reorganization energy. By comparing the molecular HOMO orbital size, one may conclude that a smaller sized HOMO orbital will induce larger outer sphere reorganization energy. It was recommended that the design of rigid conjugated molecules that are potentially lower in reorganization energy is preferred for pursuing faster intermolecular charge transfer on metal oxide surfaces.
Figure 1.9 The calculated reorganization energies including the inner sphere and outer sphere reorganization energies and the measured values for the ruthenium polypyridyl series, organic indoline dye series, and metal phthalocyanine series compounds. Taken from reference 70.
Qing Wang and coworkers compared $D_{\text{app}}$ of ruthenium polypyridyl compounds bearing different substituent groups at the 4,4'-position of the bipyridine ligands or with replacement of one of the bipyridine ligands by isothiocyanate ligands.\textsuperscript{71} One of the key discoveries was that the existence and orientation of two isothiocyanate ligands was vital to rapid hole percolation. The presence of isothiocyanate ligands expose the relatively large HOMO orbitals involved in hole hopping to the electrolyte that increases the electronic coupling for intermolecular hole transfer. The $cis$- orientation of two isothiocyanate ligands were able to promote a stacking configuration on the TiO$_2$ surface, acting as a hole hopping relay, Figure 1.10. These arguments were further supported by comparing the CV for Ru(dmb)(dcb)(NCS)$_2$ dye with and without a Hg$^{2+}$ solution treatment. As Hg$^{2+}$ ion was confirmed to bind to the sulfur end of the isothiocyanate ligand, the anodic current was significantly attenuated because of the lack of electronic communication between neighboring Ru-NCS moieties.

The influence molecular structure exhibits on hole percolation was further investigated in detail by Durrant’s group based on two structurally related ruthenium complex: $cis$-di(thiocyanato)(2,20-bipyridyl-4,40-dicarboxylic acid)-(2,20-bipyridyl-4,40-tridecyl) ruthenium(II), N621, and $cis$-di(thiocyanato)(2,20- bipyridyl-4,40- dicarboxylic acid)- (2,20-bipyridyl-4,40- bis(vinyltriphenyl amine)) ruthenium(II), HW456.\textsuperscript{72} HW456 had two pendent triphenyl amine groups on one of the bipyridine ligands whereas N621 had two long redox inactive alkyl chains. Surprisingly, with the same isothiocyanate ligand configuration, the $D_{\text{app}}$ of HW456 showed more than 20 times faster hole hopping rate than N621. Hg$^{2+}$ treatment blocked hole percolation for N621 and increased hole hopping for HW456. It was clearly revealed that N621 had similar hole hopping pathway as was shown by Wang, but the main pathway for HW456 was from triphenyl amine radical cations that did not react with Hg$^{2+}$. This study also implied that triphenyl amine based hole transfer moiety potentially had faster hopping properties than Ru-NCS compounds.
Figure 1.10  Schematic model showing the configuration of Ru(dmb)(dcb)(NCS)$_2$ on the (101) surface of anatase TiO$_2$. ‘dmb’ is 4,4’-dimethyl-bipyridine and ‘dcb’ is 4,4’-dicarboxy-bipyridine. Taken and modified from reference 71.\textsuperscript{71}
Surface modification is another factor that may influence charge hopping. In 2001, our group found an unexpected cation dependence for intermolecular hole transfer. Intermolecular hole transfer of ruthenium polypyridyl compounds in TBAClO$_4$ electrolyte was turned off when the TiO$_2$ or ZrO$_2$ substrates were base pretreated. Other small cations like H$^+$ or Li$^+$ on the other hand could turn on intermolecular hole transfer. This observation was interpreted with respect to the anchoring group binding mode to the metal oxide surfaces. The flexibility of carboxylic acid binding in the presence of protons with respect to carboxylate binding might enhance translational mobility, hence leading to a higher probability of transferring charges intermolecularly. The Meyer and Galoppini groups later studied the dependence of intermolecular charge transfer on the ruthenium hole–metal oxide surface distance. Tripodal type ruthenium polypyridyl compounds were employed that separated the ruthenium center away from the surface for ~17 Å. Comparison was made between the tripodal compounds and the model compound, [Ru$^{III/II}$ (bpy)$_2$(dcb)]$^{3+/2+}$ by measuring $D_{app}$ with chronoabsorptometry. Similar $D_{app}$ values of ~10$^{-11}$ cm$^2$/s were obtained, indicating little dependence on the distance and insignificant influence of specific ion adsorption on the surface.

The identity of the surface anchoring groups can also play a role in intermolecular hole transfer reactions. Hanson and coworkers studied with a series of two, four, and six phosphonic acids derivatized ruthenium polypyridyl compounds (compound 1-3, Figure 1.11) anchored on TiO$_2$ in 0.1 M HClO$_4$ aqueous solution. Another series with a methylene spacer between the anchoring group and bipyridine ligand (compound 1C-3C, Figure 1.11) was also tested. Minor variations were observed between series 1-3 and series 1C-3C with respect to the $D_{app}$ measured by chronoabsorptometry. However, large difference of $D_{app}$ with in each series was observed. a larger number of phosphonic acid anchoring groups led to slower hole hopping rate, with $D_{app}$ value smaller by a factor of 20. It was conjectured that hydrogen bonding or other types of ion pairing
to the non-anchoring phosphonic acids in such an aqueous environment may increase the reorganization energy for hole or electron transfer.
Figure 1.11  Structures of the phosphonate-derivatized polypyridyl complexes. Taken from reference 75.75
1.3.3 Charge Hopping Mediation

Charge hopping can be strongly influenced not only by the molecules that deliver charges but also by the electrolyte species or the TiO$_2$ conduction band that mediates charges and forms another charge hopping pathway.

In 1999, the Meyer group first discovered that intermolecular hole hopping of an [Os(bpy)$_2$(dcb)]$^{2+}$ compound on mesoporous nanocrystalline TiO$_2$ substrate could be mediated by an external redox active species present in the electrolyte.$^{76}$ They reduced the surface coverage of [Os(bpy)$_2$(dcb)]$^{2+}$ to 60% of the saturation surface coverage, a coverage where hole hopping could turned on with an applied external electrochemical bias at 1.3 V vs Ag/AgNO$_3$. The addition of $3\times10^{-5}$ M [Ru(bpy)$_3$]$^{2+}$ in the TBAPF$_6$ acetonitrile electrolyte greatly facilitated oxidation of the surface bound osmium compounds with an increased $D_{app}$ from $<1\times10^{-11}$ cm$^2$/s to $3.3\times10^{-10}$ cm$^2$/s, but not the reversed reduction. The presence of $3\times10^{-5}$ M [Os(bpy)$_3$]$^{2+}$ facilitated rapid oxidation of surface bound osmium compounds and the subsequent reduction when the applied potential was stepped back to 0 V. The phenomenon of solution redox species mediated intermolecular hole hopping was attributed to a sequence of redox reactions. The first oxidation took place at the ITO contact where [Ru$^0$(bpy)$_3$]$^{2+}$, for instance, was oxidized to [Ru$^{II}$(bpy)$_3$]$^{2+}$, that diffused to the immobilized [Os(bpy)$_2$(dcb)]$^{2+}$/TiO$_2$ and then, electron transfer occurred. The fact that only one way mediation was realized with [Ru(bpy)$_3$]$^{2+}$ while [Os(bpy)$_3$]$^{2+}$ mediated both oxidation and reduction was explained in terms of the redox potentials of mediators with respect to the surface bound species. Because of similar redox potentials of [Os(bpy)$_3$]$^{2+}$ and [Os(bpy)$_2$(dcb)]$^{2+}$, both mediation directions occurred with only a slight difference in $D_{app}$. With an unfavorable driving force of 0.36 V, the reduction of [Os(bpy)$_2$(dcb)]$^{3+}$ in the presence of [Ru(bpy)$_3$]$^{2+}$ could not be achieved.

Intermolecular charge hopping can also be mediated by surface coating. Bignozzi’s group introduced a poly(methyl methacrylate) (PMMA) coated TiO$_2$ film.$^{77}$ They first co-attached an
electron donor compound, \([\text{Ru(dcbH}_2\text{)}_2(\text{CN})_2]\) where dcbH\(_2\) is 2,2’-bipyridine-4,4’-dicarboxylic acid and a mixed-valence electron acceptor compound, \([\text{HOOCpyRu}^{\text{III}}(\text{NH}_3)_4(\text{NC})\text{Ru}^{\text{II}}(\text{CN})_5]^-\) where HOOCpy is pyridine-4-carboxylic acid in a 1:4 molar ratio on a 6 \(\mu\)m thick TiO\(_2\) film. With light excitation, \([\text{Ru(dcbH}_2\text{)}_2(\text{CN})_2]\) injected an electron into the TiO\(_2\) conduction band that was subsequently trapped on \([\text{HOOCpyRu}^{\text{III}}(\text{NH}_3)_4(\text{NC})\text{Ru}^{\text{II}}(\text{CN})_5]^-\). After 2 minutes of irradiation, the light was turned off and recovery of the ground state was monitored by UV-Vis absorption. This process took around 80 minutes to complete. Under similar conditions but with a PMMA coated TiO\(_2\) film, the recovery of the ground state took more than 36 hours. Also, it was suggested that O\(_2\) could strongly affect the hole hopping that led to charge recombination. Superoxide as a one electron reduced species of O\(_2\) was invoked.

Similar charge hopping that was initiated with light was also studied in our group for \([\text{Ru(bpy)}_2(\text{dbq})]/\text{TiO}_2\) where dbq is 4,4’-dicarboxy-2,2’-biquinoline.\(^{78}\) In purely electrochemical experiments, it was found that the reduction of the film was much faster than oxidation. Chronoabsorptometry analysis revealed that \(D_{\text{app}}(\text{Ru}^{2+/-})=(3.3\pm0.3)\times10^{-12}\) m\(^2\)/s, more than 10-fold larger than \(D_{\text{app}}(\text{Ru}^{\text{III}}/\text{II})=(2\pm1)\times10^{-13}\) m\(^2\)/s. The discrepancy of apparent rate constants between the two electron or hole hopping processes might be beyond the self-exchange reactions. Reduced dye electron hopping might go through the biquinoline \(\pi^*\) orbitals as it was a lower energy lying orbital while the oxidized dye hole hopping had to involve the ruthenium \(t_2g\) orbitals. Analogously, the trend of charge hopping rate was different from \([\text{Ru(bpy)}_3^{2+}]\) in fluid acetonitrile solution as Ru\(^{\text{III}/\text{II}}\) self-exchange rate constant was \(2\times10^9\) M\(^{-1}\) s\(^{-1}\) and the Ru\(^{2+/-}\) constant was \(8\times10^8\) M\(^{-1}\) s\(^{-1}\).\(^{79-82}\) The discrepancy might be due to different reorganization energy changed by surface anchoring. A more likely explanation suggested by the authors was that reduced dye electron hopping might be mediated by the conduction band of TiO\(_2\) that had proximate energy level as the reduced biquinoline. Later, the TiO\(_2\) conduction band mediated electron hopping mechanism was further confirmed by surface anchored heme, which was well explained by the Gerischer-type model,
Scheme 1.3. The characteristic of the Fe$^{III/II}$, i.e. hemin/heme, redox couple is that the $E_{1/2}$ reduction potential is -0.68 V vs Fe$^{+/0}$, where Fe stands for ferrocene. The $E_{1/2}$ was isoenergetic with the conduction band edge of TiO$_2$, rendering the reduction of Fe$^{III}$ to Fe$^{II}$ easier by electron transfer through the TiO$_2$ acceptor states compared to the oxidation of Fe$^{II}$ to Fe$^{III}$ as the Fe$^{II}$ donor state was below the TiO$_2$ acceptor states. Indeed, the $D_{app}$ measured was much smaller for the oxidation of heme than the reduction of hemin and there was no percolation threshold observed even though the surface coverage was below 10%.
Scheme 1.3  Gerischer-type model representing the overlap of donor and acceptor state of 
$[\text{Ru(bpy)}_2(\text{dcbq})]^{0/-}$ (a) and hemin/heme (b) with TiO$_2$ conduction band edge. Taken from reference 
83.83
1.3.4 Kinetic Modeling for Charge Hopping

The quantitation values of $D_{app}$ were obtained with an electrochemical assay that corresponded to full oxidation or reduction of a sensitized thin film. Hence, it was not possible to monitor single self-exchange reactions spectroscopically as the process does not induce any absorption change. Ardo in the Meyer group at Johns Hopkins University pioneered the use of transient polarization spectroscopy to monitor the self-exchange reactions transiently.\textsuperscript{84,85} For vertically polarized light excitation, the surface anchored molecules are preferentially excited at the north and south poles on TiO$_2$ nanocrystallites assuming the vectorial transition dipole moments are perpendicular to the surface. This is usually valid as MLCT transitions of most of the ruthenium polypyridyl sensitizers occurs from the ruthenium center to the surface anchoring dcb ligand. After excited state electron injection, the oxidizing equivalent will hop among adjacent molecules before charge recombination. The intermolecular hole hopping process will decrease the initial anisotropy and therefore an anisotropy assay can be used to evaluate photoinduced intermolecular charge transfer kinetics. One of the advantages of the anisotropy assay over other electrochemical methods is that intermolecular charge transfer can be studied in the absence of electrolyte. Furthermore, the influence of electrolyte species of high ionic strength on intermolecular charge transfer is capable of being studied.

Anisotropy decay data for two widely studied sensitizers cis-Ru(dnb)(dcb)(NCS)$_2$ (Z907) and cis-Ru(dcb)$_2$(NCS)$_2$ (N3) were quantified and the data are shown in Figure 1.12. Within the charge recombination time scale, Z907 showed complete anisotropy decay with highly skewed kinetics. The stretched exponential function, Equation 1.6 was used to satisfactorily simulate the anisotropy decay with an abstracted hole hopping correlated time constant of 9.6 $\mu$s. However, the little to no anisotropy decay for N3 within the charge recombination window made the analysis difficult. The faster hole hopping rate of Z907 over N3 was consistent with the argument by Wang
and coworkers that the preferential NCS group alignment between adjacent molecules for Z907 upon surface anchoring aided fast hole hopping.

The authors also measured the anisotropy decay for \([\text{Ru(dt}b)_2(\text{dcb})]^{2+}/\text{TiO}_2\) where dtb is 4,4'-ditert-butyl bipyridine. It was found that intermolecular hole transfer could only be activated in the presence of 10 mM LiClO_4 electrolyte. The different behavior was intriguing comparing with Z907 that displayed intermolecular hole hopping whether electrolyte was present or not. It was postulated that ion compensation was necessary for highly charged \([\text{Ru(dt}b)_2(\text{dcb})]^{2+}\) to have intermolecular hole hopping occur whereas it was not for neutral Z907. However, care needed to be taken to compare or relate the photoinduced charge hopping kinetics with electrochemically observed ones as \(D_{\text{app}}\) measurement required the oxidation or reduction of the whole mesoporous film while photo-generated charge carriers were a small portion. Necking regions of interconnected TiO_2 nanoparticles might affect the charge hopping and propagation whereas photo-generated charge might not need to hop through the necking regions before charge recombination.
Figure 1.12 Transient absorption difference magic-angle (left axis) and anisotropy (right axis) changes for cis-Ru(dnb)(dcb)(NCS)$_2$/TiO$_2$ (black, solid) and cis-Ru(decb)$_2$(NCS)$_2$/TiO$_2$ thin films immersed in neat acetonitrile monitored at 465 nm after pulsed laser excitation. Overlaid in green, on the anisotropy kinetics, are fits to a stretched exponential function. Taken from reference 85.
There was one particular hole hopping situation that could be monitored spectroscopically. Hoertz and coworkers discovered that for [Os(bpy)$_2$(dcbq)]/TiO$_2$ following 417 nm light excitation, an electron would be injected into TiO$_2$ and quickly trapped to the low lying biquinoline ligand on another compound.$^{78}$ This formed a long-lived charge separated state with equal concentrations of [Os$^{III}$(bpy)$_2$(dcbq)]/TiO$_2$ and [Os(bpy)$_2$(dcbq$^-$)]/TiO$_2$. The recovery of the ground state was a result of intermolecular hole and electron transfer across the surface. The process could be monitored by transient absorption change formulated as $\Delta A = A(M^{III}) + A(M^+) - 2A(M^{II})$, where M represented [Os(bpy)$_2$(dcbq)]/TiO$_2$. The kinetics could be well modeled by a stretched exponential function mentioned in Equation 1.6, Figure 1.13. The fit yielded a rate constant $k$ of $(8 \pm 5) \times 10^5$ s$^{-1}$ and $\beta = 0.25 \pm 0.05$.

In chapter 2 of this thesis, transient absorption spectroscopy was used to monitor another similar hole hopping event. Long lived charge separated state was also observed that spanned the time scale from hundreds of nanoseconds to milliseconds. The advancement was that the kinetics were simulated by a random walk model (Monte Carlo Simulation). The satisfactory modeling provided an average hole hopping frequency of $(130$ ns$)^{-1}$. The abstracted value gave insights into how fast we could use intermolecular hole hopping processes to accumulate multiple holes on one catalytic site.
Figure 1.13  Absorption change monitored at 570 nm following 417 nm laser light excitation of [Os(bpy)$_2$(dcbq)]/TiO$_2$ ($\Gamma = 6.5 \times 10^{-8}$ mol/cm$^2$). Overlaid on the data is a best fit (while line) to Equation 1.6. Residuals for the fit are shown below. Taken from reference 78.$^{78}$
1.3.5 Influence of Charge Hopping on DSSC Performance

There are two possible effects discussed in the literature about charge hopping on DSSC performance. The positive side is regeneration by redox mediators might be facilitated. The possible down side is an increased charge recombination with TiO$_2$(e$^-$).

Parkinson’s group in 1999 first discovered that the absorbed photon-to-current conversion efficiency (APCE) was dependent on the surface coverage of N3. At surface coverages lower than 30% of the saturation surface coverage, the APCE dropped dramatically. One of the possibilities inferred by the authors was that intermolecular hole hopping was helping oxidized dyes to be regenerated by iodide more efficiently. The conjecture was depicted in Scheme 1.4. At high surface coverage, a hole percolation path formed so that oxidized dyes in the inner pores or the necking regions were able to hop out to areas that iodide could access. On the contrary, isolated N3 dyes at low surface coverage might not be efficiently regenerated by iodide so that a loss of current response was observed. Li and coworkers calculated the mean hole diffusion length in operational DSSC given the lifetimes for the oxidized dyes N621 and HW456. They found that HW456 could have hole diffusion length as long as 8 nm which is about half the diameter of a TiO$_2$ nanoparticle. This is long enough for holes at small pores or necking region to escape. The authors thus concluded that redox mediators or hole transporting materials in solid state DSSCs are more likely to reach oxidized dyes with fast hole hopping rates and long diffusion lengths. Meanwhile, the authors also put forward a caveat that efficient hole hopping might help surface impurities gather holes resulting in deleterious faster charge recombination.
Scheme 1.4 A cartoon showing how hole hopping at high surface coverage of N3 dye was able to help facilitate regeneration by iodide while isolated N3 at low surface coverage did not. Taken from reference 86.86
1.3.6 Molecular Wiring of Insulators for Lithium-Ion Battery Application

Molecular charge hopping process imparts redox activity to an insulator. In the case of mesoporous nanocrystalline TiO$_2$ or ZrO$_2$ for anchoring of molecules, they acted only as a high surface area scaffold. Wang, Grätzel and coworkers first anchored molecules on the surface of olivine-structured LiFePO$_4$, a promising cathode material for lithium-ion batteries. In this case, LiFePO$_4$ was not only a scaffold but also did redox chemistry. The use of LiFePO$_4$ as a cathode material in lithium-ion batteries suffered from low electronic conductivity. The material could intercalate Li$^+$ upon reduction, but did not delithiate upon charging unless the conductivity was improved by a carbon coating.

The conductive nature of electron/hole transport of redox active molecules at surface coverage larger than the percolation threshold offered a unique way of solving the conductivity challenge for LiFePO$_4$. The self-assembled monolayer contributed little weight and occupied little space for the purpose of maintaining the highest possible energy density for lithium-ion batteries. Wang and coworkers used 4-[bis(4-methoxyphenyl)amino]benzylphosphonic acid (BMABP) as the anchoring molecules because of close redox potential (3.5 V vs. Li$^+$/Li) comparing with LiFePO$_4$ (3.45 V vs. Li$^+$/Li). Upon positive polarization of the LiFePO$_4$ electrode, holes propagated through the BMABP monolayer and injected into the valence band of LiFePO$_4$. As a result, Li$^+$ was ejected from the LiFePO$_4$ lattice. Conversely, oxidized BMABP could propagate electrons upon electrode reduction and the reduced molecules injected electrons into the conduction band of FePO$_4$ accompanied by the uptake of Li$^+$, Figure 1.14.

Cyclic voltammograms showed no current response for bare LiFePO$_4$ electrode while a significant current response was observed for both delithiation and lithiation process when LiFePO$_4$ was wired with BMABP at saturation concentration of LiPF$_6$, Figure 1.15. The current plateaued at higher potentials as well as at lower potentials, showing the catalytic behavior of BMABP. The CV is significantly different from BMABP derivatized Al$_2$O$_3$ film that only showed diffusion
limited current response. Employment of the BMABP derivatized LiFePO$_4$ cathode along with Li$_4$Ti$_5$O$_{12}$ as the anode in an operational lithium-ion battery achieved a voltage of 1.9 V, which had little overpotential.

More researches on the topic of molecular wiring of insulators were carried out later for targeting other battery materials with different redox active molecules.$^{88-91}$ Ruthenium polypyridyl compounds typically has higher redox potentials, $>4$ V vs. Li$^+/Li$. They were chosen to wire olivine type cathode materials with higher potentials like LiMnPO$_4$ which is $\approx$4.1 V.$^{91}$ The disadvantage was that the current would drop upon cycling. The decreased activity was attributed to the phase change while LiMnPO$_4$ was releasing or uptaking Li$^+$. 
Figure 1.14 Band and density of states (DOS) diagrams showing the working principle of charging and discharging of an insulating battery material by a surface-confined molecular charge transport layer. The shaded and unshaded Gaussian functions represent the occupied and unoccupied electronic states of the redox relay, their intersection defining the Fermi level of the molecular hole transporter. (a) Structure of LiFePO$_4$ and surface anchored BMABP. (b) Band diagram and density of electronic states (DOS) curves of the integrated electrode system at equilibrium. (c) Charging the cathode by hole propagation through the molecular monolayer; hole injection from BMABP$^+$ into LiFePO$_4$ and Li$^+$ release from LiFePO$_4$. (d) Discharging the electrode by reversing these three processes. Taken from reference 87. $^{87}$
Figure 1.15 Cyclic voltammograms (CV) of BMABP-derivatized LiFePO₄ (red, blue) and mesoscopic Al₂O₃ (green) electrodes. The black line shows the curve of a bare LiFePO₄ electrode. The scan rate is 0.1 V/s. The current of BMABP-derivatized mesoscopic Al₂O₃ has been normalized according to its surface area. The electrolyte was a saturated solution of LiPF₆ in a 1:1 (w/w) mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) except for the blue curve, where 0.5 M LiPF₆ was used. Taken from reference 87.⁸⁷
1.3.7 Multi-electron Redox Catalysis Using Cross-Surface Electron/Hole Transfer

A DSSC is a device that converts light energy into electricity. Light absorption in a DSSC inherently generates one electron and one “hole”. The efficiency is seriously dependent on the sunlight condition and does not function during the night when energy is often most needed. Hence DSSCs like all PV materials suffer from being unable to store energy. Converting day light energy into the form of chemical bonds, also known as chemical fuels, is another strategy to overcome the shortcoming of DSSCs. Figure 1.16 showed a general design of such a device termed a dye sensitized photoelectrosynthesis cell (DSPEC). The ultimate goal was to oxidize water to molecular oxygen at the photoanode by molecular water catalysis while the electrons were shuttled to the cathode through the outer circuit to reduce carbon dioxide to possibly methane by a CO\textsubscript{2} reduction catalyst. Therefore, solar energy was stored in C-H bond and O-O bond that could be later used in a fuel cell to generate electricity whenever needed. The key step in the DSPEC was multi-electron redox catalysis to form C-H or O-O bonds.

Several molecular designs were investigated to achieve multiple hole or electron accumulation at single catalytic site including metal oxidize clusters or chromophore-catalyst assemblies. However, great synthetic efforts needed to be taken to make such an assembly. Separating the chromophore and the catalyst would be hugely beneficial in this manner. Cross-surface intermolecular hole/electron transfer would be a viable way to achieve multiple charge accumulation at single catalytic site. With this idea, several reports have stepped forward toward the goal.
Figure 1.16  Dye sensitized photoelectrosynthesis cell (DSPEC) for water oxidation to molecular oxygen at the photoanode and CO$_2$ reduction to methane at the cathode. Taken from reference 92.\textsuperscript{92}
In an attempt to show the charge accumulation at a catalytic site by intermolecular hole hopping, Ardo and Meyer first co-anchored Z907 and Co\textsuperscript{II}(TCPP) where TCPP is tetracarboxyphenyl porphyrin with a molar ratio of 100 to 1 on TiO\textsubscript{2} thin film.\textsuperscript{84} Upon 683 nm pulsed laser light excitation, Z907 excited state injected electrons into TiO\textsubscript{2}. The oxidized molecule Z907\textsuperscript{+} then hopped across the surface to find Co\textsuperscript{II}TCPP and oxidized the cobalt center from the formal oxidation state of two to three. This electron transfer reaction was downhill by a free energy change of -1.1 eV. Z907\textsuperscript{+} was considered to perform a random walk and more steps were expected to reach Co\textsuperscript{II}TCPP while the microsecond to millisecond time scale interfacial charge recombination would kill some of the photo-initiated Z907\textsuperscript{+}. Nevertheless, around 10\% of the co-anchored Co\textsuperscript{II}TCPP were oxidized with a quantum yield of electron transfer of 3\% from Z907\textsuperscript{+} based on the transient absorption modeling as shown in Figure 1.17. The longer time scale kinetics that extended to the seconds time scale were attributed to the charge recombination between TiO\textsubscript{2}(e\textsuperscript{-}) and Co\textsuperscript{II}TCPP.

With the proof of concept, Song, Meyer and coworkers investigated a water oxidation catalyst that required accumulation of four holes to do catalysis.\textsuperscript{95} The chromophore employed was [Ru(bpy)\textsubscript{2}((4,4\textquoteleft-(OH)\textsubscript{2}PO\textsubscript{2}bpy)]\textsuperscript{2+}, abbreviated as Ru\textsuperscript{II}P\textsuperscript{2+} and the catalyst was [Ru(Mebimpy)((4,4\textquoteleft-(OH)\textsubscript{2}PO-CH\textsubscript{2})\textsubscript{2}bpy)(OH\textsubscript{2})]\textsuperscript{2+} where Mebimpy was 2,6-bis(1-methylbenzimidazol-2-yl)pyridine, abbreviated as Ru\textsuperscript{II}OH\textsubscript{2}\textsuperscript{2+}. The sensitization was configured as 8×10\textsuperscript{-8} mol cm\textsuperscript{-2} Ru\textsuperscript{II}P\textsuperscript{2+} and 4×10\textsuperscript{-8} mol cm\textsuperscript{-2} Ru\textsuperscript{II}OH\textsubscript{2}\textsuperscript{2+} on TiO\textsubscript{2} in 0.1 M HClO\textsubscript{4} in water. 532 nm laser light excitation revealed that ~73\% of the oxidative equivalents at Ru\textsuperscript{III}OH\textsubscript{2}\textsuperscript{3+}/TiO\textsubscript{2} was generated from intermolecular hole hopping of the photo-initiated Ru\textsuperscript{III}P\textsuperscript{3+} within 20 ns, with an overall catalyst oxidation of 83\%. The fast production of one electron oxidized catalyst was attributed to the number and proximity of the photo-initiated Ru\textsuperscript{III}P\textsuperscript{3+} to the catalyst. A decreased yield of ~14\% of the initial formation of Ru\textsuperscript{III}OH\textsubscript{2}\textsuperscript{3+}/TiO\textsubscript{2} with ~40\% of the previous surface coverage proved the hypothesis. The second oxidative equivalent accumulation was further studied.
by transient absorption spectroscopy. The starting oxidation state of the catalyst was fixed to Ru\textsuperscript{III} and the formation of Ru\textsuperscript{IV}OH\textsuperscript{3+} was monitored after laser excitation of Ru\textsuperscript{II}P\textsuperscript{2+}/Ru\textsuperscript{III}OH\textsuperscript{2+}/TiO\textsubscript{2}. However, due to fast back electron transfer to the pre-oxidized Ru\textsuperscript{III}OH\textsuperscript{2+} and low signal-to-noise in the UV region where the Ru\textsuperscript{III}OH\textsuperscript{2+} and Ru\textsuperscript{IV}OH\textsuperscript{3+} showed the most significant difference in absorption, the formation of the second oxidative equivalent of Ru\textsuperscript{IV}OH\textsuperscript{3+} was difficult to discern.

The more encouraging results came from steady state illumination of 5.1×10\textsuperscript{-8} mol cm\textsuperscript{-2} Ru\textsuperscript{II}P\textsuperscript{2+} and 8.0×10\textsuperscript{-9} mol cm\textsuperscript{-2} Ru\textsuperscript{II}OH\textsuperscript{2+} on TiO\textsubscript{2} with 0.2 V applied bias. Spectral modeling showed that 1.5×10\textsuperscript{-9} mol cm\textsuperscript{-2} of Ru\textsuperscript{IV}=O\textsuperscript{2+} formed as the doubly oxidized species on TiO\textsubscript{2}, Figure 1.18. This is remarkable as intermolecular hole transfer could contribute to the accumulation of multiple hole equivalents on single water oxidation catalyst. With further modification of the surface like the core-shell structure to retard charge recombination,\textsuperscript{96} more equivalents of holes will be expected to accumulate and water oxidation may be achievable via intermolecular electron/hole hopping mechanism.
Figure 1.17 Transient absorption difference signals after 683 nm pulsed laser excitation of a TiO\textsubscript{2} thin film electrode cofunctionalized with Z907 and CoTCPP in an $\sim$100:1 molar ratio and immersed in 100 mM TBAClO\textsubscript{4}/CH\textsubscript{3}CN (absorbed fluence $\approx$ 2.65 mJ/cm\textsuperscript{2}). (A) Spectra at the indicated delay times; the 85 $\mu$s data are modeled by spectral addition of Co\textsuperscript{II}, Co\textsuperscript{III}, TiO\textsubscript{2}(e$^-$), and Ru\textsuperscript{III} in a -1:1:9:8 mol ratio (orange). (B) Kinetics monitored at 436 nm that correspond to (i) Z907$^+$ + Co\textsuperscript{II} followed by (ii) Co\textsuperscript{III} + TiO\textsubscript{2}(e$^-$) to yield the initial state, Ru\textsuperscript{II}/TiO\textsubscript{2}/Co\textsuperscript{II}. Taken from reference 84.\textsuperscript{84}
Figure 1.18  Spectral changes of $5.1 \times 10^{-8}$ mol cm$^{-2}$ Ru$^{3+}$P$^2+$ and $8.0 \times 10^{-9}$ mol cm$^{-2}$ Ru$^{2+}$OH$^2+$ coloaded on TiO$_2$ photoanodes with 0.2 V applied bias upon 445 nm (8.3 mW) irradiation for $\sim$200–300 s (to approach photoequilibrium). Taken from reference 95.95
1.4 Summary

Harnessing solar energy and converting it to useful electrical work has been the main theme of this thesis work. Dye-sensitized solar cells represent a promising third generation photovoltaic technology that could enable renewable energy for future generations if important challenges are addressed. In the following chapters, many of these challenges will be discussed and addressed. These include the search for more robust and red sensitizing dye molecules, deeper understanding of the relationship among intramolecular hole transfer, charge recombination and \( V_{oc} \), Chapter 2, the effect of sensitizer regeneration on \( V_{oc} \), Chapter 3, dye aggregation and surface modification, Chapter 4, sensitizer-redox mediator interaction and its influence on charge recombination and \( V_{oc} \), Chapter 5, and finally performance improvement based on excited state hot injection, Chapter 6.

Harnessing solar energy in the form of chemical bonds is also part of the interest of this thesis work. Utilizing cross surface intermolecular electron transfer or hole hopping is one of the strategies to accumulate multiple holes on one catalytic site. In Chapter 2, this vital process for possible chemical fuel production will be discussed and insights will be given from a kinetic perspective.
1.5 References


(10) The National Center for Photovoltaics (NCPV) at NREL http://www.nrel.gov/ncpv/.


Chapter 2: Intramolecular and Lateral Intermolecular Hole Transfer at the Sensitized TiO$_2$ Interface

In part a compilation of two publications.$^{1,2}$

This work was collaborative in conjunction with Kiyoshi C. D. Robson$^\dagger$, Evan E. Beauvilliers$^\ddagger$, Patrik G. Johansson$^\ddagger$, Eduardo Schott$\S$, Ximena Zarate$\S$ Ramiro Arratia-Perez$\dagger$ and Curtis P. Berlinguette$^\dagger$

$^\dagger$Johns Hopkins University, Baltimore, MD, USA

$^\ddagger$University of Calgary, Calgary, Canada

$\S$Universidad Bernardo O’Higgins, Santiago, Chile

$^\dagger$Universidad Andres Bello, Santiago, Chile

2.1 Introduction

Molecules with two or more redox active groups have provided insights into interfacial electron transfer reactions at semiconductor interfaces that could not have been obtained from molecules with a single redox active group.$^{1,3-9}$ A relatively common motif used for solar energy conversion in dye-sensitized solar cells is shown generically in Scheme 2.1. A sensitizing dye molecule S, absorbs a photon to create an excited state that initiates two charge transfer reactions: 1) electron transfer to a TiO$_2$ nanocrystallite; and 2) intramolecular-hole transfer to a covalently
linked donor. The net result is an interfacial charge separated state comprised of an injected electron and an oxidized donor. Here we report a study of ten electron donor-acceptor compounds where the quantum yield for intramolecular-hole transfer was systematically controlled.
Scheme 2.1 Excited state electron injection and intramolecular hole transfer for a Sensitizer-linker-Donor compound anchored on TiO$_2$ surface.
Previous studies have shown that intramolecular-hole transfer can lead to a dramatic enhancement of the lifetime of the electron that was injected into the semiconductor.\textsuperscript{3,6} However, hole transfer comes at the expense of a significant loss in free energy that is not always compensated for by the longer lifetime. It is therefore of interest to examine whether the driving force for hole transfer can be reduced without a loss in lifetime. Under such conditions, an ‘equilibrium’ like that shown in Scheme 2.2 is expected. This is not a true equilibrium as recombination of the injected electron with the dye molecule is necessarily thermodynamically favored. Nevertheless, this recombination reaction is known to require milliseconds for completion\textsuperscript{10} while intramolecular electron transfer is sub-nanosecond\textsuperscript{4} such that a quasi-equilibrium is expected on intermediate time scales and under steady-state illumination. Quantification of such a redox equilibrium is further complicated by the non-ideal behavior of molecules anchored to conductive surfaces.\textsuperscript{11,12} To our knowledge with the one exception described below, no previous studies have characterized such interfacial equilibria and examined how this influenced recombination or the free energy stored in the interfacial charge separated state as reported by the open circuit photovoltage.
Scheme 2.2 The interfacial redox equilibrium under study.
In this chapter, electron transfer studies of five ruthenium terpyridyl compounds with a tridentate cyclometalated ligand conjugated to a triaryl amine donor were reported at TiO$_2$ interfaces, Scheme 2.3. Light excitation of these sensitized materials led to rapid excited state injection with hole transfer yields that could be qualitatively predicted based on the solution reduction potentials. Surprisingly, charge recombination rates were insensitive to the location of the oxidizing equivalent, i.e. Ru$^{III}$ or NAr$_3$$^{•+}$, while the open circuit photovoltages were consistently larger for the compound that had undergone hole transfer. The coincidence of redox potentials and charge recombination kinetics suggested that the interfacial dipole moment contributed to the measured open circuit photovoltage. Herein, DFT calculations have been employed to quantify the dipole moments before and after light excitation. A total of ten donor-acceptor compounds have been characterized with a broad range of Ru$^{III/II}$ and NAr$_3$$^{•+/0}$ reduction potentials so that the redox equilibrium in Scheme 2.1 could be systematically probed. *In situ* spectroelectrochemical results showed non-Nernstian behavior that provided new insights into the factors that control non-ideality at semiconductor interfaces. In addition, a novel remote excited state injection from a NAr$_3$ donor was observed under conditions where the ruthenium center was in the formal oxidation state of three. This excited state injection was followed by rapid back electron transfer that was fast enough to compete with iodide oxidation. A lateral intermolecular hole hopping process was identified and modeled by Monte Carlo simulations.
Scheme 2.3 Molecular structures of the compounds with the indicated Ru$^{III/II}$ (blue) and NAr$_3$$^{+/-}$ (red) reduction potentials.
2.2 Experimental

Materials. Acetonitrile (Burdick & Jackson, spectrophotometric grade); methanol (Sigma-Aldrich, spectrophotometric grade, > 99.9%); tert-butanol (Fisher Scientific); lithium perchlorate (Aldrich, 99.99%); tetra-n-butylammonium hydroxide (1 M in methanol, Sigma-Aldrich); argon gas (Airgas, > 99.998%); oxygen gas (Airgas, industrial grade); titanium(IV) isopropoxide (Sigma-Aldrich, 97%); fluorine-doped, SnO₂-coated glass (FTO; Hartford Glass Co., Inc., 2.3 mm thick, 15 Ω/sq); and glass microscope slides (Fisher Scientific, 1 mm thick). The sensitizers in this study, C₁-C₅ in Scheme 2.3 and the methyl ester derivatives, abbreviated similarly E₁-E₅, were available from previous studies.¹³

Sensitized Metal Oxide Thin Films. Mesoporous nanocrystalline TiO₂ thin films were prepared as previously described.¹⁴ The films were then immersed in C₁-C₅ dye solutions in methanol with 1 equivalent TBAOH to help solubility or in E₁-E₅ dye solutions in acetonitrile tert-butanol mixture (v:v = 50:50). Films were then washed with neat CH₃CN and diagonally positioned in a standard 1 cm² quartz cuvette containing 0.5 M LiClO₄ acetonitrile solution. The electrolyte solutions were purged with argon gas for at least 30 min prior to experimentation.

Spectroscopy. UV-Vis Absorption. Steady-state UV-vis absorption spectra were obtained on a Varian Cary 50 spectrophotometer. All experiments done were performed at room temperature unless mentioned otherwise.

Transient Absorption Spectroscopy. Nanosecond transient absorption measurements were obtained with an apparatus similar to that which has been previously described.¹⁴ Samples were photo-excited by a frequency doubled, Q-switched, pulsed Nd:YAG laser (Quantel USA (BigSky) Brilliant B; 532 nm, 5-6 ns full width at half-maximum (fwhm), 1 Hz, ~10 mm in diameter) directed 45° to the film surface. A 150 W Xenon arc lamp coupled to a 1/4 m monochromator (Spectral Energy, Corp. GM 252) served as the probe beam (Applied Photophysics) that was aligned
orthogonally to the excitation light. For detection at sub-100 μs time scales the lamp was pulsed with 80 V. Detection was achieved with a monochromator (Spex 1702/04) optically coupled to an R928 photomultiplier tube (Hamamatsu). Transient data were acquired on a computer-interfaced digital oscilloscope (LeCroy 9450, Dual 350 MHz). Typically 30-50 laser pulses were averaged at each observation wavelength over the range 380-800 nm for full spectra generation and 120-200 laser pulses were averaged for single wavelength measurements. For the low temperature studies (−45 °C), the sample temperature was maintained to ± 0.1 °C using a liquid nitrogen cryostat (UniSoku CoolSpek USP-203-B).

**Infrared Absorption Spectroscopy.** Attenuated Total Reflectance (ATR) spectra were obtained using a Thermo Scientific Nicolet Nexus 670 spectrophotometer. The measurements were made under an N₂ gas flow, and the spectra were averaged for 128 scans with 1 cm⁻¹ resolution.

**Electrochemistry.** A potentiostat (BAS model CV-50W) was employed for measurements in a standard three-electrode arrangement with a sensitized TiO₂ thin film deposited on a FTO substrate working electrode, a platinum disk counter electrode and a Ag/AgCl reference electrode (Bioanalytical Scientific Instruments, Inc.) in 0.5 M LiClO₄ acetonitrile solution. All potentials are reported versus the normal hydrogen electrode (NHE). The ferrocenium/ferrocene (Fc⁺/Fc) half-wave potential was measured at room temperature before and after each experiment and was used as an external standard to calibrate the reference electrode. Conversion constant of -630 mV from NHE to Fc⁺/Fc was used in acetonitrile at 25 °C.¹⁵

**Spectroelectrochemistry.** Steady state UV-vis absorption spectra were recorded in concomitant with bulk electrolysis of a standard three-electrode cell. External biases were applied to the sensitized TiO₂ thin film deposited on a FTO substrate working electrode positioned diagonally in a 1 cm cuvette. Each potential step was held for around 2 to 3 minutes until the spectrum was invariant with time and the next potential was applied.
**Computation. Data Analysis.** Kinetic data fitting was performed in Origin 8.5 and least-squares error minimization was accomplished using the Levenberg-Marquardt iteration method. For the transient absorption spectral modeling and spectroelectrochemical determination of concentrations of redox active states, a method for the standard addition of known spectra, written in Wolfram Mathematica 8.0, was implemented to realize least-squares error minimization.

**Intermolecular Hole Hopping Kinetics Simulation.** Monte Carlo simulations to model lateral hole hopping process for C1+/TiO2 at variable laser fluences were performed with Wolfram Mathematica 8.0 and 9.0 on a personal computer (PC). Monte Carlo runs were repeated 1000 times for a single TiO2 particle simulation (S/N ≥ 1000) while 50 times were implemented for TiO2 particle arrays (S/N ≥ 1350). The TiO2 particle arrays were set to be 2×2×2 or 3×3×3, as larger arrays could not be minimized in a reasonable time period with a PC equipped with 16 GB RAM.

**DFT Calculation.** The geometry optimizations and properties calculations of the ground state and of the oxidized complexes were performed using the ADF2010.01 code. The calculations were carried out using the ZORA Hamiltonian incorporating scalar (sc.) relativistic corrections and with the triple-ζ Slater basis set plus one polarization function (STO-TZP). The molecular structures were fully optimized without symmetry constriction, and via analytical energy gradient techniques, implemented by Versluis and Ziegler, employing non-local correction of exchange and correlation (XC) incorporated via general gradient approximation (GGA), within the BP86 functional, which is composed of the exchange of Becke and the correlation of Perdew. Solvation effects were modeled by the conductor-like screening model for real solvents (COSMO) using acetonitrile as solvent for all the calculations.
2.3 Results

The carboxylic forms of the compounds anchored to mesoporous anatase TiO$_2$ thin films with high surface coverages ($> 3 \times 10^{-8}$ mol/cm$^2$) within 1 hr reaction times in methanol solutions at room temperature. The ground state absorption of these sensitized thin films immersed in 0.5 M LiClO$_4$/CH$_3$CN are shown in Figure 2.1(a). The methyl ester forms of the compounds (E1-E5) displayed much slower kinetics for surface binding. The visible absorption spectra of the TiO$_2$ thin films sensitized with the ester form of the compounds measured in the 0.5 M LiClO$_4$/CH$_3$CN are shown in Figure 2.1(b). In both case, the visible absorption spectra of the sensitized thin film, abbreviated C#/TiO$_2$ or E#/TiO$_2$, were very similar to that observed for the compounds in neat acetonitrile and indicated that the molecules anchored to the surface without measurable degradation.
Figure 2.1 The visible absorption spectra of the indicated sensitized thin films immersed in 0.5 M LiClO$_4$ CH$_3$CN solutions.
Figure 2.2 The UV-vis-NIR absorption spectra of C1/TiO2 (a) and C5/TiO2 (b) measured at variable applied potentials in 0.5 M LiClO4 CH3CN solutions. The arrows indicate the direction of absorption changes with increased positive applied potential. The insets show the fraction (x) of dye molecules present in C1/TiO2, C5/TiO2 (black solid squares), C1+/-TiO2, C5+/-TiO2 (red solid squares) and C12+/-TiO2, C52+/-TiO2 (green solid squares) states. Overlaid on the data are fits to a modified Nernst equation.
Cyclic voltammetry of the sensitized thin films showed significant overlap of two redox waves with peak-to-peak splittings greater than 200 mV at a scan rate of 100 mV/s. Therefore, spectroelectrochemistry was carried out to estimate reduction potentials and assign the redox processes. Figure 2.2(a)-(b) showed representative UV-vis-NIR spectral changes upon oxidation for C1/TiO2 and C5/TiO2. Other data are shown in Figure A2.1. Initial oxidation of C1/TiO2 to C1+/TiO2 showed an absorption increase at 470 nm. Bleaches of the metal-to-ligand charge transfer (MLCT) bands at 433 nm and 531 nm indicated that oxidation occurred at the ruthenium metal center. The weak absorption band in the red and near infrared region was attributed to ligand-to-metal charge transfer (LMCT). Further oxidation beyond 1035 mV versus NHE resulted in the loss of the initial isosbestic points and the formation of new ones at 423 nm and 526 nm. A marked absorption band around 980 nm characteristic of NAr3•+ absorption was observed that served as a probe of hole transfer in transient absorption studies. In the case of C5/TiO2, the order of the redox chemistry was reversed. The immediate appearance of a strong absorption band from ~580 nm to the near infrared region indicated that the first oxidation was NAr3 centered. This was followed by the ruthenium centered oxidation at more positive potentials. Standard addition method based on global modeling was used to calculate the fraction of the species present at each applied potential and representative values are shown as the insets in Figure 2.2. Overlaid on the data in orange are sigmoidal fits, \( x=1/(1+10^{(E_{\text{app}}-E^\circ)/a \times 59 \text{mV}}) \), where \( x \) is the fraction of molecules present at a given applied potential, \( a \) is the non-ideality factor, and \( E^\circ \) is the formal reduction potentials of RuIII/II and NAr3+/0 taken as the applied potential where concentration of the oxidized and reduced forms were equal. These data are summarized in Table 2.1.
Figure 2.3 Calculated dipole moment vectors for a) C2; b) C4; c) C5; d) C2⁺; e) C4⁺; f) C5⁺. The table in each image is the percentage contribution of the ruthenium (Ru), Terpyridine’ (Tp) and the triarylamine (NAr₃) to the HOMO and LUMO orbitals.
Theoretical characterization of three representative compounds (C2, C4 and C5) by density functional theory (DFT) was completed for the compounds in the ground and one-electron oxidized states in the fully protonated form and with one of the carboxylic acid groups deprotonated. These calculations were performed to assess the molecular orbitals involved in the electron transfer chemistry and to quantify the change in dipole moment that accompanied sensitizer oxidation. The frontier molecular orbitals are shown in Figure A2.2-Figure A2.3. The HOMO of the oxidized compounds was located over the phenyl rings of the NAr3 donor while the LUMO was composed of orbitals on the terpyridyl rings with contributions from the Ru d orbitals. Shown in Figure 2.3 are the calculated dipole moment vectors for the ground states and one electron oxidized states of C2, C4 and C5 in the diprotonated form. The calculated dipole moment (μ) components are reported in Table A2.1. It was found that the magnitudes of μ for the ground state of C2, C4 and C5 were 27.4 D, 28.1 D and 30.1 D and after one electron oxidation the dipole moments increased to 46.3 D, 50.8 D and 55.5 D, respectively. The 9.2 D larger for C5+ relative to C2+ resulted from the ‘hole’ in C5+ being localized on the NAr3 donor group rather than the metal center.
Figure 2.4 Absorption difference spectra measured at 100 ns delay time after pulsed 532 nm excitation of (a) C1/TiO$_2$-C5/TiO$_2$ and (b) E1/TiO$_2$-E5/TiO$_2$ immersed in 0.5 M LiClO$_4$/CH$_3$CN solution. Highlighted regions in pink are where NAr$_3$$^{+}$ absorbs light strongly.
Nanosecond transient absorption spectroscopy was used to quantify interfacial charge recombination between TiO$_2$(e$^-$)s and the oxidized compounds. Figure 2.4 shows absorption difference spectra of the sensitized materials in an acetonitrile electrolyte at 100 ns delay time after 532 nm laser excitation. A single product was observed after laser excitation consistent with excited state injection and hole transfer occurring on a sub-10 ns time scale. At early observation times, evidence of a faster component was observed for C5/TiO$_2$ and measurements at -45 °C revealed a ~5 ns rise time for the appearance of the oxidized NAr$_3$$^+$, Figure A.2.4. This process was within the instrument response time, but indicated that hole transfer occurs on a hundreds of ps to few ns time scale. A progressive increase of the absorption band in the red region attributed to NAr$_3$$^+$ was observed from C1 to C5 or from E1 to E5 that was correlated with larger values of $[E^\circ$(Ru$^{III}$/II)$-E^\circ$(NAr$_3$$^+$/0)]]. The kinetics measured for charge recombination between the injected electrons and the oxidized dye molecules were in good agreement with an earlier communication for C2$^+$/TiO$_2$(e$^-$), C4$^+$/TiO$_2$(e$^-$) and C5$^+$/TiO$_2$(e$^-$). Here with an additional two sensitized films, it was again found that within experimental error there was no difference in charge recombination rate constants, i.e. recombination was insensitive to the identity of the compound Figure A.2.5. The influence of surface coverage was also quantified, Figure A.2.6. Decreasing the surface coverage from the saturation value 6×10$^{-8}$ mol/cm$^2$ to values of ~1/5 saturation resulted in only a very minor change to the charge recombination kinetics.
Figure 2.5 The UV-vis absorption spectra of C4/TiO2 immersed in 0.5 M LiClO4 CH3CN (black) and immersed in 0.5 M LiClO4/1.0 × 10^{-4} M H2SO4 CH3CN (red). The upper inset shows the absorption difference spectra measured 45 ns after pulsed 532 nm excitation of C4/TiO2 and the lower inset shows the same data for an H2SO4 treated C4/TiO2 thin film; overlaid in solid curves are simulations; highlighted regions in pink are where NA3•+ absorbs strongly.
Addition of sulfuric acid at concentrations as low as 1.0×10^-4 M to a C4/TiO2 thin film immersed in 0.5 M LiClO4/CH3CN induced a noticeable bathochromic shift and increase of the MLCT absorption band throughout the visible region, Figure 2.5. Spectral changes were preserved even after the C4/TiO2 thin film was re-immersed in fresh 0.5 M LiClO4/CH3CN. Laser excitation of the acid exposed C4/TiO2 thin film in 0.5 M LiClO4/CH3CN resulted in rapid excited state electron injection to TiO2 (k_{inj} > 10^8 s^{-1}). A significant absorption increase in the red region indicated a larger extent of intramolecular hole transfer relative to that for untreated C4/TiO2, Figure 2.5 insets. Spectral modeling indicated that the sulfuric acid treatment increased the hole transfer yield from 0.25 to 0.51. The ATR-FTIR spectra showed that the acid treatment resulted in the appearance of an intense carbonyl stretch at 1712 cm^{-1} that was at the same energy as that measured for a C4 powder in the solid state, Figure A2.7.
Figure 2.6 The data shown in panels (a), (c), and (e) are absorption difference spectra measured after pulsed laser excitation ($\lambda_{ex}=532$ nm) of C1/TiO$_2$ biased to 890 mV vs. NHE (C1/TiO$_2$ : C1$^+/TiO_2$ = 50 : 50), 960 mV vs. NHE (C1/TiO$_2$ : C1$^+/TiO_2$ = 15 : 85) and 1035 mV vs. NHE (C1/TiO$_2$ : C1$^+/TiO_2$ = 0 : 100) at the indicated delay times. Overlaid in solid lines are simulations based on the the absorption profiles of C1/TiO$_2$, C1$^+/TiO_2$, C1$^{2+}$/TiO$_2$ shown in Figure A2.8 and the 1$^{st}$ derivative spectrum of C1$^+/TiO_2$, the fractional concentrations of which (black square is C1/TiO$_2$, red circle is C1$^+/TiO_2$, and green triangle is C1$^{2+}$/TiO$_2$) were shown in (b), (d) and (f) as a function of time.
The presence of two stable oxidation states enabled studies where the Ru\textsuperscript{II} or NAr\textsubscript{3} group was oxidized prior to light excitation. Due to the proximity of the Ru\textsuperscript{III/II} and NAr\textsubscript{3}•+/0 reduction potentials for C2-C5, C1 was chosen for the study as the reduction potentials were the most separated. Absorption difference spectra of C1/TiO\textsubscript{2} displayed in Figure 2.6 (a), (c), and (e) were acquired in 0.5 M LiClO\textsubscript{4} CH\textsubscript{3}CN at 890, 960 and 1035 mV applied potentials after 532 nm excitation. At these potentials, the ratio of sensitizers present prior to light excitation were calculated from the spectroelectrochemical data. Spectral modeling based on the measured absorption spectrum of C1, C1\textsuperscript{+}, C1\textsuperscript{2+}, Figure A2.8, and the TiO\textsubscript{2}(e\textsuperscript{-}) were necessary to simulate the measured spectra. Spectral shifts due to an underlying Stark effect were also evident and inclusion of the first derivative absorption spectrum of C1\textsuperscript{+}/TiO\textsubscript{2} improved the spectral modeling as has been previously described.\textsuperscript{27,28} The fractions of C1, C1\textsuperscript{+}, and C1\textsuperscript{2+} generated after 532 nm light excitation over the total number of molecules (C1+C1\textsuperscript{+}+C1\textsuperscript{2+}) as a function of delay times were deconvoluted from the time resolved spectral data and shown in Figure 2.6 (b), (d), and (f). Because the concentration of each oxidation state was determined, the injection yield of C1\textsuperscript{+}/TiO\textsubscript{2} was calculated to be ~0.1 at a 20 ns delay time, Figure 2.6(b).
Figure 2.7 Absorption changes monitored at 507 nm after pulsed light excitation at the indicated applied potentials ($\lambda_{ex} = 532$ nm, 1.4 mJ/cm$^2$). Overlaid in yellow are the fits to the KWW model ($\beta_{KWW}=0.17$).
A single wavelength of 507 nm was chosen to monitor the interfacial charge recombination of TiO$_2$(e$^-$) with the oxidized sensitzers, Figure 2.7. Absorption changes as a function of time were satisfactorily described by the Kohlrausch–Williams–Watts (KWW) model$^{29,30}$, Equation (2.1) with a fixed $\beta_{KWW}$ value of 0.17 under all bias conditions. The rate of this process was found to be dramatically increased when more oxidized compounds, i.e. more positive potentials, were generated on TiO$_2$ surfaces. The increase of charge recombination rate was found to be universal within the series of compounds, C1-C5. The charge recombination behavior of C$_5^+/TiO_2$(e$^-$) with applied positive biases was also shown in Figure A2.9.

\[
\Delta \text{Abs} = A \exp[-(kt)^{\beta_{KWW}}] \tag{2.1}
\]
Figure 2.8 Absorption changes monitored at 540 nm after pulsed light excitation with five irradiances ($\lambda_{ex} = 532$ nm 0.3-1.5 mJ/cm$^2$) of C1/TiO$_2$ immersed in 0.5 M LiClO$_4$ CH$_3$CN and biased at 1035 mV versus NHE. Overlaid as solid lines are absorption profiles abstracted from Monte Carlo simulations of 1 (a) and 27 (b) nanoparticles.
Shown in Figure 2.8 is time resolved absorption data measured after pulsed laser excitation of a C1/TiO2 thin film held at an applied bias of +1035 mV vs. NHE. At this applied potential, the ruthenium center was oxidized to the formal oxidation state of three and is therefore better formulated as C1+/TiO2. Excited state injection was rapid and efficient ($k_{inj} > 10^8$ s$^{-1}$ and $\phi_{inj} = 0.1$). The data were recorded at five different irradiances from 0.3 to 1.5 mJ/cm$^2$. Two different Monte Carlo simulation methods were carried out to understand the lateral intermolecular hole hopping process that occurred after interfacial electron transfer to a second dye molecule. In the first method, 536 dye molecules were evenly distributed on a single 15 nm diameter sphere with an average intermolecular distance of 11.5 Å. The second method took 27 similar spheres and packed them into a 2×2×2 or a 3×3×3 cubic array with nearest neighbor center-to-center interparticle distances of 14.8 nm. In these arrays, dye molecules in the necking regions between spheres were removed. In both methods, after excited state electron injection, the injected electron quantitatively recombined with a different molecule to yield equal numbers of C1 and C12+ randomly positioned on the surface. The random walk of each C1 or C12+ was controlled by a pseudo-random number generator either to the six adjacent C1+ sites with equal probability for one sphere or weighted exponentially (decay constant $\beta = 0.35$ Å$^{-1}$)$^{31,32}$ by the distance to every other site. The Ru$^{III/II}$ and NAr3•+/0 hopping rates were assumed to be the same, such that an “effective” hopping rate was calculated. This assumption was supported by the spectroelectrochemical data, which showed that the time required to oxidize 40% of the NAr3 donors in C5/TiO2 was only about 1.5 times shorter than that required to oxidize the same percentage of Ru$^{II}$ sites in C1/TiO2, implying that the hopping rates were indeed very similar. Hole transfer from C12+ to C1 to yield two C1+ compounds was assumed to be quantitative when the two were adjacent. For both methods, the initial number of C1 and C12+ molecules created with light was an important parameter that influenced the kinetic behavior for lateral hole hopping. Hole-hopping simulations for cases where one, two three, four or five charge-separated pairs were created on each TiO2 particle as well as 27, 54, 81, 108, or 135 pairs for each 27 particle array were performed. The best fit of the simulation data to the
experimental data as determined by chi-squared analyses, Figure A2.12, are shown as the solid curves overlaid on the transient data in Figure 2.8. Hopping rate of \((160 \text{ ns})^{-1}\) for the single-particle case and \((130 \text{ ns})^{-1}\) for the particle arrays were found. Simulations based on the array of nanoparticles gave rise to a more well-defined minimum and were found to be in better agreement with the experimental data, particularly those data measured on the longer time scales (Figure A2.11 and Figure A2.12).
2.4 Discussion

The redox and photoinduced electron transfer properties of TiO$_2$ thin films sensitized with five different cyclometalated ruthenium compounds with conjugated triarylamine donor groups were quantified. The presence of two redox active portions of these compounds, Ru$^{III/II}$ and NAr$_3$$^{+/-}$, provided new insights into interfacial redox reactions that could not have been obtained with a single chromophoric sensitizer. In the discussion below, emphasis is placed on published literature on solar energy conversion that relates to: 1) the non-Nernstian nature of the interfacial redox chemistry; 2) intramolecular hole transfer; 3) dipole moment contributions to the stored Gibbs free energy; and 4) lateral intermolecular hole transfer across the TiO$_2$ surface.

2.4.1 Non-Nernstian Redox Chemistry.

The Nernst equation predicts that for a one electron transfer process at room temperature a 59 mV shift in potential will arise when the ratio of the concentrations of the reduced and oxidized forms are changed by a factor of ten.$^{33}$ This relation has been phenomenally successful in fluid electrolyte solutions, particularly when activities are used in place of concentrations.$^{33}$ However, non-Nernstian behavior has been noted at chemically modified electrode surfaces, and has been quantified by inclusion of a non-ideality factor, $a$, into the Nernst equation.$^{11,12,34-36}$ When $a = 1$ in Equation 2.2, the Nernst equation results. When $a > 1$ non-ideality results, behavior most often attributed to intermolecular interactions accompanying the redox chemistry as described by Frumkin.$^{37,38}$ The availability of two redox active groups in these compounds, the Ru$^{III/II}$ center, and the NAr$_3$$^{+/-}$ group that is expected to be further from the TiO$_2$ surface, enabled interrogation of the origin of non-ideality by spectroelectrochemistry.

$$E = E^° + \frac{aRT}{nF} \ln \frac{[Ox]}{[Red]} \quad (2.2)$$
It was found that in order to achieve a factor of ten change in concentration, more than 59 mV of applied potential was needed and hence non-ideality factors had to be introduced to model all the interfacial electrochemical data. For instance, a non-ideality factor $a = 1.45$ was measured for the Ru$^{III/II}$ of C1/TiO$_2$ that indicated that an ~ 90 mV potential step was required for a factor of ten change in concentration. Interestingly, the Ru$^{III/II}$ redox reactions for all five compounds revealed higher non-ideality factors than the covalently linked NAr$_3^{+/0}$ groups, $1.37 \pm 0.08$ versus $1.15 \pm 0.09$. The Ru$^{III/II}$ non-ideality factors were larger than those of NAr$_3^{+/0}$ regardless of which redox center was oxidized first in the compound. For example, the ruthenium center in C2 was oxidized first and second in C5 yet both displayed non-ideality factors of ~1.32. As counter ions and solvent reorganize as a consequence of the redox chemistry, the insensitivity of the non-ideality factors to the total oxidation state of the molecule implies that such interfacial reorganization was not the cause of the non-ideality. It could well have been the case that the second group oxidized displayed the larger ideality factors due to the higher charge on the molecule, but this was not observed.

The origin of the non-ideality is instead consistent with either intermolecular interactions, as proposed by Frumkin, or a surface electric field model. The former seems less likely as space filling models indicate that the rigid thiophene linker results in similar Ru-Ru and NAr$_3$-NAr$_3$ intermolecular distances. Therefore, the surface electric field experienced by the redox active group is most likely the origin of the non-ideality as such fields are known to decrease with distance from the semiconductor surface. The only previously related literature report was a recent study of a cobalt porphyrin anchored to TiO$_2$, where both Co$^{III/II}$ and Co$^{II/I}$ reactions were quantified. While this chemistry was complicated somewhat by coordination number changes that accompany this redox chemistry, larger non-ideality factors were observed for Co$^{II/I}$ relative to Co$^{III/II}$. Like the Ru$^{III/II}$ and NAr$_3^{+/0}$ redox chemistry reported herein the Co$^{III/II}$ redox potentials occurred within the forbidden band gap of TiO$_2$ and hence required a percolation pathway from the
transparent conductive substrate to the molecules (see Intermolecular Hole Hopping below), while
the direct reduction of TiO$_2$ accompanied the conversion of Co(II) to Co(I). Electrons injected into
TiO$_2$ produce a large electric field, $E = 3$ MV/cm, that has been observed by electro-absorption
spectroscopy, i.e. Stark spectroscopy, and reported to be distance dependent.$^{27,40-42}$ Hence the
enhanced non-ideality factors reported for Co$^{II/II}$ redox chemistry were also attributed to a surface
electric field, consistent with the conclusions drawn here.

The appearance of non-ideal redox chemistry raises the issue of what the true reduction
potentials of the surface anchored compounds are. This question is particularly relevant to
operational solar cells when an electric field mechanism for non-ideality is operative as the
reduction potentials would no longer be fixed values and would instead change with the solar flux.
For the purposes of this study, the formal reduction potential was taken as the potential where the
equilibrium concentrations of the oxidized and reduced forms were equal with the understanding
that these potentials do likely shift to more negative values with the TiO$_2$ quasi-Fermi level under
solar illumination. Comparisons of these ‘dark’ potentials with those measured for the free
compounds in fluid electrolytes was difficult as the carboxylic acid forms of the compounds were
nearly insoluble in CH$_3$CN. However, the ester derivatives were soluble and the NAr$_3$$^{+/0}$ reduction
potentials measured were in good agreement with the interfacial values. In contrast, the Ru$^{III/II}$
potentials were generally 70-90 more positive than those measured at the TiO$_2$ interface. This shift
is consistent with an inductive effect where the electron donating nature of carboxylate binding
groups yield less positive Ru$^{III/II}$ potentials than do the electron withdrawing ester groups. Thus the
formal reduction potentials do not appear to be significantly altered upon surface binding once the
change from carboxylic acid (or ester) to carboxylate that accompanies surface binding is accounted
for. Nevertheless, the non-ideality of the molecular redox chemistry at the TiO$_2$ interface perturbs
the equilibrium for intramolecular hole transfer in a quantifiable manner as is described below.

2.4.2 Intramolecular Hole Transfer.
It was of interest to calculate the extent of hole transfer from the oxidized ruthenium center to the covalently linked triarylamine moiety based on the spectroelectrochemical data as these values can be compared to those measured experimentally after pulsed laser excitation. To account for the non-idealities and to be consistent with the spectroelectrochemical results, the Ru$^{III/II}$ and NAr$_3$$^{+/-}$ redox reactions were considered to be independent of each other even though they were covalently linked, Equation 2.3. The equilibrium constants and hole transfer yields were calculated with Equations 2.4 and 2.5, respectively. The hole transfer yields were calculated with and without the inclusion of non-ideality factors, $\Phi_{\text{calc}}$ and $\Phi_{\text{calc,a}}$, where $a_1$ represents the ideality factor for Ru$^{III}$ and $a_2$ for NAr$_3$$^{+/-}$, and are summarized in Table 2.1.

\[
\begin{align*}
\text{Ru}^{III} + \text{NAr}_3 & \rightleftharpoons \text{Ru}^{II} + \text{NAr}_3^{+} \\
K_{eq} &= \frac{[\text{Ru}^{II}]^{a_1}[\text{NAr}_3^{+}]^{a_2}}{[\text{Ru}^{III}]^{a_1}[\text{NAr}_3^{0}]^{a_2}} \\
\Phi_{\text{calc}} &= \frac{[\text{NAr}_3^{+}]}{[\text{NAr}_3^{0}] + [\text{NAr}_3^{+}]} = \frac{K_{eq}^{1/a_1+a_2}}{1 + K_{eq}^{1/a_1+a_2}}
\end{align*}
\]

The inclusion of ideality factors, in essence, broadens the potential range over which Ru$^{III/II}$ and NAr$_3$$^{+/-}$ redox chemistry occurs. This is conveniently depicted through the chemical capacitance as was first suggested by Murray, Scheme 2.4. The representitve chemical capacitance data for C2/TiO$_2$, C4/TiO$_2$, and C5/TiO$_2$ are shown in Figure A2.13. Three different scenarios are possible for the hole transfer reaction under study. In the first, the driving force for hole transfer is small and $K_{eq} << 1$. This is the case for C3/TiO$_2$, $K_{eq} = 4.3 \times 10^{-3}$, and the inclusion of ideality factors increases the overlap region and hence the fraction of Ru$^{III}$ that can oxidize the NAr$_3$ group as is shown in Scheme 2.4a. Hence non-ideality is expected to increase the yield of hole transfer after excited state injection when $K_{eq} << 1$. For C3/TiO$_2$ the magnitude of the effect was about a factor of two. The second scenario is where $K_{eq} = 1$; where little change in the yield of
hole transfer is expected provided that the non-ideality factors are similar. The third scenario is where the driving force for hole transfer is large and $K_{eq} >> 1$; as was found to be the case for $\text{C5/TiO}_2$ where $K_{eq} = 1.1 \times 10^2$. Now the inclusion of non-ideality factors results in a larger fraction of $\text{NAr}_3$ groups that cannot be oxidized by $\text{Ru}^{\text{III}}$. As a result the expected hole transfer quantum yield decreases, by about 16% in the case of $\text{C5/TiO}_2$. 
Scheme 2.4 The chemical capacitance of C3/TiO2 (a) and C5/TiO2 (b) as a function of applied potential. The solid curves represent best fits to the experimental data with the indicated non-ideality factors. The dashed curves represent ideal Nernstian behavior. The overlap of the chemical capacitance represents potentials where both triaryl amine and ruthenium redox chemistry occurs.
The quantum yields for hole transfer measured after pulsed laser excitation of the sensitized thin films were in better agreement with the calculated values when the non-ideality factors were included, particularly for C4/TiO2 and C5/TiO2 that displayed hole transfer yields greater than 0.25. Therefore as shown through steady state equilibrium measurements and transient kinetic studies, non-ideal redox behavior is detrimental for hole transfer when the Gibbs free energy change for the reaction is favorable. It should be kept in mind that the hole transfer yields were calculated from data measured in the absence of injected electrons while the experimental data was measured after excited state electron transfer where the injected electron itself was expected to give rise to non-ideal behavior. Had the non-ideality resulted from intermolecular interactions, i.e. Frumkin like behavior, one might anticipate that it would be absent in the photoinduced charge separation studies where the number of oxidized dye molecules is small, on average less than five per nanocrystallite. Therefore, this suggests that non-idealities need to be taken into account for prediction of hole transfer yields and that the origin of the non-ideality is likely due to the surface electric field.

The yield for photoinduced intramolecular hole transfer measured experimentally was highly sensitive to the interfacial conditions as both increased proton concentration and the presence of ester groups resulted in enhanced hole transfer yields. Methyl ester derivatives of the sensitizers were found to anchor to the TiO2 surface with a pronounced ATR-FTIR absorption peak at 1730 cm⁻¹ indicative of unhydrolyzed methyl ester groups. Enhanced hole transfer yields were measured for thin films sensitized with these compounds relative to their carboxylic acid derivatives. This can be rationalized by the inductive electron withdrawing nature of the unhydrolyzed ester groups relative to the electron donating carboxylate groups present on the TiO2 surface. Indeed, the same behavior was observed after protonation of free carboxylate groups by a dilute H2SO4/CH3CN solution. For example, light excitation of an acid treated C4/TiO2 resulted in a factor of two increase in the hole transfer yield. These data show that the hole transfer yield was highly sensitive to environmental conditions such as the interfacial pH.
Table 2.1 Electrochemical and photophysical data for the sensitized thin films

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E^{0}_{1/2}$ (Ru$^{III/II}$) $^a$ (a$_1$) $^b$</th>
<th>$E^{0}_{1/2}$ (NAr$_3$•+/0) $^a$ (a$_2$) $^b$</th>
<th>$K_{eq}$ $^c$</th>
<th>$\Phi_{ht,calc}$</th>
<th>$\Phi_{ht,a}$</th>
<th>$\Phi_{ht,meas}$</th>
<th>$E^{0}_{1/2}$ (Ru$^{III/II*}$)</th>
<th>$\Delta G_{es}$</th>
<th>Abs max</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>890 (1.45 ± 0.04)</td>
<td>1155 (1.22 ± 0.04)</td>
<td>3.31 × 10$^{-3}$</td>
<td>&lt; 0.01</td>
<td>0.02</td>
<td>&lt; 0.02$^e$</td>
<td>-0.76</td>
<td>1.65</td>
<td>435, 534</td>
</tr>
<tr>
<td>C2</td>
<td>945 (1.30 ± 0.04)</td>
<td>1150 (1.21 ± 0.04)</td>
<td>3.42 × 10$^{-3}$</td>
<td>0.02</td>
<td>0.04</td>
<td>&lt; 0.02$^e$</td>
<td>-0.72</td>
<td>1.65</td>
<td>431, 529</td>
</tr>
<tr>
<td>C3</td>
<td>1010 (1.44 ± 0.03)</td>
<td>1150 (1.24 ± 0.02)</td>
<td>4.30 × 10$^{-3}$</td>
<td>0.06</td>
<td>0.12</td>
<td>0.05$^e$</td>
<td>-0.67</td>
<td>1.68</td>
<td>427, 519</td>
</tr>
<tr>
<td>C4</td>
<td>870 (1.33 ± 0.03)</td>
<td>960 (1.11 ± 0.03)</td>
<td>3.01 × 10$^{-2}$</td>
<td>0.15</td>
<td>0.19</td>
<td>0.25</td>
<td>-0.81</td>
<td>1.68</td>
<td>439, 532</td>
</tr>
<tr>
<td>C5</td>
<td>1060 (1.33 ± 0.04)</td>
<td>940 (1.04 ± 0.03)</td>
<td>1.07 × 10$^{2}$</td>
<td>0.91</td>
<td>0.88</td>
<td>0.74</td>
<td>-0.62</td>
<td>1.68</td>
<td>431, 520</td>
</tr>
</tbody>
</table>

$^a$ $E^{0}_{1/2}$ given as mV versus NHE; $^b$a$_1$ and a$_2$ are the non-ideality factor described in Equation 2.3 and 2.4; $^c$ $K_{eq}$ defined in Equation 2.4; $^d$ $\Delta G_{es}$ was estimated from the corrected photoluminescence spectrum measured for sensitized ZrO$_2$; $^e$Estimated from the absorption amplitude at 720-750 nm relative to C5/TiO$_2$. 
2.4.3 The Role of Dipole Moments.

Charge recombination from TiO$_2$(e$^-$) to the oxidized compounds was insensitive to whether the hole was localized on Ru$^{III}$ or NAr$_3^{+}$. Therefore, for these compounds there was no kinetic advantage gained by hole transfer from Ru to the NAr$_3$ group. An explanation for this behavior remains unknown, but may emanate from the conjugated thiophene bridge that links the triarylamine to the cyclometalated ligand that provides a delocalized LUMO with metal d and NAr$_3$ orbital character for all the compounds studied. Back electron transfer may hence always occur to the Ru center. This would also be expected to occur when the redox equilibrium shown in Scheme 2.2 is established on the electron transfer time scale: the injected electron reduces Ru$^{III}$ and this shifts equilibrium concentrations to the left and hence more Ru$^{III}$ is generated. Kinetic evidence that the quasi intramolecular redox equilibrium was established on the time scale before back interfacial electron transfer comes from the fact that the hole transfer rate constant for Ru$^{III} \rightarrow$ NAr$_3$ occurred on a time scale greater than $k_{ht} > 1 \times 10^8$ s$^{-1}$ for all the sensitized materials while recombination required milliseconds.

Regardless of the mechanism, charge recombination of the injected electron with the oxidized sensitizer was remarkably insensitive to the sensitizer employed. At the same time, the open circuit voltage, $V_{oc}$, measured in the absence of a redox mediator was approximately 100 mV larger for C5/TiO$_2$ that displayed the highest quantum yield for hole transfer to the amine donor, Figure A2.10. This was unexpected as the spectroelectrochemical data showed that the acceptor states in TiO$_2$ were insensitive to the identity of the dye molecules present on the surface and hole transfer results in a loss in free energy. Therefore, if anything hole transfer should have given rise to a smaller $V_{oc}$ value for C2/TiO$_2$ than C5/TiO$_2$. In many previous studies, this loss in free energy was compensated by a decrease in the charge recombination rate constant as predicted by the diode equation. However, an ~100 fold diminution of this rate constant would be needed to account for the $V_{oc}$ values measured and this simply was not observed. Other factors such as inefficient
sensitizer regeneration,\textsuperscript{8,28,44} acid-base chemistry\textsuperscript{45} and/or interfacial dipole moments the ground state dyes are also known to influence $V_{oc}$.\textsuperscript{46-48}

It is asserted here that the enhancement in $V_{oc}$ reported here results from the increase dipole moment that accompanies hole transfer. This assertion comes in part from an elimination of all other possibilities such as the recombination kinetics described above. Furthermore, spectroelectrochemical studies showed that the TiO$_2$ density of acceptor states was insensitive to the identity of the dye molecule and hence specific sensitizer effects, like the protonation state of the dye molecule as reported by Nazeeruddin and coworkers, were not operative in this homologous series of dye molecules.\textsuperscript{45} In addition, it has previously been shown that the orientation of molecular dipole moments at the TiO$_2$ surface influences $V_{oc}$ through the electrostatic field generated.\textsuperscript{49,50} Dipoles oriented toward the surface increase $V_{oc}$ due to the upshift of the conduction band of the TiO$_2$ nanoparticle, while those are directed away decrease $V_{oc}$. Before comparing this experimental data to previous studies, it is important to point out a key experimental detail: the open circuit photovoltage data reported here was measured against a pseudo-reference electrode in the absence of redox mediators while most other literature reports are for an operational solar cell with a redox mediator present, typically I$^-$/I$_3^-$. For this reason, previous workers used the inherent dipole of the surface anchored dye molecule, or co-adsorbed non-chromophoric dipolar molecules, and attributed the measured $V_{oc}$ to the ground state, i.e. the non-illuminated thin film.\textsuperscript{46-49} This was reasonable as the steady state concentrations of excited and oxidized sensitizers were thought to be vanishingly small and hence would not contribute to the measured $V_{oc}$ values. In contrast, the data reported here is very sensitive to the concentration of the oxidized dye molecules as no regenerator is present. When the sensitized thin films were illuminated in such a non-regenerative cell, oxidized dye molecules were formed along with injected electrons that raised the TiO$_2$ quasi-Fermi level toward the vacuum level. These oxidized states had dipole moments that were almost twice as large as their ground states as shown by DFT calculation. In addition, the calculated dipole
moments were largest when the hole was predominantly localized on the NAr₃ group. For example, Ru³⁺ → NAr₃ hole transfer in C5⁺/TiO₂ gave rise to a 9.2 D increase in dipole moment relative to C2⁺/TiO₂ where the hole was predominantly localized on the Ru³⁺ center.

The dipole moment data can be used to calculate the dipole moment induced electrostatic potential drop (Δφ_{dipole}), Equation 2.6.

\[ \Delta \phi_{\text{dipole}} = \frac{N \Delta(\mu \cos \theta)}{\epsilon \epsilon_0} \]  

This equation predicts that the \( V_{oc} \), should be dependent on the change in the surface dipole moment that accompanies excited state injection, \( \Delta(\mu \cos \theta) \), and the surface coverage of oxidized molecules, \( N \), assuming that the permittivity of the molecular layer \( \epsilon_0 = 5 \). At most about 10% of the dye molecules injected electrons at the highest irradiance employed, \( N \) would be \( \sim 7 \times 10^{16} \) molecules/m². When the full range of tilt angles and dipole moments of different protonation states of the dye molecule were considered (see Table A2.1), a range of \( \Delta \phi_{\text{dipole}} = 40-60 \) mV were calculated to accompany hole transfer which is in reasonable agreement with the value of 100 mV measured experimentally.

One could rightly argue that the \( V_{oc} \) data reported here has little relevance to an operational dye sensitized solar cell that necessarily contains a redox mediator. However, with some organic dye molecules compelling evidence was found that inefficient sensitizer regeneration lowers \( V_{oc} \). Hence some fraction of the injected electrons leak back to the oxidized dye molecule under conditions where the number of injected electrons is large. More recently Wang and coworkers reported clear evidence that this also occurs for highly optimized dye molecules like Ru(dcbH₂)(dnb)(NCS)₂ (Z907), where dcbH₂ is 4,4’-(CO₂H)₂-2,2’-bipyridine and dnb is 4,4’-dinonyl-bipyridine. In one previous comparative study of donor-acceptor sensitized thin films where the charge recombination kinetics were correlated with the kinetics for back interfacial electron transfer to the oxidized donor, the enhanced \( V_{oc} \) that accompanied hole transfer was
measured in the presence and absence of the redox mediator.\textsuperscript{3} Taken together, this suggests that one cannot rule out the possibility that dipole moment measurements made without a redox mediator do have some relevance to operational solar cells. In any event, such measurements appear to be the most useful for fundamental studies of the interfacial dipole moment changes that follow excited state injection.

2.4.4 Intermolecular Hole Hopping.

It has long been known that molecules with formal reduction potentials that lie within the forbidden band gap, where TiO\(_2\) is expected to be an insulator, can be reversibly oxidized in these mesoporous thin films.\textsuperscript{51} The established mechanism is that oxidation is initiated at the transparent conductive oxide (TCO) substrate and proceeds by lateral intermolecular hole hopping throughout the film provided that a percolation threshold has been achieved.\textsuperscript{52,53} Recently, lateral hole hopping has also been observed to occur after excited state injection by time resolved anisotropy spectroscopic measurements.\textsuperscript{32} The sensitized interfaces under study here enabled lateral hole hopping reactions to be induced with light and monitored by transient absorption spectroscopy, Scheme 2.5. Such reactions are important in photoelectrosynthetic cells as they provide a means for translating oxidizing equivalents to a catalyst after excited state injection.
Scheme 2.5 Electron transfer and hole hopping processes observed after 532 nm laser excitation of C1+/TiO₂: excited state electron injection (a); interfacial charge recombination (b); lateral intermolecular hole hopping (c).
\[ TiO_2|Ru^{III} - NAr_3 \rightarrow TiO_2(e^-)|Ru^{III} - NAr_3^{\text{**}} \] (2.7)

\[ TiO_2(e^-)|Ru^{III} - NAr_3 \rightarrow TiO_2|Ru^{II} - NAr_3 \] (2.8)

\[ TiO_2|Ru^{III} - NAr_3^{\text{**}} + TiO_2|Ru^{II} - NAr_3 \rightarrow 2(TiO_2|Ru^{II} - NAr_3) \] (2.9)

When the Ru\textsuperscript{III} center in C1/TiO\textsubscript{2} was electrochemically oxidized to yield C1\textsuperscript{+}/TiO\textsubscript{2} (i.e. Ru\textsuperscript{III}-NAr\textsubscript{3}), a new visible absorption band centered at 470 nm was observed that was assigned to be an intra-ligand charge transfer band from the triaryl amine donor to the substituted terpyridine ligand (NAr\textsubscript{3}→ terpy*), that is very similar in energy and band width to that observed for organic D-\pi-A molecules with triaryl amine donors.\textsuperscript{28} In addition, DFT calculations of the one electron oxidized forms of these compounds reveal that the HOMO is largely centered on the NAr\textsubscript{3} group and the LUMO on the terpyridyl ligand, Figure A2.3. Light excitation into this band resulted in the immediate appearance of the doubly oxidized sensitizer, i.e. where both Ru and NAr\textsubscript{3} were oxidized, confirming excited state electron injection into TiO\textsubscript{2} from C1\textsuperscript{+}, Scheme 2.5(a) and Equation 2.7. Interfacial electron injection yield measured by comparative actinometry on a 50 ns time scale was 0.1. It was unclear whether this low yield resulted from rapid back electron transfer or to intramolecular reductive quenching by the proximate Ru\textsuperscript{III} center followed by rapid back electron transfer.

Excited state electron injection was followed by interfacial back electron transfer to a neighboring C1\textsuperscript{+} molecule, Equation 2.8. This process was investigated as a function of applied bias that created different concentrations of singly oxidized C1. It was found that charge recombination rates were much larger when oxidized compounds were present. Kinetic modeling did not show a simple relationship between the rate constants abstracted from a KWW analysis and the concentration of the oxidized dye molecules. However, at one extreme where all the compounds were oxidized, the KWW rate constants were three orders of magnitude faster than the condition where no dye molecules had been electrochemically oxidized. Increased charge
recombination was due to a higher probability of the injected electron to encounter a \( \text{C1}^+/\text{TiO}_2 \).

Quantitative interfacial back electron transfer in principle yielded \( \text{C1}/\text{TiO}_2 \) and \( \text{C1}^{2+}/\text{TiO}_2 \) in equal concentrations.

Hole transfer from \( \text{C1}^{2+}/\text{TiO}_2 \) to \( \text{C1}/\text{TiO}_2 \) was favored by 270 mV of Gibbs free energy, Equation 2.9, and occurred after lateral intermolecular hole hopping across the TiO\(_2\) surface brought the two reactants close to each other. A significant absorption change accompanied this recombination reaction process that could not be adequately described by first- or second- order kinetic models. Instead the data were fit to a random walk model based on Monte Carlo simulation. Scheme 2.6a shows a representative Monte Carlo simulation of three \( \text{C1} \) molecules (blue points) and three doubly oxidized, \( \text{C1}^{2+} \) molecules (red points) randomly positioned on a 15 nm diameter sphere that represents a TiO\(_2\) nanocrystal. Time dependent concentrations were calculated as the intermolecular hopping rate was varied and was compared to experimental data measured at five different excitation irradiances. The simulations agreed with experiment when an intermolecular hole hopping rate constant of \((160 \text{ ns})^{-1}\) was used. The experimental and simulated data were in best agreement on the microseconds and short time scales that represented greater than 70% of the recombination. The poor agreement on longer time scales might arise from cases where inter-particle hopping occurred.\(^{54}\) The necking regions could allow lateral hole hopping from one TiO\(_2\) nanoparticle to the other, thus decreasing the recombination rates. To test this hypothesis, an array of 27 particles was used in a similar simulation that allowed for inter-particle hopping (Scheme 2.6b). The best fit of the simulation data to the experiment was achieved with a hopping rate of \((130 \text{ ns})^{-1}\). A chi-squared error analysis of the respective fits showed significant improvement of the multi-particle simulation over the single particle simulation and residuals revealed that it was the longer time scale data where the fit to experimental data was most improved, Figure A2.12. On average, the hole hopped about 16 nm before encountering a reduced compound. Due to the
random nature of the walk, ~1800 nm total distance would be reached if the path could be directed
in a single direction.
Scheme 2.6 Monte Carlo simulation of lateral intermolecular hole hopping on spherical TiO$_2$ nanocrystallites. Black dots represent the C1$^+$ sites that are evenly distributed on the surface. Red spheres are C1$^{2+}$ and blue spheres are C1. Thirty steps of random walks are shown.
The (130 ns)\(^{-1}\) hopping rate recovered has relevance to photoelectrosynthetic water splitting cells where accumulation of oxidizing equivalents at catalytic sites is required.\(^{55-58}\) In one embodiment of such cells, the hole must hop to an oxidation catalyst after excited state injection. This hole hopping is kinetically competitive with back electron transfer. At the lowest irradiance conditions studied, and with an average charge recombination rate constant of \(2 \times 10^5\) s\(^{-1}\), a single oxidizing equivalent could circumnavigate a single nanocrystallite once in search of a catalyst before recombination. Unfortunate for this goal was the finding that charge recombination occurred on the same time scale as did hole hopping when every sensitizer had been oxidized by one electron. In this case, back electron transfer and efficient accumulation at a catalyst would not be expected. This finding emphasizes the need to isolate the catalyst from the TiO\(_2\) surface for the realization of efficient photoelectrosynthetic cells.
2.5 Conclusions

The characterization of TiO$_2$ sensitized to visible light with molecules that possessed two redox active groups has provided new insights into the kinetics and thermodynamics of interfacial electron and hole transfer reactions. The redox chemistry was non-Nernstian, behavior reasonably attributed to the electric field present at the interface, and accounted for the hole transfer yields measured after pulsed laser excitation. The charge recombination kinetics and the density of TiO$_2$ acceptor states were the same for all the sensitized materials that were characterized, while the open circuit photovoltage was largest for the sensitizer that displayed the highest yield for hole transfer demonstrated the importance of the oxidized sensitizer dipole moment. Finally, a novel photo-initiated intermolecular hole transfer process occurred with a hole hopping rate of (130 ns)$^{-1}$ that was sufficient to translate the hole a considerable distance from the site of excited state injection, provided that the concentration of holes was small.
2.6 Appendix

Figure A2.1  UV-vis absorption spectra of (a) C2/TiO2 (b) C3/TiO2 (c) C4/TiO2 measured at different applied potentials in 0.5 M LiClO4 CH3CN solutions. The insets show the fraction (x) of dye molecules present in the fully reduced state (black squares), singly oxidized state (red squares) and doubly oxidized state (green squares). Overlaid are sigmoidal fits, x=1/(1+10exp((E_{app}-E^{0}_1/2)/a×59mV)), where a is the non-ideality factor.
Table A2.1 Calculated Dipole Moments vector components, orientation with respect to the TiO\textsubscript{2} surface normal and electrostatic potential drop for C\textsubscript{2}, C\textsubscript{4} and C\textsubscript{5} in their two protonation studied states (a. triprotonated and b. diprotonated) and in their two oxidation state (Ru(II) and Ru(III)).

<table>
<thead>
<tr>
<th></th>
<th>(\mu_x)</th>
<th>(\mu_y)</th>
<th>(\mu_z)</th>
<th>(\theta) (°)</th>
<th>(\phi_{\text{dipole}}) (mV)</th>
<th>(\Delta \phi_{\text{dipole}}) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground State</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{2}</td>
<td>1.61</td>
<td>2.64</td>
<td>-4.29</td>
<td>5.3</td>
<td>27.61</td>
<td>-25</td>
</tr>
<tr>
<td></td>
<td>0.88</td>
<td>23.84</td>
<td>-13.44</td>
<td>27.4</td>
<td>43.63</td>
<td>-105</td>
</tr>
<tr>
<td>C\textsubscript{4}</td>
<td>1.87</td>
<td>3.91</td>
<td>-3.15</td>
<td>5.4</td>
<td>40.49</td>
<td>-22</td>
</tr>
<tr>
<td></td>
<td>9.15</td>
<td>23.70</td>
<td>-12.05</td>
<td>28.1</td>
<td>41.96</td>
<td>-110</td>
</tr>
<tr>
<td>C\textsubscript{5}</td>
<td>1.30</td>
<td>4.74</td>
<td>-5.74</td>
<td>7.6</td>
<td>43.07</td>
<td>-29</td>
</tr>
<tr>
<td></td>
<td>10.36</td>
<td>24.44</td>
<td>-14.11</td>
<td>30.1</td>
<td>39.58</td>
<td>-122</td>
</tr>
<tr>
<td>Oxidized State</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{2} \textsuperscript{+}</td>
<td>17.56</td>
<td>4.09</td>
<td>-9.86</td>
<td>20.5</td>
<td>9.54</td>
<td>-107</td>
</tr>
<tr>
<td></td>
<td>35.10</td>
<td>26.98</td>
<td>-13.60</td>
<td>46.3</td>
<td>26.05</td>
<td>-220</td>
</tr>
<tr>
<td>C\textsubscript{4} \textsuperscript{+}</td>
<td>29.57</td>
<td>7.48</td>
<td>-6.15</td>
<td>31.1</td>
<td>-0.85</td>
<td>-164</td>
</tr>
<tr>
<td></td>
<td>43.55</td>
<td>23.29</td>
<td>-11.69</td>
<td>50.8</td>
<td>17.38</td>
<td>-256</td>
</tr>
<tr>
<td>C\textsubscript{5} \textsuperscript{+}</td>
<td>29.81</td>
<td>7.34</td>
<td>-11.75</td>
<td>32.9</td>
<td>-4.62</td>
<td>-173</td>
</tr>
<tr>
<td></td>
<td>47.93</td>
<td>24.16</td>
<td>-14.18</td>
<td>55.5</td>
<td>18.28</td>
<td>-278</td>
</tr>
</tbody>
</table>
Figure A2.2 Frontier Molecular Orbitals for the three studied complexes in their ground state.
Figure A2.3 Frontier Molecular Orbitals for the three studied complexes in their oxidized state with one carboxylic acid group deprotonated.
Figure A2.4 Absorption change monitored at 640 nm after 532 nm light excitation for C5/TiO2 immersed in 50 mM LiClO4 CH3CN at -45 °C. The data correspond to intra-molecular RuIII → NAr3 hole transfer with an overlaid fit to a first-order kinetic model.
Figure A2.5 Absorption change monitored at 550 nm after pulsed light excitation (532 nm) of C1-C5/TiO$_2$ immersed in 0.5 M LiClO$_4$ CH$_3$CN. Overlaid in yellow is the best fit to the KWW kinetic model.
Figure A2.6  Absorption change monitored at 740 nm after pulsed light excitation (532 nm) of C5/TiO2 immersed in 0.5 M LiClO4 CH3CN at 1/5 saturation surface coverage (black) and saturation surface coverage (red).
Figure A2.7 The ATR-FTIR spectra of C4/TiO2 (blue), H2SO4 treated C4/TiO2 (red) and C4 powder (black). The green dashed line serves as a guide line for the peaks appearing at 1712 cm⁻¹.
Figure A2.8 The UV-vis absorption of C1/TiO$_2$, C1$^+$/TiO$_2$ and C1$^{2+}$/TiO$_2$
Figure A2.9 Absorption change monitored at 442 nm after pulsed 532 nm light excitation of C5/TiO2 at the indicated applied potentials. Overlaid in yellow are the fits to the KWW model. Inset: a $t_{1/2}$ analysis of this data plotted against the fraction of oxidized triarylamines.
Figure A2.10  Plot of open circuit voltages of $\text{C2}/\text{TiO}_2$, $\text{C4}/\text{TiO}_2$ and $\text{C5}/\text{TiO}_2$ in 0.5 M LiClO$_4$ CH$_3$CN non-regenerative electrolyte versus steady state irradiances.
Figure A2.11  Absorption changes monitored at 540 nm after pulsed light excitation with five irradiances ($\lambda_{\text{ex}} = 532$ nm 0.3-1.5 mJ/cm$^2$) of C1/TiO$_2$ immersed in 0.5 M LiClO$_4$ CH$_3$CN and biased at 1035 mV versus NHE. Overlaid as solid lines are absorption profiles abstracted from Monte Carlo simulations of 8 TiO$_2$ nanoparticles (2×2×2 array).
Figure A2.12 Chi-Squared analysis (a) and residuals for the highest S/N data (b) of Monte Carlo simulations for lateral hole transfer reactions occurring on a single nanocrystal (black), an 8 nanocrystal array (red) and a 27 nanocrystal array (blue). Chi-squared values were calculated using 1000 points evenly spaced on a logarithmic scale. Experimental values were a 21-point moving average of the raw data.
Figure A2.13  The interfacial density of states for C2/TiO2, C4/TiO2, and C5/TiO2 measured by spectroelectrochemistry in 0.5 M LiClO4/CH3CN electrolyte.
2.7 References


126


Chapter 3: Atomic Level Resolution of Dye Regeneration in the Dye Sensitized Solar Cell

In part a compilation of one publication.¹

This work was collaborative in conjunction with Kiyoshi C. D. Robson‡, Gerald J. Meyer† and Curtis P. Berlinguette‡

‡Johns Hopkins University, Baltimore, MD, USA
†University of Calgary, Calgary, Canada

3.1 Introduction

Dye-sensitized solar cells (DSSC) continue to be actively pursued as low cost alternatives to traditional photovoltaics.² The successful utilization of Co³⁻/²⁺ diimine compounds as redox mediators³⁻⁶ removes some of the inherent thermodynamic limitations of the I⁻/I₃⁻ mediators⁷ and could soon enable a leapfrog jump in efficiency. Also impressive is the molecular detail in which DSSCs can now be optimized.⁸,⁹ Isotopic substitution has also been shown to enhance excited state electron injection yields.¹⁰ Indeed, several recent reports demonstrate that exchange of a single atom, or a few atoms, in a dye molecule markedly changes the efficiencies of DSSCs comprised of them. While the magnitude of the efficiency change can be quite dramatic, the origin(s) generally remains speculative. Adducts comprised of one of the exchanged atoms with redox mediators present in the electrolyte are generally invoked to rationalize photoelectrochemical behavior.¹¹,¹² In all cases investigated thus far, adduct formation lowers DSSC efficiencies. The findings
disclosed herein suggest that adduct formation, most likely involving iodide activation, can results in enhanced power conversion efficiencies when the position of the exchanged atom within the dye structure is carefully taken into account.

One would indeed expect changes in DSSC efficiency when heteroatoms in a dye molecule are exchanged. Adduct formation between the dye and the semiconductor surface and/or species present in the electrolyte alter redox potentials and hence the interfacial electron-transfer kinetics that govern electrical power generation. O’Regan and Palomares have reported evidence of N-I and S-I binding.\textsuperscript{11,13} The iodine species was thought to be the oxidized form of the redox mediator present in the electrolyte, either molecular iodine, I\textsubscript{2}, or tri-iodide, I\textsubscript{3}\textsuperscript{−}. The high surface concentration of these iodine-based electron acceptors at the TiO\textsubscript{2} interface results in conditions that favor unwanted charge recombination and hence lower the quasi-Fermi level of the illuminated TiO\textsubscript{2} thin film.\textsuperscript{14} Based largely on this novel work, it is now widely accepted that the presence of sulfur heteroatom(s) in a dye molecule have a deleterious influence on energy conversion when employed in DSSCs. This conclusion is unfortunate as large classes of organic dye, such as polythiophenes and phenothiazines, possess S atoms.

In order to resolve the nature of these interactions, two oxygen atoms in the donor-acceptor organic dye \((E)-3-\{(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-2-cyanoprop-2-enoic acid (\textbf{Dye-O})\}\textsuperscript{15} were replaced with two sulfur atoms, \((E)-3-\{(5-(4-(bis(4-(hexylthio)phenyl)amino)phenyl)thiophen-2-yl)-2-cyanoprop-2-enoic acid) (\textbf{Dye-S})\) shown in Figure 3.1. The dye molecules are ‘donor-acceptor’ or ‘push-pull’ type organic dyes wherein charge transfer for the triphenylamine group (TPA) to the cyanoacetic acid moiety that can bind to the TiO\textsubscript{2}. This orbital arrangement allows for efficient charge separation and vectorial electron transfer towards the TiO\textsubscript{2} surface subsequent to light absorption. Moreover, these donor and acceptor units are common modalities in high performance organic and/or inorganic DSSC sensitzers.\textsuperscript{16-20}
In this study the location of the substitution of the two-atom changes was carefully taken into consideration. As shown in Figure 3.1, there is a sizable orbital coefficient on the heteroatom (either O or S, for Dye-O and Dye-S, respectively) in the lowest-unoccupied spin orbital (LUSO) of the oxidized forms of the dyes (i.e., Dye-O⁺ and Dye-S⁺). Consequently, the delocalization of the LUSO onto the heteroatoms offers the opportunity to interrogate how S and O atoms can affect DSSC performance, particularly in view of the fact that it is this same portion of the oxidized sensitizer that directly interacts with the redox mediator. Comparative interfacial electron transfer studies were therefore conducted with Dye-O and Dye-S anchored to mesoporous TiO₂ thin films in the presence and absence of Co₃⁺/²⁺ and I₃⁻/I⁻ redox mediators to gain insight into the role of specific adducts. It is shown that the identity of the heteroatom can have a profound effect on dye regeneration, and in turn the open-circuit voltage (Vₜₜ), as the S atoms enhance the rate of the reaction between the oxidized dye and the redox mediator by 3-fold with Co-based mediators, and 25-fold with iodide-based mediators.
Figure 3.1 Molecular structures of the organic dyes Dye-O and Dye-S. The heteroatoms that have an effect on the regeneration reaction with redox mediators are indicated. The β-LUSO (lowest-unoccupied spin orbital) for the oxidized forms of each dye, Dye-O⁺ and Dye-S⁺, are provided below each structure to highlight the delocalization of the wavefunction onto the heteroatoms of interest (the terminal hexyl substituents were replaced with methyl substituents for the calculations).
3.2 Experimental

Preparation of Compounds. All reactions and manipulations were performed using solvents passed through an MBraun solvent purification system prior to use. All reagents were purchased from Aldrich. Purification by column chromatography was carried out using silica (Silicycle: Ultrapure Flash Silica). Analytical thin-layer chromatography (TLC) was performed on aluminum-backed sheets pre-coated with silica 60 F254 adsorbent (0.25 mm thick; Merck, Germany) and visualized under UV light. Routine $^1$H and $^{13}$C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature. Chemical shifts ($\delta$) are reported in parts per million (ppm) from low- to high-field and referenced to residual non-deuterated solvent in the Supporting Information Section. Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; t = triplet; m = multiplet. All $^1$H chemical shifts follow the general labeling scheme in Figure A3.1. Organic and inorganic compounds Dye-O$^{15}$ and P1-S,$^{21}$ P2-S,$^{21}$ P3-S,$^{21}$ 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane,$^{22}$ 1,3-dimethylimidazolium iodide (DMII),$^{23}$ [Co(bpy)$_3$](PF$_6$)$_2$, and [Co(bpy)$_3$](PF$_6$)$_3$,$^{6}$ were synthesized according to literature reports.

Substrate Preparations. Mesoporous nanocrystalline TiO$_2$ thin films were prepared as previously described.$^{24}$ Film thickness was determined to be about 5 μm by profilometry. The films were briefly immersed in acetonitrile solution containing dye (~75 μM) and coadsorbent chenodeoxycholic acid (~3.7 mM). Films were then washed with neat CH$_3$CN and diagonally positioned in a standard 1 cm$^2$ quartz cuvette containing 0.5 M LiClO$_4$ acetonitrile solution. In some experiments the sensitized thin films were sandwiched against a glass microscope with a vinyl film (Warps, 8 mil Vinyl-Pane) spacer that contained desired concentrations of Co(bpy)$_3^{2+}$ or LiI in 0.5 M LiClO$_4$ acetonitrile solutions. The electrolyte solutions were purged with Ar gas for at least 30 min prior to experimentation.
**Spectroelectrochemistry.** Steady-state UV-visible absorption spectra were obtained on a Varian Cary 50 spectrophotometer at room temperature. A potentiostat (BAS model CV-50W) was employed for measurements in a standard three-electrode arrangement with a sensitized TiO$_2$ thin film deposited on a FTO substrate working electrode, a platinum disk counter electrode and an Ag/AgCl reference electrode (Bioanalytical Scientific Instruments, Inc.) in 0.5 M LiClO$_4$ acetonitrile solution. All potentials are reported versus the normal hydrogen electrode (NHE). The ferrocenium/ferrocene half-wave potential was measured at room temperature before and after each experiment and was used as an external standard to calibrate the reference electrode. Conversion constant of -640 mV from NHE to Fc$^+/Fc$ was used in acetonitrile at 25 °C.

**Transient Absorption Spectroscopy.** Nanosecond transient absorption measurements were obtained with an apparatus similar to that which has been previously described.$^{24}$ Briefly, samples were excited by a frequency doubled Q-switched, pulsed Nd:YAG laser (Quantel USA (BigSky) Brilliant B; 532 nm, 5-6 ns full width at half-maximum (fwhm), 1 Hz, ~10 mm in diameter) directed 45° to the film surface. A Glan-Taylor polarizer was employed in the laser path to attenuate the pulse fluence. A 150 W Xenon arc lamp coupled to a 1/4 m monochromator (Spectral Energy, Corp. GM 252) served as the probe beam (Applied Photophysics) that was aligned orthogonally to the excitation light. For detection at sub-100 μs time scales the lamp was pulsed with 80 V. Detection was achieved with a monochromator (Spex 1702/04) optically coupled to an R928 photomultiplier tube (Hamamatsu). Transient data were acquired on a computer-interfaced digital oscilloscope (LeCroy 9450, Dual 350 MHz) with 2.5 ns resolution terminated at 50 Ω for sub-100 μs; for longer time scales, the signal was terminated with a 10 kΩ resistor and bandwidth limited at 80 MHz. Typically, 30-50 laser pulses were averaged at each observation wavelength over the range 380-710 nm for full spectra generation. 300-500 laser pulses were typical averages for single wavelength measurement to achieve satisfactory S/N. Kinetic data fitting and spectral modeling
was performed in Origin 8 and least-squares error minimization was accomplished using the Levenberg-Marquardt iteration method.

**DFT Calculations.** Density functional theory (DFT) calculations were carried out using B3LYP and the 6-31G(d) basis set. All geometries were fully optimized in the ground states (closed shell) and the +1 oxidized states (open shell). Time-dependent density functional theory (TD-DFT) calculations were performed with an IEFPCM solvation model (CH$_3$CN) using a spin-restricted formalism to examine low-energy excitations at the ground-state geometry. All calculations were carried out with the Gaussian 03W software package.$^{25}$

**Cell Fabrication.** Photoanodes were prefabricated by Dyesol Inc. (Australia) with screen-printable TiO$_2$ pastes (18-NRT and WER4-O, Dyesol$^{\text{TM}}$). The active area of the TiO$_2$ electrodes were 0.28 cm$^2$ with a thickness of 6 μm (18-NRT) and 3 μm (WER4-O) on fluorine-doped tin-oxide [FTO; TEC8 (8 Ω cm$^{-2}$)]. The TiO$_2$ substrates were treated with TiCl$_4$(aq) (0.05 M) at 70 °C for 30 min and subsequently rinsed with H$_2$O and then dried prior to heating. The electrodes were heated to 450 °C for 20 min in an ambient atmosphere and left to cool to 80 °C prior to immersing into an acetonitrile solution containing the dye (~0.25 mM) and chenodeoxycholic acid (~2.5 mM) for 16 h. The stained films were then rinsed with copious amounts of CH$_3$CN and dried. The cells were fabricated using Pt-coated counter-electrode [FTO TEC-15 (15 Ωcm$^{-2}$)] and sealed with a 30 μm Surlyn (Dupont) gasket by resistive heating. Two electrolytes were used for this study: (i) I$_3^+$/I$^-$ [1.0 M 1,3- dimethylimidazolium iodide (DMII), 60 mM I$_2$, 0.5 M tert-butylpyridine, 0.05 M NaI and 0.1 M GuNCS in a mixed solvent system of acetonitrile and valeronitrile (85:15, v/v)]; (ii) Co$^{III/II}$ [0.21 M [Co(bpy)$_3$](PF$_6$)$_2$, 0.033 M [Co(bpy)$_3$](PF$_6$)$_3$, 0.1 M NaClO$_4$ and 0.2 M tert-butylpyridine in acetonitrile]. Each electrolyte was introduced into the two sandwiched electrodes via vacuum backfilling through a hole in the counter electrode. In the cases where the I$_3^+$/I$^-$ electrolyte was used, the hole was sealed with an aluminum-backed Bynel® foil (Dyesol$^{\text{TM}}$). In the cases where the Co$^{III/II}$ electrolyte was used, the hole was covered with a thin Surlyn (25 μm) microscope slide;
aluminum foil was then taped to the back of the cell. Silver bus bars were added to all cells after sealing.

**Cell Characterization.** Photovoltaic measurements were recorded with a Newport Oriel solar simulator (Model 9225A1) equipped with a class A 150 W xenon light source powered by a Newport power supply (Model 69907). The light output (area = 5 cm x 5 cm) was calibrated to AM 1.5 using a Newport Oriel correction filter to reduce the spectral mismatch in the region of 350-700 nm to less than 1.5%. The power output of the lamp was measured to 1 Sun (100 mW cm\(^{-2}\)) using a certified Si reference cell. The current-voltage (I–V) characteristic of each cell was obtained by applying an external potential bias to the cell and measuring the generated photocurrent with a Keithley digital source meter (Model 2400). All cells were measured with a mask size of 0.13 cm\(^2\). IPCE measurements were performed on a QEX7 Solar Cell Spectral Response Measurement System from PV Instruments, Inc. The system was calibrated with a photodiode that was calibrated against NIST standard I755 with a transfer uncertainty of less than 0.5% between 400-1000 nm, and less than 1% at all other wavelengths. All measurements were made in AC mode at a 10-Hz chopping frequency under a bias light. The system was calibrated and operated in Beam Power mode.
3.3 Results

3.3.1 Synthesis and Characterization.

The preparation of Dye-O followed a previously reported literature procedure.\textsuperscript{15} A similar protocol was followed for Dye-S with the exception of the generation of the P2-S precursor, which was isolated following an electrophilic aromatic substitution reaction between P1-S and C_6H_5S- (Scheme A3.1, Supporting Information). A subsequent electrophilic bromination step with NBS furnished the bromoderivative P3-S, which could undergo reaction with 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane under Suzuki cross-coupling conditions to yield P4-S. A Vilsmeier-Haack formylation was employed to install the –CHO group (P5-S), which was condensed with cyanoacetic acid to yield the target Dye-S.

The optical spectra of Dye-O and Dye-S recorded in CH_3CN are very similar (Figure 3.2a). Dye-O is characterized by an intense charge-transfer absorption band centered at \( \lambda_{\text{max}} = 478 \text{ nm} \) (\( \varepsilon = 2.84 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \)), while that of Dye-S is slightly hypsochromically shifted to \( \lambda_{\text{max}} = 470 \text{ nm} \) (\( \varepsilon = 3.16 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \)). The slight differences in absorption are attributed to less orbital overlap of the sulfur lone pairs with the \( \pi \) system of the aryl rings of the TPA groups relative to those of the oxygen atoms, which was corroborated by the \(^1\text{H} \) NMR chemical shifts and redox chemistry (\textit{vide infra}) of the two complexes.\textsuperscript{21} Time-dependent DFT indicates that, for both Dye-O and Dye-S, the HOMO, HOMO-1, and HOMO-2 orbitals are localized to the electron-rich TPA moiety, and the LUMO and LUMO+1 levels are confined to the cyanoacetic acid portion of the molecule; the lowest energy transition (\textit{i.e., \( \lambda_1 \); Figure A3.2 and Figure A3.3}) is a LUMO \( \leftrightarrow \) HOMO transition. Light excitation into the charge transfer absorption bands resulted in room temperature fluorescence, Figure A3.4.

The dyes were found to bind to thin films of anatase, mesoporous TiO_2 with high surface coverages over 1\( \times 10^{-7} \) mol/cm\(^2\), and are herein abbreviated Dye-O/TiO_2 and Dye-S/TiO_2. When
the sensitized thin films were measured in neat CH$_3$CN, the absorption maxima were slightly blue shifted from that observed in fluid solution (Figure 3.2b). The presence of 0.5 M LiClO$_4$ induced a significant bathochromic (red) shift in both cases, measured to be 870 cm$^{-1}$ for Dye-O/TiO$_2$ and 750 cm$^{-1}$ for Dye-S/TiO$_2$ (Figure A3.5). Lewis acidic cations, such as Li$^+$, bind to anatase TiO$_2$ and the local field generated are known to induce a bathochromic shift of dye molecules anchored to the same surface.\textsuperscript{26}

The cyclic voltammograms of Dye-O or Dye-S in 0.1 M NBu$_4$BF$_4$/CH$_3$CN electrolyte displayed quasi-reversible TPA$^{+}$/TPA$^0$ redox waves at +0.96 and +1.06 V vs. NHE, respectively as shown in Figure A3.6. Cyclic voltammetry of the sensitized thin films showed broad waves with large peak-to-peak splittings (Figure A3.7). Spectroelectrochemistry was therefore used to estimate the reduction potentials of Dye-O/TiO$_2$ and Dye-S/TiO$_2$. Oxidation of Dye-O/TiO$_2$ or Dye-S/TiO$_2$ resulted in characteristic absorption changes attributed to the oxidized triphenylamine (Figure 3.3). Isosbestic points were maintained and the spectral changes were reversible upon stepping the potential back to less positive values. The insets of Figure 3.3 show the fraction of molecules in the given redox state at each applied potential, E$_{app}$. This fraction of (x) was calculated by \( x = 1/(1+10^{((E_{app}-E^o)/a\times59\text{ mV})}) \). The formal reduction potential, E$^o$, was taken as the equilibrium potential where the fraction present was 0.5, and was measured to be +1090 mV vs. NHE for Dye-S/TiO$_2$ while +1015 mV for Dye-O/TiO$_2$. An ideality factor of \( a = 1.27 \) for Dye-O/TiO$_2$ and \( a = 1.05 \) for Dye-S/TiO$_2$ were required to fit the data.\textsuperscript{14} In some cases, the fractional surface coverage was converted to a chemical capacitance in units of mF/cm$^2$ by \( (-d\chi/dE_{app})\times\Gamma\times F \times 10^6 \), where \( \Gamma \) is the surface coverage in mol/cm$^2$ and F is Faraday’s constant (96,485 C·mol$^{-1}$).
Figure 3.2 UV-vis absorption spectra of Dye-O (red) and Dye-S (blue) in a) fluid CH$_3$CN solution and b) anchored to TiO$_2$ immersed in CH$_3$CN solution at 298 °K.
The $E_{0,0}$ energy was calculated to be 2.31 eV and 2.32 eV for Dye-O and Dye-S, respectively, from the intersection of the absorption and fluorescence spectra (Table 3.1 and Figure A3.4). The excited state reduction potential, $E(S^*/S)$, was then calculated by $E(S^*/S) = E(S^*/S) - E_{0,0}$ to be -1.35 and -1.26 V vs. NHE for Dye-O and Dye-S, respectively.

The application of negative applied potentials to the sensitized thin films immersed in 0.5 M LiClO$_4$/CH$_3$CN resulted in reduction of TiO$_2$ and the characteristic absorption of the trapped TiO$_2$ electron, TiO$_2$(e$^-$). The potential dependence of this reduction was found to be the same for Dye-O/TiO$_2$ and Dye-S/TiO$_2$, and were well described by a single exponential fit, Figure A3.8.

The measured absorbance was related to the number of TiO$_2$(e$^-$)s per 15 nm diameter spherical particle though Beer’s law and the extinction coefficient $\varepsilon = 1000 \text{ M}^{-1}\cdot\text{cm}^{-1}$ with an effective optical path length for a 5 $\mu$m thick film of 50% porosity positioned 45$^\circ$ to the probe light. For example, the absorption due to 20 electrons per particle was calculated as $\text{Abs} = \varepsilon \cdot b \cdot c(TiO_2(e^-)) = 1000 \text{ M}^{-1}\cdot\text{cm}^{-1} \times 5 \text{ (}\mu\text{m}) \times 1.414 \times 10^{-4} \text{ (cm}\cdot\text{mm}^2) \times 50\% \times 20 / (4/3\times\pi\times(7.5\times10^{-9}\text{m}))^3\times\text{N}_A/10^3\text{(L} \cdot \text{m}^{-3}) = 0.007.$
Figure 3.3  Visible absorption spectra of (a) Dye-O/TiO₂ (dye surface coverage Γ = 1.0×10⁻⁷ mol·cm⁻²) and (b) Dye-S/TiO₂ (Γ = 5.3×10⁻⁷ mol·cm⁻²) measured at the indicated applied potentials in 0.5 M LiClO₄ CH₃CN solution. The insets show the fraction (x) of dye molecules present in the reduced (black squares, ■) and the oxidized state (red circles, ●). Overlaid on this data is a sigmoidal fit, $x = 1/(1+10^{(E_{\text{app}}-E^{\circ}/a×59 \text{ mV})})$, where a is the ideality factor determined to be 1.27 for Dye-O/TiO₂ and 1.05 for Dye-S/TiO₂.
Table 3.1  Summary of Spectroscopic and Electrochemical Properties for **Dye-O** and **Dye-S** in solution and anchored to TiO$_2$.

<table>
<thead>
<tr>
<th>compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{PL}}$ (nm)</th>
<th>$E_{1/2}$ (V vs NHE)</th>
<th>$E_{0.0}$ (eV)</th>
<th>$E(S^+/S^-)$ (V vs NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dye-O</strong></td>
<td>478 (2.84)</td>
<td>598</td>
<td>0.96</td>
<td>2.31</td>
<td>-1.35</td>
</tr>
<tr>
<td><strong>Dye-O/TiO$_2$</strong></td>
<td>468</td>
<td>-</td>
<td>1.02</td>
<td>2.03</td>
<td>-1.01</td>
</tr>
<tr>
<td><strong>Dye-S</strong></td>
<td>469 (3.16), 318 (2.96)</td>
<td>623</td>
<td>1.06</td>
<td>2.32</td>
<td>-1.26</td>
</tr>
<tr>
<td><strong>Dye-S/TiO$_2$</strong></td>
<td>453</td>
<td>-</td>
<td>1.09</td>
<td>2.12</td>
<td>-1.03</td>
</tr>
</tbody>
</table>

*a*Corresponds to maximum of lowest-energy absorption band recorded in CH$_3$CN; values indicated in parentheses with units of $\times 10^4$ M$^{-1}$ cm$^{-1}$.

*b*Fluorescence maxima determined in CH$_3$CN after excitation at a wavelength corresponding to $\lambda_{\text{max}}$.  *Corresponds to TPA$^{•+}$/TPA$^{0}$ redox couple.

Data collected in 0.1M NBu$_4$BF$_4$ CH$_3$CN solutions at 100 mV/s and referenced to [Fc]$^{+}$/[Fc] (+640 mV vs NHE). Data for sensitized TiO$_2$ thin films was collected in 0.5 M LiClO$_4$ CH$_3$CN solutions by density of states measurements (see Figure 3.10).  *In fluid solution, $E_{0.0}$ was estimated from the intersection of the normalized absorption and fluorescence spectra (See Figure A3.4). For the sensitized TiO$_2$ thin films, $E_{0.0}$ was estimated from the intercept of a tangent line drawn on the red edge of ground state absorption.  *Estimated using $E(S^+/S^-) = E_{1/2} - E_{0.0}$. 

141
Figure 3.4 Absorption difference spectra measured at the indicated delay times after pulsed 532 nm excitation of a) Dye-O/TiO$_2$ and b) Dye-S/TiO$_2$ immersed in 0.5 M LiClO$_4$ CH$_3$CN solution. Overlaid in purple are simulated spectra.
3.3.2 Interfacial Charge Recombination.

Nanosecond transient absorption spectroscopy was used to quantify interfacial electron transfer from TiO$_2$ to the oxidized sensitizers. Absorption difference spectra of Dye-O/TiO$_2$ and Dye-S/TiO$_2$ displayed in Figure 3.4 were acquired in 0.5 M LiClO$_4$ CH$_3$CN after pulsed 532-nm excitation of the sensitized thin films. Simulations based on a 1:1 stoichiometry of oxidized dyes and injected electrons, Dye$^+$/TiO$_2$(e$^-$), plus the first derivative of the ground state absorption were in good agreement with the experimental data. Normalization of the measured spectra at different observation times revealed that the bleach in the initial spectra were red shifted relative to those observed at longer delay times. The first derivative absorption feature is consistent with previous studies and the presence of an underlying electric field that influences the sensitizer absorption spectra in a manner similar to that observed in Stark spectroscopy. The time dependent spectral changes are due to screening of the electric field by solvents and ions.$^{26,27}$ The immediate appearance of the absorption spectrum of the oxidized dye molecule indicated that electron injection occurred with a rate constant $k_{inj} > 10^8$ s$^{-1}$.

Shown in Figure 3.5 are absorption changes measured after pulsed light excitation of Dye-O/TiO$_2$ and Dye-S/TiO$_2$ in 0.5 M LiClO$_4$/CH$_3$CN that correspond to charge recombination between the injected electron and the oxidized sensitizer. Both sensitized thin films had a ground state absorption of 0.43 at the 532-nm excitation wavelength. The kinetics were non-exponential but were satisfactorily modeled by Kohlrausch-Williams-Watts (KWW) function, Equation 3.1, with a $\beta$ value of 0.20 $\pm$ 0.01 for both sensitizers on mesoporous nanocrystalline TiO$_2$ surface.$^{28}$ Average charge recombination rate constants, $k_{cr}$, were calculated as the first moment$^{29}$ of the underlying Lévy distribution of rate constants, Equation 3.2.

\[
\Delta A_{bs} = A \exp[-(kt)^{\beta}] \tag{3.1}
\]

\[
k_{cr} = \left[ \frac{1}{k_{\beta}} \times \Gamma \left( \frac{1}{\beta} \right) \right]^{-1} \tag{3.2}
\]
Figure 3.5 Absorption change monitored at 635 nm after pulsed light excitation (532 nm; laser fluence: 0.3 mJ/cm$^2$) of Dye-O/TiO$_2$ (left) and Dye-S/TiO$_2$ (right) immersed in 0.5 M LiClO$_4$/CH$_3$CN at the indicated applied potentials. Overlaid in yellow are best fits to the KWW kinetic model.
In the absence of an applied bias, the $k_{cr}$ values were found to be within experimental error the same, $k_{cr} = 1.3 \pm 0.1 \times 10^2 \text{ s}^{-1}$ for Dye-O/TiO$_2$ and $k_{cr} = 1.4 \pm 0.1 \times 10^2 \text{ s}^{-1}$ for Dye-S/TiO$_2$, Figure A3.9. The reduction of TiO$_2$ with forward bias had a marked influence on the average charge recombination rate constants. The $k_{cr}$ values were found to increase exponentially with the applied potential from +100 to -300 mV vs NHE, Figure A3.10.

The $V_{oc}$ was measured in the absence of redox mediator under the same condition as the charge recombination measurement described previously. Over 2 decades of irradiances, the $V_{oc}$ values for Dye-O/TiO$_2$ and Dye-S/TiO$_2$ were within experimental error the same (Figure A3.11).
Figure 3.6 Absorption changes measured after pulsed laser excitation of the sensitized film in the presence of the indicated concentration of [Co(bpy)$_3$](ClO$_4$)$_2$ (a) Dye-O/TiO$_2$ and (b) Dye-S/TiO$_2$ or LiI (c) Dye-O/TiO$_2$ and (d) Dye-S/TiO$_2$ in 0.5 M LiClO$_4$ CH$_3$CN. Absorbance changes were monitored at a probe wavelength of 635 nm (excitation wavelength: 532 nm; laser fluence: 0.1 mJ/cm$^2$). Overlaid in yellow are the best fits to bi-exponential kinetic model.
Figure 3.7 Plots of observed regeneration rate constants ($\bar{k}_{\text{obs}}$) of Dye-O/TiO$_2$ (solid squares, ■) and Dye-S/TiO$_2$ (solid circles, ●) obtained from the kinetics fits versus titrated a) [Co(bpy)$_3$$^{2+}$] and b) iodide concentrations.
Table 3.2  Second-order regeneration rate constants \( (k_{\text{reg}}) \) abstracted for \textbf{Dye-O}/TiO\(_2\) and \textbf{Dye-S}/TiO\(_2\) in 0.5 M LiClO\(_4\)/CH\(_3\)CN containing cobalt- and iodide-based redox mediators.

<table>
<thead>
<tr>
<th></th>
<th>[Co(bpy)](_3)(^{2+})</th>
<th>Iodide</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{\text{reg}} ) (M(^{-1})·s(^{-1}))</td>
<td>( G^{0,a} ) (V)</td>
<td>( k_{\text{reg}} ) (M(^{-1})·s(^{-1}))</td>
</tr>
<tr>
<td><strong>Dye-O/TiO(_2)</strong></td>
<td>1.1×10(^6)</td>
<td>-0.46</td>
</tr>
<tr>
<td><strong>Dye-S/TiO(_2)</strong></td>
<td>3.5×10(^6)</td>
<td>-0.53</td>
</tr>
</tbody>
</table>

\(^a\)\( E^0([\text{Co(bpy)}]^{3+/2+}) = 0.56 \) V vs. NHE. \(^b\)Calculated free energy change for outer-sphere reactions based on \( E^0(I/I) = 1.23 \) V vs. NHE or \(^c\)\( E^0(I_2^-/2I) = 0.93 \) V vs. NHE
3.3.3 Sensitizer Regeneration.

The regeneration of Dye-O*/TiO₂(e⁻) and Dye-S*/TiO₂(e⁻) by iodide and [Co(bpy)₃]²⁺ donors were investigated. A laser pulse was used to generate the interfacial charge separated state, Dye-O*/TiO₂(e⁻) or Dye-S*/TiO₂(e⁻), in an electrolyte that contained known amounts of I⁻ or [Co(bpy)₃]²⁺. The data were recorded at an observation wavelength of 635 nm where the oxidized dye predominately absorbed light, Figure 3.6. Increased donor concentrations significantly increased the regeneration rates. The observed kinetic data could not be fit to a single exponential function, but were adequately described by a sum of two exponential functions, from which an average rate constant was calculated, Equations 3.3 and 3.4.

\[ \Delta \text{Abs} = A_0 + A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t) \]  \hspace{1cm} (3.3)

\[ \bar{k}_{obs} = \frac{A_1/k_1 + A_2/k_2}{A_1/k_1^2 + A_2/k_2^2} \]  \hspace{1cm} (3.4)

The \( \bar{k}_{obs} \) values were plotted against Co(bpy)₃²⁺ and I⁻ concentrations. A linear relation was observed as is shown in Figure 3.7. The slopes from the linear fits provided the second-order rate constants for dye regeneration. The values are summarized in Table 3.2.

The regeneration efficiency, \( \phi_{\text{reg}} \), was quantified based on the charge recombination and regeneration rate constants, Equation 3.5

\[ \phi_{\text{reg}} = \frac{k_{\text{reg}}[D]}{(k_{\text{cr}} + k_{\text{reg}}[D])} \]  \hspace{1cm} (3.5)

where D is the donor concentration. The \( \phi_{\text{reg}} \) values reflect the facts that charge recombination rate constants were highly sensitive to the extent of forward bias and that regeneration rate constants were larger for Dye-S*/TiO₂(e⁻), Table 3.3.
Table 3.3 Regeneration efficiencies calculated by Equation 3.5 at the indicated forward bias conditions

<table>
<thead>
<tr>
<th>Bias (mV vs. NHE)</th>
<th>$\Phi_{reg}$ 0.5 M I$^+$</th>
<th>$\Phi_{reg}$ 0.2 M Co$^{II}$(bpy)$_3^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>-70</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>-140</td>
<td>0.97</td>
<td>0.91</td>
</tr>
<tr>
<td>-200</td>
<td>0.83</td>
<td>0.60</td>
</tr>
<tr>
<td>-270</td>
<td>0.57</td>
<td>0.28</td>
</tr>
<tr>
<td>Dye-O/TiO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>30</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>-40</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>-110</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>-180</td>
<td>0.99</td>
<td>0.95</td>
</tr>
<tr>
<td>-240</td>
<td>0.99</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Dye-S/TiO$_2$
Transient absorption spectra were also recorded after pulsed laser excitation in the presence of iodide. At long observation times (> 10 μs) the injected electron and I$_3^-$ were observed as well as a derivative feature attributed to a shift in the ground state absorption of the dye molecules due to the injected electrons (an electro-absorption or Stark effect)$^{26,27}$, Figure A3.12. Recombination of the injected electron with I$_3^-$ was found to be well modeled by KWW function with a β value of 0.8, Figure A3.13. An average rate constant was calculated to be 2.3 ± 0.4 s$^{-1}$ using Equation 3.2.

At short observation times, there was clear kinetic evidence for the presence of I$_2^\cdot$. It was of interest to test whether injected electrons recombined with I$_2^\cdot$. This was accomplished by a method that was previously described.$^{30}$ The absorption change at 396 nm, where both I$_3^-$ and I$_2^\cdot$ absorbed light, was measured at a sufficiently long delay time (10 μs) to ensure that all of the photogenerated I$_2^\cdot$ had disproportionated. The initial amplitude of the absorption change expected if quantitative I$_2^\cdot$ disproportionation occurred was then calculated, based on and the known relative extinction coefficients of I$_3^-$ and I$_2^\cdot$, and compared to the experimentally measured value. After a small correction for contributions from the oxidized dye, the calculated and experimentally measured values were within experimental error the same for Dye-S/TiO$_2$, consistent with quantitative I$_2^\cdot$ disproportionation, Figure A3.14. In other words, all the I$_2^\cdot$ that was photogenerated underwent disproportionation with no evidence for a TiO$_2$(e$^-$) + I$_2^\cdot$ → reaction. This same conclusion could not be reached for Dye-O/TiO$_2$ due to the more sluggish regeneration rates that made kinetic analysis difficult.

3.3.4 Light-to-Electrical Energy Conversion.

Photocurrent density-voltage plots are shown for DSSCs with Dye-O and Dye-S using an iodide- and cobalt-based electrolytes, Figure 3.8. The DSSCs fabricated with Dye-S display similar power conversion efficiencies (PCEs) to those fabricated with 1 with the I$_3$/I$^-$ based electrolytes, Table 3.4. The DSSCs fabricated with Dye-O and Dye-S and an I/I$_3^-$ based electrolyte displayed
PCEs of 6.1 ± 0.2 % and 6.2 ± 0.3 %, respectively. The DSSCs fabricated with **Dye-O** or **Dye-S** and the CoIII redox mediator displayed PCEs of 4.6 ± 0.4 % and 6.3 ± 0.7 %, respectively.

Photocurrent action spectra, measured as the incident photon-to-current efficiency (IPCE) versus wavelength (Figure 3.9), were in good agreement with the absorptance spectra. The slight decrease in photocurrent efficiency that was measured below 420 nm with the iodide containing electrolyte is due to competitive light absorption by tri-iodide. The **Dye-O** absorbed light to about 650 nm. When corrections were made for light scattering and absorption by the FTO substrate, the efficiency was near 100%.
Table 3.4 Solar Cell Performance Parameters Obtained Under Simulated AM 1.5 Illumination (1 Sun) for Dye-O and Dye-S.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electrolyte&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$J_{sc}$ (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>$V_{oc}$ (mV)</th>
<th>Fill Factor</th>
<th>PCE (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye-O</td>
<td>I&lt;sup&gt;-&lt;/sup&gt;/I&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>11.7 ± 0.2</td>
<td>734 ± 21</td>
<td>70.5 ± 1.5</td>
<td>6.1 ± 0.2</td>
</tr>
<tr>
<td>Dye-S</td>
<td>I&lt;sup&gt;-&lt;/sup&gt;/I&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>10.3 ± 0.6</td>
<td>798 ± 24</td>
<td>74.4 ± 2.2</td>
<td>6.2 ± 0.3</td>
</tr>
<tr>
<td>Dye-O</td>
<td>Co&lt;sup&gt;III/II&lt;/sup&gt;</td>
<td>10.1 ± 0.5</td>
<td>714 ± 31</td>
<td>63.7 ± 4.8</td>
<td>4.6 ± 0.4</td>
</tr>
<tr>
<td>Dye-S</td>
<td>Co&lt;sup&gt;III/II&lt;/sup&gt;</td>
<td>10.8 ± 0.4</td>
<td>828 ± 38</td>
<td>70.0 ± 3.6</td>
<td>6.3 ± 0.7</td>
</tr>
</tbody>
</table>

<sup>a</sup>The I<sub>3</sub>/<I<sub>3</sub><sup>-</sup> electrolyte solution is composed of 1.0 M 1,3-dimethylimidazolium iodide (DMI), 60 mM I<sub>2</sub>, 0.5 M tert-butylpyridine, 0.05 M NaI and 0.1 M GuNCS in a mixed solvent system of acetonitrile and valeronitrile (85:15, v/v) while the Co<sup>III/II</sup> electrolyte is composed of 0.21 M [Co(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>, 0.033 M [Co(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>, 0.1 M NaClO<sub>4</sub> and 0.2 M tert-butylpyridine in acetonitrile. <sup>b</sup>A 0.13 cm<sup>2</sup> mask was used.
Figure 3.8 Current-voltage curves for DSSCs fabricated with Dye-O and Dye-S at AM1.5 illumination using (A) I/I₃ and (B) Co³⁺II redox mediators.
Figure 3.9 Incident-photon-to-current efficiency for DSSCs fabricated using a) $\Gamma/I_3^-$ and b) $\text{Co}^{III/II}$ redox mediators.
3.4 Discussion

The two dyes investigated in this study, that differ only by a two-heteroatom change from oxygen to sulfur within the donor unit, revealed nearly quantitative short-circuit photocurrent efficiencies when employed in DCCS with iodide or cobalt redox mediators. However, the open circuit photovoltage, $V_{oc}$, was found to be largest for Dye-S under all conditions investigated. It is not the absolute values of the conversion efficiencies that are novel in this study as Wang et al. have reported more optimal data\textsuperscript{15} and even higher values for structurally related organic dyes have been realized by Bai and coworkers.\textsuperscript{31} Instead this comparative study reveals an improvement with Dye-S that stands in stark contrast to the commonly accepted view that sulfur atoms incorporated within the organic framework of a dye molecule enhance recombination and hence lower the overall light-to-electrical energy conversion efficiency. Indeed, recombination of the injected electrons with the oxidized dye was within experimental error the same for the two sensitized materials. Likewise, recombination of injected electrons with oxidized iodide ions was also sensitizer independent. Surprisingly, the origin of the disparate $V_{oc}$ values was instead traced to an enhanced regeneration rate and efficiency for Dye-S. Detailed mechanistic studies revealed that regeneration was optimal at the short circuit condition for both dye molecules, but was not rapid enough for Dye-O to compete with $\text{Dye-O}^{+}/\text{TiO}_2(e^-) \rightarrow \text{Dye-O}/\text{TiO}_2$ recombination as the number of electrons trapped in TiO$_2$ was raised toward the values expected at the open circuit condition. Below we discuss these two key findings in regard to the interfacial energetics, kinetics, and conversion efficiency in dye sensitized solar cells.

3.4.1 Interfacial Energetics.

Spectroelectrochemistry of the sensitized thin films revealed that the electrochemical reduction of TiO$_2$ was insensitive to the identity of the surface anchored dye molecules. Reduction of TiO$_2$ results in a blue-black coloration of the film that has been attributed to trapped TiO$_2(e^-)$s,
most probably as Ti$^{\text{III}}$ sites.$^{32}$ Employing the approach of Bisquert and coworkers,$^{33}$ the potential-dependent redox chemistry was converted to a chemical capacitance. A key assumption was that electrons could be independently added and removed from the TiO$_2$; i.e., the electrons are screened from each other. With this assumption, molecular excited states with reduction potentials as low as 0 V vs. NHE would be able to inject electrons into TiO$_2$, Figure 3.10. Dye-O and Dye-S are much more potent reductants and quantitative injection was expected. The knowledge that the $E(S^*/S*)$ potential is $\sim$ 600 mV higher than needed for efficient electron injection, allows for future work on developing these sensitizers by extending the $\pi$-bridge to lower the $E(S^*/S*)$ and consequently covering a larger portion of the solar spectrum.
Figure 3.10 Interfacial energetics of Dye-O/TiO₂ and Dye-S/TiO₂ in 0.5 M LiClO₄/CH₃CN solution.
The dye molecules could be reversibly oxidized and the potential dependence is displayed in the form of chemical capacitance. The peak of the distributions shown corresponds to the potential where equal concentrations of the oxidized and reduced forms were present. This value was taken as the formal reduction potential and was found to be 75 mV more positive for Dye-$\text{S/TiO}_2$ than Dye-$\text{O/TiO}_2$. This difference was attributed to the poorer orbital overlap of lone pair of the sulfur atom with the phenyl ring. Nevertheless, measurements of the photovoltage generated in the absence of redox mediators showed that the free energy stored in the Dye-$\text{O}^+/\text{TiO}_2(e^-)$ and Dye-$\text{S}^+/\text{TiO}_2(e^-)$ interfacial charge-separated states were within experimental error the same. Taken together this data indicates that the change of heteroatoms did not appreciably influence interfacial thermodynamics for Dye-$\text{O/TiO}_2$ and Dye-$\text{S/TiO}_2$.

### 3.4.2 Interfacial Kinetics.

Charge recombination between the injected TiO$_2(e^-)$ and the oxidized dye molecules were within experimental error the same for both Dye-$\text{O/TiO}_2$ and Dye-$\text{S/TiO}_2$. This observation was expected as the driving force for the reactions differed by merely 75 mV. The average rate constants, $k_{cr}$, abstracted from a distributional analysis of the kinetic data were highly sensitive to the presence of excess TiO$_2(e^-)$s. This behavior was first recognized by Durrant and coworkers for cis-Ru(decb)$_2$(NCS)$_2$/TiO$_2$ and was immediately apparent for the organic dyes studied herein. The $k_{cr}$ values increased exponentially with the applied forward bias that, given the exponential density of states known for TiO$_2$, implies a reaction that is first-order in TiO$_2(e^-)$ concentration.

The kinetics for sensitizer regeneration were quantified spectroscopically. With [Co(bpy)$_3$]$^{2+}$ as the electron donor, second-order rate constants of the order of $10^6$ M$^{-1}$·s$^{-1}$ were measured for reaction 3.6.

$$\text{Dye-X}^+/\text{TiO}_2 + \text{Co}^{II}(\text{bpy})_3^{2+} \rightarrow \text{Dye-X/\TiO}_2(e^-) + \text{Co}^{III}(\text{bpy})_3^{3+} \quad (X = \text{O or S}) \quad (3.6)$$
At high [Co(bpy)$_3$]$^{2+}$ concentrations (i.e., above 0.13 M) and low concentrations of trapped TiO$_2$(e$^-$)s, the regeneration step was quantitative, consistent with the high photocurrent efficiencies measured at the short circuit condition. The high photocurrents also indicated that the unwanted charge recombination of the injected electron with the oxidized cobalt compound, [Co(bpy)$_3$]$^{3+}$ was inefficient. This likely emanates from the well-known spin change that accompanies Co$^{III/II}$ redox chemistry and results in anomalously small self-exchange rate constants.$^{37,38}$ The [Co(bpy)$_3$]$^{2+}$ compound has a $d^7$ high spin electron configuration, ($t_{2g}^5e_g^{*2}$) and [Co(bpy)$_3$]$^{3+}$ has a $d^6$ low-spin configuration, ($t_{2g}^6$). Consistent with other sensitizers that have displayed high solar conversion efficiencies with a Co$^{III/II}$ redox mediator, the long hexyl hydrocarbon chains are postulated to effectively shield the TiO$_2$ surface from the [Co(bpy)$_3$]$^{3+}$.3

Iodide oxidation has been the subject of many studies$^{39,40}$ and occurs by two different mechanisms: one that is first-order in iodide to generate the iodine atom; and the other that is second-order in iodide to yield an iodine radical anion called di-iodide, I$_2^\cdot$. It remains unclear which mechanism(s) are operative at sensitized TiO$_2$ interfaces. This ambiguity is due in part to the rapid reactivity of the iodine atom with iodide to yield the same I$_2^\cdot$ product. However, the latter mechanism is generally thought to be operative in solar cells as the thermodynamics for this outer-sphere electron transfer pathway are more favorable.$^7$ For example, the free energy change for regeneration of the classical N$3$ sensitizer, cis-Ru(dcb)$_2$(NCS)$_2$ to yield the iodine atom is endergonic by +140 mV ($E^\circ$(I$^\cdot$/I$^-$) =1.23 V vs NHE), while it is exergonic by -160 mV for I$_2^\cdot$ formation, ($E^\circ$(I$_2^\cdot$/2I$^-$) = 0.93 V vs NHE).$^{41}$ The corresponding driving forces for regeneration of Dye-S/TiO$_2$ studies here are essentially identical, suggesting specific interactions between the oxidized dye and iodide. While these arguments are not definitive as inner-sphere dye-iodide adducts may activate iodide and significantly alter the thermodynamics,$^{42}$ ion-pairing with the oxidized dye is generally invoked to explain regeneration mechanisms at sensitized TiO$_2$ interfaces, Reaction 3.7.$^{43}$
\[ [\text{I}^-, \text{Dye-X}^+/\text{TiO}_2] + \text{I}^- \rightarrow \text{Dye-X}/\text{TiO}_2 + \text{I}_2^- \quad (X = \text{O or S}) \]  

(3.7)

In the present case, the rate constant for regeneration differs by a factor of 25 with only a 75-mV change in driving force for \( \text{Dye-O}^+ \) and \( \text{Dye-S}^+ \). This finding is striking in that previous kinetic data indicate that a 75 mV change in driving force would not have such a dramatic influence on the electron transfer rate constant.\(^{12,31}\) For example, Palomares and coworkers observed a four-fold enhancement of regeneration with an additional 60-mV driving force,\(^{12}\) while O’Regan and coworkers observed a 20-fold enhancement of regeneration with over 300-mV driving force.\(^{44}\) Clearly the dependence of the measured electron transfer rate constants on \(-\Delta G\) will be a function of where they sit on the Marcus parabola. Reactions that occur near the top of the parabola, \textit{i.e.}, where \(-\Delta G = \lambda\), may show a very shallow \(\Delta G\) dependence where those that are highly unfavored show a stronger dependence. Nevertheless, a 25-fold change in rate constant cannot reasonably be attributed to only a 75 mV change in driving force.

Inspection of the molecular orbitals of the two dyes reveals a higher orbital coefficient on the S atom relative to the O atom. This description is more predominant in the oxidized forms of the dyes, which is the more relevant form to be considered here. \textbf{Dye-O} and \textbf{Dye-S} offer the first examination of how different heteroatoms affect the regeneration step, where the heteroatoms constitute the portion of the molecule that will be interacting with the electrolyte. Previous studies on the heteroatom effect in metal-based dyes place the heteroatom at a position that will not necessarily interact with the dyes, Figure 3.11. Consequently, the previous studies produced differences in behavior that were manifest in the recombination step, but not necessarily the regeneration step. The reaction between the oxidized forms of \textbf{Dye-O} and \textbf{Dye-S} and the redox mediator will almost certainly involve the portion of the molecule bearing the triaryl fragment bearing the heteroatoms of interest. Consequently, the much faster rates of dye regeneration provide incontrovertible evidence that the S atoms mediate an interaction with the redox mediator that is favorable relative to the O atoms.
Adduct formation between iodide and the soft more polarizable sulfur atom as the Lewis base at the regeneration site would provide an inner-sphere electron transfer pathway that could enhance electronic coupling and hence alter the electronic transmission coefficient. Alternatively, the higher rate of the reaction could simply be a result of the greater orbital coefficient on the S atom on the O atom.
Figure 3.11 Molecular structures of two ruthenium(II)-based dyes studies by O'Regan and coworkers\textsuperscript{11} indicating the site where the heteroatoms have been changed. The $\beta$-LUSO (lowest-unoccupied spin orbital) for the oxidized form of the ruthenium dye where $X = S$ is shown to the left of the $\beta$-LUSO for \textbf{Dye-S}\textsuperscript{+} (also shown in Figure 3.1) to highlight that there is no orbital character over the S atoms in the metal dye and significant orbital character over the S atoms in the organic dye. The portions of the respective dyes that ostensibly interact with the redox mediator are illustrated. The equivalent spin-density plots are found in Figure A3.15.
In either event, transient absorption data clearly show that the unwanted charge recombination reaction with oxidized iodide species were not influenced by the presence of the sulfur atoms positioned near the donor site of these organic dyes as was invoked previously for the ruthenium-based sensitizers.\textsuperscript{11} Recombination of the injected electrons with I\textsuperscript{−} or I\textsubscript{2} was within experimental error the same for the two dye sensitized TiO\textsubscript{2} materials, 2.3 ± 0.4 s\textsuperscript{−1}. Di-iodide, an intermediate in the regeneration reaction and a I\textsuperscript{3−} reduction product, is also a potential electron acceptor,\textsuperscript{45,46} yet there was no evidence for a reaction between \textbf{Dye-S}/TiO\textsubscript{2}(e\textsuperscript{−}) and I\textsuperscript{2−}. Instead, the I\textsuperscript{2−} formed during regeneration underwent disproportionation with a quantum yield and reaction rate constant that was unchanged from that measured in fluid acetonitrile solution.\textsuperscript{29}

The question remains whether more rapid regeneration by \textbf{Dye-S}/TiO\textsubscript{2}(e\textsuperscript{−}) could account for the larger open circuit photovoltage, \(V_{oc}\), measured in the DSSCs. Generally speaking, the observation of quantitative short circuit photocurrents and IPCE values has led previous authors to conclude that regeneration is optimal.\textsuperscript{8} However, at short circuit the injected electrons are rapidly removed from TiO\textsubscript{2} thin film whereas at the open circuit condition many electrons are trapped within each nanocrystallite; behavior that is known to enhance charge recombination.\textsuperscript{36} Indeed as TiO\textsubscript{2} electrons were thermally transferred to TiO\textsubscript{2} with an external potentiostat, recombination to these oxidized organic dyes increased significantly and the corresponding regeneration efficiency decreased. At \(-200 \text{ mV}\) vs. NHE, the regeneration efficiency for \textbf{Dye-S}/TiO\textsubscript{2}(e\textsuperscript{−}) was near unity for both donors while that for \textbf{Dye-O}/TiO\textsubscript{2}(e\textsuperscript{−}) had dropped by about 20\% for iodide and 40\% for Co(bpy)\textsubscript{3}\textsuperscript{2+}. The significant decrease for the cobalt mediator reflects the fact that it did not regenerate as quickly as did iodide. These regeneration efficiencies explain the smaller \(V_{oc}\) values measured for \textbf{Dye-O} as well as it is greater sensitivity to the cobalt mediator as is described more fully below.

Correlations of measurements made under potentiostatic conditions with the operational solar cell are non-trivial. Ideally, one would like to employ transient absorption spectroscopy
directly as an *in situ* characterization tool for DSSCs as has been done in pioneering studies by O’Regan and coworkers.\textsuperscript{47,48} However, transmission losses associated with the complete DSSC coupled with the necessary corrections for redox chemistry that occurs at the counter electrode have thus far precluded data of the quality presented herein. Nevertheless, about 20 electrons reside in each TiO\textsubscript{2} nanocrystallite at the power point, albeit a value noted to be quite sensitive to the distribution of TiO\textsubscript{2} particle sizes.\textsuperscript{47} With reasonable assumptions of extinction coefficient and path length, the measured TiO\textsubscript{2}(e\textsuperscript{-})\textsubscript{s} absorption at -200 mV is in good agreement with this value, and the number would be even higher at the open circuit condition. Thus, the potentiostatic kinetic data provide compelling evidence that the high short circuit photocurrents for both dyes are due to quantitative regeneration and the low \(V_{oc}\) value for Dye-O/TiO\textsubscript{2} results from poor regeneration when the TiO\textsubscript{2}(e\textsuperscript{-}) concentration is high. Hence, the detailed mechanistic studies reported herein show that the observation of quantitative short circuit photocurrents is not necessarily an indication that regeneration is optimal. Quantitative regeneration of Dye-S/TiO\textsubscript{2} as the TiO\textsubscript{2}(e\textsuperscript{-}) concentration was raised toward the values expected at the open circuit condition underlies its superior performance and \(V_{oc}\) values relative to Dye-O/TiO\textsubscript{2}. 
3.5 Conclusions

To our knowledge this study provides the first direct comparison of molecules where a simple two-atom change – *at the site of regeneration* – systematically probes the rates of regeneration by I⁻ (and Co(II)). The results of this study contrast the broadly accepted view in the field that S atoms enhance the rate of recombination between the TiO₂(e⁻) and the oxidized iodide mediator thus lowering the solar conversion efficiency of the DSSC. These disparities in reactivities are manifest in the specific positioning of the heteroatom change within the portion of the dye molecule that is most likely to react with the incoming reductant I⁻. These results highlight that the atomic composition of the dye can have a profound effect on the dye regeneration process, and that the careful design of molecular dyes can lead to an optimization of interactions with the redox mediator that can lead to further enhancements in dye regeneration. Furthermore, the data provide compelling evidence that sluggish regeneration can lower the open circuit photovoltage even when quantitative short circuit photocurrents are measured.
3.6 Appendix

**Physical Methods.** Elemental analysis (EA), electrospray ionization mass spectrometry (ESI) mass spectrometry (MS) data were collected at the Chemistry Instrumentation Facility of the University of Calgary. Electrochemical measurements were performed under anaerobic conditions with a Princeton Applied Research VersaStat 3 potentiostat using dry solvents, Pt working and counter electrodes, Ag pseudoreference electrode, and 0.1 M NBu₄BF₄ supporting electrolyte. Electronic spectroscopic data were collected on CH₃CN solutions using a Cary 5000 UV-vis spectrophotometer (Varian). Steady-state emission spectra were obtained at room temperature using an Edinburgh Instruments FLS920 Spectrometer equipped with a Xe900 450W steady state xenon arc lamp, TMS300-X excitation monochromator, TMS300-M emission monochromator, Hamamatsu R2658P PMT detector and corrected for detector response.

**Open Circuit Photovoltage (V_{oc}).** Open circuit photovoltages were measured in non-regenerative solar cells containing 0.5 M LiClO₄ acetonitrile electrolyte. The counter electrode was platinized FTO by pyrolysis of PtCl₄ isopropanol solution at 450°C for 30 minutes. The cell was washed by pre-purged 0.5 M LiClO₄ acetonitrile electrolyte twice before sealing. Cells were shorted each time before being illuminated. The photovoltages were recorded using a BASi Epsilon-EC. Incident light was achieved with a 514.5 nm line of an Innova Ar⁺ laser with a Thorlabs BE 10X beam expander, and the incident irradiance was altered using Newport neutral density filters. The cell size was typically 1.5 cm by 1.5 cm. The light intensities were scanned from low to high and then, high to low to check hysteresis. In case of hysteresis, we use points from decreasing light irradiances.
Scheme A3.1  Synthesis of Dye-S.\textsuperscript{a}

\textsuperscript{a}Reaction conditions: a) i: HSC\textsubscript{6}H\textsubscript{13}, KO\textsubscript{t}Bu, THF, 2 h; ii: DMF, reflux, 18 h; b) N-bromosuccinimide, EtOAc, dark, 25 °C, 24 h; c) Na\textsubscript{2}CO\textsubscript{3}, Pd(PPh\textsubscript{3})\textsubscript{4}, THF/H\textsubscript{2}O (9:1, v/v), N\textsubscript{2}, reflux, 16 h; d) i: DMF, CHCl\textsubscript{3}, 0 °C; ii: POCl\textsubscript{3}, reflux, 7 h; e) NCCH\textsubscript{2}CO\textsubscript{2}H, piperidine, CH\textsubscript{3}, N\textsubscript{2}, reflux, 20 h.
Figure A3.1 Labelling scheme for $^1$H NMR signal assignments.
4-(hexylthio)-N-(4-(hexylthio)phenyl)-N-(4-(thiophen-2-yl)phenyl)aniline (P4-S). A mixture of 4-bromo-N,N-bis(4-(hexylthio)phenyl)aniline (P3-S)\(^{21}\) (0.47 g, 0.84 mmol), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane\(^{22}\) (0.213 g, 1.01 mmol), Na\(_2\)CO\(_3\) (0.900 g, 8.44 mmol) and Pd(PPh\(_3\))\(_4\) (0.100 mg, 8.00 µmol) were stirred in a sparged THF/H\(_2\)O (9:1, v/v, 50 mL) solution under N\(_2\) at reflux for 16 h. The solution was then cooled to room temperature and the product was extracted with EtOAc (3 x 30 mL). The organic layers were pooled and dried over MgSO\(_4\) prior to removal of solvent in vacuo. The resultant residue was purified by chromatography [SiO\(_2\) 8:2 hexanes/CH\(_2\)Cl\(_2\); \(R_t = 0.16\)] to yield 0.29 g (55%) of the product as a yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.51\) (d, 2H, \(^3J = 8.7\) Hz, \(H_j\)), 7.28-7.25 (m, 6H, \(H_l, H_k, H_g\)), 7.09-7.04 (m, 7H, \(H_h, H_i, H_m\)), 2.91 (t, 4H, \(^3J = 7.3\) Hz, \(H_f\)), 1.72-1.65 (m, 4H, \(H_e\)), 1.50-1.43 (m, 4H, \(H_d\)), 1.37-1.30 (m, 8H, \(H_c, H_b\)), 0.93 (t, 6H, \(^3J = 6.9\) Hz, \(H_a\)); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 146.9, 145.7, 144.3, 131.1, 130.9, 129.2, 128.2, 127.0, 124.8, 124.3, 124.1, 122.5, 34.8, 31.6, 29.5, 28.7, 22.7, 14.2; HRMS (ESI): \(m/z = 559.2396\) [(M)\(^+\)] (calcd for C\(_{34}\)H\(_{41}\)NS\(_3\)\(^+\): m/z = 559.2396).

5-(4-(bis(4-(hexylthio)phenyl)amino)phenyl)thiophene-2-carbaldehyde (P5-S). P4-S (110 mg, 0.20 mmol) and DMF (44 µL, 0.61 mmol) were dissolved in anhydrous CHCl\(_3\) (10 mL) under a nitrogen atmosphere. After the solution was cooled to 0 °C, phosphorus oxychloride (0.1 mL, 0.4 mmol) was added dropwise to the reaction mixture. After the mixture was left at reflux for 7 h, 20 mL of water was added. Sodium acetate was then added to neutralize the mixture prior to extraction of the product by CH\(_2\)Cl\(_2\) (3 x 20 mL). The pooled organic layers were dried over MgSO\(_4\), and then separated by filtration before the solvent was removed in vacuo. The residue was purified by chromatography [SiO\(_2\): 9:1, hexanes/EtOAc, \(R_t = 0.24\)] to yield 0.084 g (72 %) of the product as an orange solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.84\) (s, 1H, \(H_n\)), 7.67 (d, 1H, \(^3J = 4.0\) Hz, \(H_l\)), 7.50 (d, 2H, \(^3J = 8.8\) Hz, \(H_j\)), 7.28 (d, 1H, \(^3J = 4.0\) Hz, \(H_k\)), 7.23 (d, 4H, \(^3J = 8.7\) Hz, \(H_e\)), 7.04-7.01 (m, 6H, \(H_h, H_i\)), 2.88 (t, 4H, \(^3J = 7.3\) Hz, \(H_f\)), 1.68-1.60 (m, 4H, \(H_c\)), 1.45-1.38 (m, 4H, \(H_d\)), 1.31-
1.35 (m, 8H, Hc, Hb), 0.87 (t, 6H, 3J = 6.9 Hz, Ha); 13C NMR (100 MHz, CDCl3): δ = 182.7, 154.6, 148.9, 145.0, 141.7, 137.8, 132.1, 130.9, 127.5, 126.8, 125.6, 123.2, 122.8, 34.7, 31.6, 29.4, 28.7, 22.7, 14.2; HRMS (ESI): m/z = 588.2418 [(M+H)+] (calcd for C35H42NOS3+: m/z = 588.2423).

(E)-3-(5-(4-(bis(4-(hexylthio)phenyl)amino)phenyl)thiophen-2-yl)-2-cyanoprop-2-enoic acid (Dye-S). P5-S (80 mg, 0.14 mmol), cyanoacetic acid (30 mg, 0.41 mmol) and piperidine (0.1 mL, 1 mmol) were dissolved in CH3CN under a nitrogen atmosphere and left at reflux for 20 h. The solvent was then removed in vacuo and the product was purified by column chromatography [SiO2: 9.5:0.5 CH2Cl2 /AcOH, Rf = 0.46] to yield 63 mg (71%) as a dark orange solid. 1H NMR (400 MHz, CDCl3): δ = 8.30 (s, 1H, Ha), 7.75 (d, 1H, 3J = 4.2 Hz, Hı), 7.53 (d, 2H, 3J = 8.8 Hz, Hj), 7.31 (d, 1H, 3J = 3.9 Hz, Hk), 7.24 (d, 4H, 3J = 8.7 Hz, Hı), 7.04-7.00 (m, 6H, Hı, Hl), 3.94 (t, 4H, 3J = 7.3 Hz, Hı), 1.68-1.61 (m, 4H, Hı), 1.45-1.38 (m, 4H, Hı), 1.32-1.25 (m, 8H, Hı, Hı, Hı), 0.88 (t, 6H, 3J = 6.9 Hz, Hı); 13C NMR (100 MHz, CDCl3): δ = 168.0, 156.2, 149.4, 148.0, 144.8, 140.6, 134.0, 132.5, 130.8, 127.8, 126.1, 125.8, 123.7, 122.4, 116.0, 95.9, 34.5, 31.6, 29.4, 28.7, 22.8, 14.2; HRMS (ESI): m/z = 655.2327 [(M-H)-] (calcd for C38H41N2O2S3: m/z = 655.2338).
Figure A3.2 The calculated HOMO and LUMO for Dye-O.
Figure A3.3  The calculated HOMO and LUMO for \textbf{Dye-S}. 
Figure A3.4  Normalized absorption spectra of Dye-O (solid red line) and Dye-S (solid blue line) and normalized fluorescence spectra of Dye-O (dashed red line) and Dye-S (dashed blue line) in CH$_3$CN solutions at 298 °K.
Figure A3.5 Ground state UV-visible absorption spectra of Dye-O (red) and Dye-S (blue) anchored to nanocrystalline TiO$_2$ films in neat CH$_3$CN. The corresponding dash-dot lines are for the same films immersed in 0.5 M LiClO$_4$ CH$_3$CN solutions.
Figure A3.6 Cyclic voltammograms of Dye-O (red trace) and Dye-S (blue trace) in 0.1 M NBu$_4$BF$_4$ CH$_3$CN solutions at 298 °K using a Pt working electrode, 100 mV/s scan rate. Dashed line indicates $E_{1/2}$ value.
Figure A3.7  Cyclic voltammetry of Dye-O/TiO$_2$ (A) ($E_{pa} = 1190$ mV, $E_{pc} = 860$ mV, dye surface coverage $\Gamma = 1.0 \times 10^{-7}$ mol·cm$^{-2}$) and Dye-S/TiO$_2$ (B) ($E_{pa} = 1183$ mV, $E_{pc} = 996$ mV, $\Gamma = 5.3 \times 10^{-8}$ mol·cm$^{-2}$) immersed in 0.5 M LiClO$_4$ CH$_3$CN solution at r.t. (scan rate: 100 mV/s).
Figure A3.8  Density of TiO$_2$ acceptor states measured by spectroelectrochemistry. The extinction coefficient of TiO$_2$(e$^-$) was assumed to be 1000 M$^{-1}$ cm$^{-1}$ at 800 nm. The solid and dashed lines were single exponential fits for Dye-O/TiO$_2$ and Dye-S/TiO$_2$ in 0.5 M LiClO$_4$ CH$_3$CN.
Figure A3.9  Charge recombination kinetics of Dye-O/TiO$_2$ (black) and Dye-S/TiO$_2$ (red) immersed in 0.5 M LiClO$_4$ CH$_3$CN monitored at 635 nm (excitation wavelength: 532 nm; laser fluence: 0.3 mJ/cm$^2$). Overlaid in yellow (Solid: Dye-O/TiO$_2$, Dashed: Dye-S/TiO$_2$) are the fits using KWW function ($\beta = 0.19$).
Figure A3.10  Plot of Log ($k_{cr}$) abstracted from KWW fits shown in Figure 3.5 through equation 2, plotted as a function of the applied bias for the indicated sensitized thin films.
Figure A3.11  Open circuit photovoltage of Dye-O/TiO$_2$ (triangle) and Dye-S/TiO$_2$ (cross) measured in 0.5 M LiClO$_4$ without redox mediators (steady state excitation wavelength: 514.5 nm).
Figure A3.12 Absorption difference spectra measured at the indicated delay times after pulsed 532 nm laser excitation of a) Dye-O/TiO₂ and b) Dye-S/TiO₂ immersed in 0.2 M LiI/0.3 M LiClO₄ CH₃CN solution.
Figure A3.13 Absorption changes monitored at 720 nm after pulsed 532 nm laser excitation of the sensitized films in 0.5 M LiI CH₃CN (laser fluence: 2 mJ/cm²). Overlaid in yellow are fits to the KWW model ($\beta = 0.8$).
Figure A3.14  a) Absorption changes monitored at 396 nm at 5 different irradiances after pulsed 532 nm laser excitation of Dye-S/TiO$_2$ in 0.5 M LiI CH$_3$CN (Correction has been made for absorption changes of Dye-S$^+/TiO_2$); b) Absorption changes monitored at 635 nm under the same conditions as a).
Figure A3.15 Spin-density plots for dyes oxidized dyes \( \text{TG6}^+ \), \( \text{Dye-O}^+ \) and \( \text{Dye-S}^+ \). Note that there is no orbital character over the S atom comprising the terminal substituent of the modified bipyridine ligand in \( \text{TG6}^+ \), while there is significant orbital character over the terminal O and S atoms in \( \text{Dye-O}^+ \) and \( \text{Dye-S}^+ \).
3.7 Reference


C 2009, 113, 7469.


(17) Zeng, W.; Cao, Y.; Bai, Y.; Wang, Y.; Shi, Y.; Zhang, M.; Wang, F.; Pan, C.; 

(18) Hagberg, D. P.; Edvinsson, T.; Marinado, T.; Boschloo, G.; Hagfeldt, A.; Sun, L. 


1501.


(23) Bonhote, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. 


(25) Frisch, M. J.; al., e. Gaussian 03 Revision c.02 ed 2004, Gaussian Inc., 
Wallingford, CT.

Soc. 2010, 132, 6696.


Chapter 4: Donor-π-Acceptor Organic Hybrid TiO₂ Interfaces for Solar Energy Conversion

In part a compilation of one publication.¹

This work was collaborative in conjunction with Kiyoshi C. D. Robson‡, Gerald J. Meyer†

and Curtis P. Berlinguette§

†Johns Hopkins University, Baltimore, MD, USA

‡University of Calgary, Calgary, Canada

4.1 Introduction

Solar photons are known to initiate a wide variety of technologically and environmentally important reactions at titanium dioxide-organic interfaces ²,³. At one extreme, the organic molecule is a pollutant that can be degraded to benign chemical products via TiO₂ photocatalytic mineralization ⁴-⁶ - a popular approach for the clean-up of waste water arising from industry. At another extreme, an organic dye molecule undergoes photo-induced electron transfer reactions that can generate electrical power where no net photochemistry is wanted ⁷. Indeed, regenerative dye sensitized solar cells based on anatase TiO₂ nanocrystallites cast as a mesoporous thin films have attracted worldwide attention since the seminal report by O’Regan and Gratzel ⁸. Remarkable improvements in the efficiency of dye-sensitized solar cells based on organic dye molecules over the last decade, from less than 1% to greater than 9% ⁹, coupled with their low cost and ease in fabrication, suggest that organic molecules at TiO₂ interfaces may one day provide sustainable electrical power for future generations.
Figure 4.1 Structure of deoxycholic acid (DCA) and chenodeoxycholic acid (CDCA).
A key advance in the efficiency of dye sensitized solar cells with organic dyes was realized by Hara, Arakawa and coworkers in 2004. With coumarin dye molecules they reported what was at that time an unprecedented 7.5% global conversion efficiency. They also found, as had Gratzel and Kay before them, that the presence of deoxycholic acid as a co-adsorbent improved both the photocurrent and the photovoltage of the solar cells. The sensitivity of the energy conversion efficiency of coumarin based dye sensitized solar cells to the presence of deoxycholic acid (and tert-butyl pyridine) was remarkable as the global conversion efficiencies without such additives were only 3.6%. To this date, deoxycholic acid, or the related chenodeoxycholic acid (CDCA), shown in Figure 4.1 represent common co-adsorbents when organic dyes are utilized in dye sensitized solar cells at metal oxide interfaces. These are naturally occurring bile acids that contain a carboxylic acid functional group, for metal oxide binding, covalently linked through a propylene carbon chain to a steroid-like organic framework. The steroidal portion of the acids contains both hydrophilic and hydrophobic sites that may interact uniquely with different dye molecules; although the details of such putative interactions are not well understood.

A second highly significant advance was made by Licheng Sun and coworkers who replaced coumarin with what are termed ‘donor-acceptor,’ ‘push-pull,’ or more specifically ‘donor-π-acceptor’ type organic dyes. The modular nature of these dyes enabled independent optimization of the donor, the π bridge and the acceptor. Furthermore, the orbital arrangement realized when the acceptor was anchored to TiO₂, promoted vectorial photo-induced electron transfer towards the TiO₂ surface and inhibited thermal back electron transfer to the oxidized donor. Utilization of donor-π-acceptor organic dyes in dye sensitized solar cells resulted in efficiency of 6.7%. Furthermore, it was with this class of dye molecules that high solar conversion efficiencies were first realized with tris-chelated cobalt redox mediators as an alternative to the more standard iodide/tri-iodide mediators. In fact, Wang and coworkers reported an impressive 9.4% conversion efficiency with an organic donor-acceptor sensitizer and Co(phen)₃³⁺/²⁺ redox mediators, where phen is 1,10-phenanthroline. It was later shown that cyclometalated ruthenium...
polypyridyl dye molecules can also be utilized with cobalt redox mediators. Explanations for why cobalt mediators work well under some conditions and not under others remain speculative.

We recently reported the use of two donor-acceptor organic dyes that differed by only a two-heteroatom change from oxygen to sulfur within the donor unit. In solar cells employing either I$_3$/I$^-$ or [Co(bpy)$_3$]$^{3+/2+}$, where bpy is 2,2'-bipyridine, redox mediators, conversion efficiencies greater than 6% were achieved. Despite similar optical and redox properties for these two donor-π-acceptor organic dyes, a consistently higher open-circuit voltage ($V_{oc}$) was measured with the sulfur containing dye molecule. Mechanistic studies revealed that a 25-fold enhancement of the regeneration rate constant for iodide oxidation enhanced the regeneration yield under open circuit conditions yet had little influence on the yield at the short circuit condition. The data removed the dogma that S atoms were necessarily deleterious for energy conversion with iodide redox mediators. Here we report studies designed to better understand the role of chenodeoxycholic acid and the cobalt mediators on these donor-π-acceptor organic hybrid TiO$_2$ interfaces useful for solar energy conversion.
4.2 Experimental

Materials. Acetonitrile (Burdick & Jackson, spectrophotometric grade); lithium perchlorate (Aldrich, 99.99%); chenodeoxycholic acid (Alfa Aesar) argon gas (Airgas, > 99.998%); oxygen gas (Airgas, industrial grade); titanium(IV) isopropoxide (Sigma-Aldrich, 97%); and glass microscope slides (Fisher Scientific, 1 mm thick). [Co(bpy)₃](PF₆)₂ was synthesized according to the literature report. The two dyes were available from previous studies.

Substrate preparations. Mesoporous nanocrystalline TiO₂ thin films were prepared as previously described. Briefly, TiO₂ paste was made by sol-gel method and was doctor-bladed onto glass microscope slides. The slides were then sintered at 450 °C for 30 minutes under constant O₂ flow. The films were kept at 70 °C and then immersed in acetonitrile solution containing dye (~75 μM) and, in some cases, co-adsorbent chenodeoxycholic acid (~3.7 mM). Films were then washed with neat CH₃CN and diagonally positioned in a standard 1 cm² quartz cuvette in acetonitrile solution for UV-vis spectra measurements. In transient absorption experiments, the sensitized thin films were sandwiched against a glass microscope with a vinyl film (Warps, 8 mil Vinyl-Pane) spacer that contained concentrations of 0.2 M Co(bpy)₃²⁺ in 0.5 M LiClO₄ acetonitrile solutions. The electrolyte solutions were purged with argon gas for at least 30 min prior to experimentation.

Optical measurements.

Steady state UV-vis absorption. Steady state UV-vis absorption spectra were obtained on a Varian Cary 50 spectrophotometer. The macroscopic surface coverage (Γ in mol · cm⁻²) was determined from the measured absorption spectra with the modified Beer-Lambert law formula (Abs = 1000×ε×Γ), where ε is the molar decadic extinction coefficient in unit of M⁻¹ · cm⁻¹. The peak molar decadic extinction coefficient of the sensitized TiO₂ film was assumed to have the same value as in solution. All experiments were performed at room temperature.

Transient absorption spectroscopy. Nanosecond transient absorption measurements were obtained with an apparatus similar to that which has been previously described. Briefly, samples
were excited with nanosecond pulses of 532 nm light with a 150 W Xenon lamp as the probe beam. Optical filters were used to remove IR, UV and scattered light. Kinetic analysis was performed in Origin 8.
Figure 4.2 Molecular structure of the two organic dyes Dye-O and Dye-S.
4.3 Results and Discussion

The molecular structure of the dye molecules are (E)-3-(5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)-2-cyanoprop-2-enoic acid (Dye-O) and (E)-3-(5-(4-(bis(4-(hexylthio)phenyl)amino)phenyl)thiophen-2-yl)-2-cyanoprop-2-enoic acid) (Dye-S) shown in Figure 4.2. These molecules were prepared and characterized in a previously reported manuscript \(^{16}\).

4.3.1 Surface coverage effect of Dye-O and Dye-S on UV-vis absorption spectra

Surface coverages of Dye-O/TiO\(_2\) and Dye-S/TiO\(_2\) were varied by immersing TiO\(_2\) films in 75 μM CH\(_3\)CN solutions with 3.7 mM CDCA for different periods of time. With this approach, about a factor of ten change in surface coverage was realized based on UV-vis absorption spectroscopy, Figure 4.3a and Figure 4.4a. The absorption maximum progressively shifted toward the blue, i.e., a hypsochromic shift. This is most easily seen in the normalized spectra shown in Figure 4.3b and Figure 4.4b. Indeed the surface coverage was directly correlated with the absorption maximum. Note that the oscillation in the “absorption spectra”, that are most pronounced at low surface coverages, are interference patterns from the thin films.
Figure 4.3 (a) Ground state absorption spectra of Dye-O/TiO\textsubscript{2} immersed in neat CH\textsubscript{3}CN at different surface coverages (5.1 × 10\textsuperscript{-9} ~ 7.2 × 10\textsuperscript{-8} mol·cm\textsuperscript{-2}). (b) Normalized absorption spectra for all surface coverages of Dye-O/TiO\textsubscript{2}. Overlaid in thick red is the Dye-O solution spectrum in neat CH\textsubscript{3}CN. The arrow shows the direction for increasing surface coverages.
Figure 4.4 (a) Ground state absorption spectra of Dye-S/TiO₂ immersed in neat CH₃CN at different surface coverages ($4.9 \times 10^{-9} - 6.7 \times 10^{-8}$ mol·cm⁻²). (b) Normalized absorption spectra for all surface coverages of Dye-S/TiO₂. Overlaid in thick blue is the Dye-S solution spectrum in neat CH₃CN. The arrow shows the direction for increasing surface coverages.
Comparisons of the Dye-O or Dye-S solution spectra with that measured for the sensitized thin film were made. The absorption maximum of Dye-O was 478 nm ($\varepsilon = 2.84 \times 10^4 \text{ m}^{-1} \cdot \text{cm}^{-1}$) and for Dye-S was 469 nm ($\varepsilon = 3.16 \times 10^4 \text{ m}^{-1} \cdot \text{cm}^{-1}$) in fluid CH$_3$CN solution. The absorption maxima measured for the sensitized films were most similar to these values when the dye surface coverage was the lowest. At higher surface coverages, the absorption maximum of Dye-O/TiO$_2$ was blue shifted 730 cm$^{-1}$ and Dye-S/TiO$_2$ by 900 cm$^{-1}$ relative to these solution values, behavior attributed to dye aggregation as is discussed in the next section. In addition, the long wavelength absorption onset for the highest surface coverage films was red shifted by about 1010 cm$^{-1}$ (from 610 nm to 650 nm) for Dye-O and 540 cm$^{-1}$ (from 600 nm to 620 nm) for Dye-S. This change in the absorption onset has previously been observed for ruthenium polypyridyl and coumarin dyes and was attributed to increased delocalization of the carboxylate group into the organic $\pi$ system upon binding with Ti$^{4+}$ site on the surface $^{19,20}$. While such an interpretation seems reasonable, it is difficult to rule out intermolecular interaction between the dye molecules that could also influence the absorption onset.

### 4.3.2 Effect of CDCA coadsorption on UV-vis absorption spectra

Aggregation of some dye molecules is known to quench photoluminescence and hence is often expected to decrease the excited state injection yield and hence the overall solar cell efficiency $^{21,22}$. As mentioned in the Introduction Section, chenodeoxycholic acid (CDCA) has been used extensively at organic TiO$_2$ interfaces with the notion that it inhibits dye aggregation on the TiO$_2$ surface $^{10,20}$. Most commonly as was done in this study, this additive is placed in the dying solution such that the CDCA molecules competitively co-adsorb with the dye molecules. This co-adsorption procedure has been particularly effective when coumarin dye molecules were employed, even though it decreased the total number of dyes present at the interface $^{10}$. Computational chemistry has shown that CDCA molecules insert themselves between coumarin molecules thereby inhibiting intermolecular dye-dye interaction $^{23}$. To test whether similar behavior might occur for
these donor-π-acceptor dye molecules, surface adsorption studies were performed in the absence of CDCA. By varying the amount of time the TiO$_2$ was allowed to react with the organic dye molecules, the surface coverage could again be varied by over a factor of ten. However, the spectra were quantitatively different from those measured with CDCA. The hypsochromic shift in the absorption spectrum was evident in even the lowest surface coverage data, Figure 4.5 and Figure 4.6. Indeed the normalized spectra show that the absorption maximum were almost surface coverage independent which is in stark contrast to that observed when CDCA was present and a progressive blue shift was observed with increased surface coverage. The dramatic changes in the absorption maximum with surface coverage, that were significantly smaller in the presence of CDCA, are most easily observed in the plot shown in Figure 4.7. This data supports the theoretical predictions and suggests that these donor-π-acceptor dye molecules are aggregated, even at the lowest surface coverages $^{23}$. 
Figure 4.5  (a) Ground state absorption spectra of Dye-O/TiO$_2$ in neat CH$_3$CN without chenodeoxycholic acid at different surface coverages ($8.8 \times 10^{-9} - 6.9 \times 10^{-8}$ mol·cm$^{-2}$) and (b) their normalized spectra. Overlaid in thick red is the Dye-O solution spectrum in neat CH$_3$CN. The arrow shows the direction for increasing surface coverages.
Figure 4.6. (a) Ground state absorption spectra of Dye-S/TiO$_2$ in neat CH$_3$CN without chenodeoxycholic acid at different surface coverages ($5.1 \times 10^{-9} \sim 6.4 \times 10^{-8}$ mol·cm$^{-2}$) and (b) their normalized spectra. Overlaid in thick blue is the Dye-S solution spectrum in neat CH$_3$CN. The arrow shows the direction for increasing surface coverages.
Figure 4.7 Plot of the absorption maximum in wavenumbers and wavelength for Dye-O/TiO₂ (solid red squares: with CDCA coadsorption; open red squares: without CDCA coadsorption) and Dye-S/TiO₂ (solid blue circles: with CDCA coadsorption; open blue circles: without CDCA coadsorption) versus the surface coverages.
4.3.3 Surface coverage effect on charge recombination between TiO₂(e⁻) and [Co³⁺(bpy)₃]³⁺

Due to the intrinsic two electron redox chemistry of I₃⁻/I⁻, charge recombination between TiO₂(e⁻) in isolated states and I₃⁻ is thought to be rare in operational solar cells ²⁴. The disadvantage of utilizing I₃⁻/I⁻ redox mediator is that the one electron oxidation of I⁻ induces a series of I-I bond formation and disproportionation reactions that are accompanied by a free energy loss of around 600 mV ²⁵. This has motivated extensive explorations of alternative redox mediators and cobalt based coordination compounds appear to be the most promising. Indeed, an efficiency of over 12% was achieved by Gratzel’s group utilizing a zinc porphyrin with long alkyl chains and Co³⁺tris(bipyridyl) compounds as the redox mediator ²⁶. The long chain hydrocarbon was introduced to block close approach of the cobalt mediators with the TiO₂ surface. It was of interest to see whether evidence for such behavior could be observed by simply increasing the number of Dye-O or Dye-S molecules on the TiO₂ surface.

To accomplish this, nanosecond transient absorption spectroscopy was employed. Pulsed laser excitation of a Dye-S/TiO₂ thin film in a 0.5 M LiClO₄/CH₃CN solution that contained 0.2 M [Co(bpy)₃]²⁺ led to the immediate appearance of the oxidized sensitizer and an injected electron, Equation 4.1. Consistent with previous studies the rate constant for excited state injection could not be time resolved with nanosecond resolution, \( k_{\text{inj}} > 10^8 \text{s}^{-1} \).

\[
\text{Dye-S}^+/\text{TiO}_2 \rightarrow \text{Dye-S}^+/\text{TiO}_2(\text{e}^-) \quad (4.1)
\]

The oxidized dye was then regenerated by the [Co(bpy)₃]²⁺ present in the solution, Equation 4.2.

\[
\text{Dye-S}^+/\text{TiO}_2(\text{e}^-) + [\text{Co}^{\text{II}}(\text{bpy})_3]^{2+} \rightarrow \text{Dye-S}/\text{TiO}_2(\text{e}^-) + [\text{Co}^{\text{III}}(\text{bpy})_3]^{3+} \quad (4.2)
\]
This dye regeneration reaction was previously characterized under pseudo-first order conditions and the rate constants were found to be $1.1 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$ for \textbf{Dye-O}^+/\text{TiO}_2$ and $3.5 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$ for \textbf{Dye-S}^+/\text{TiO}_2$. The approximately 3-fold larger rate constant for \textbf{Dye-S}^+/\text{TiO}_2 presumably stems from the 70 mV more favorable driving force for the reaction, $\Delta G^\circ = -0.53$ V versus $-0.46$ V$^{16}$.

The subsequent reaction of the injected electron with the oxidized cobalt compound has not been previously reported. This recombination reaction was studied for \textbf{Dye-S}/\text{TiO}_2 at low $7.0 \times 10^{-9}$ mol cm$^{-2}$ and high $3.5 \times 10^{-8}$ mol cm$^{-2}$ surface coverages without the presence of CDCA, Equation 4.3.

\[
\text{Dye-S}/\text{TiO}_2(e^-) + [\text{Co}^{III}(\text{bpy})_3]^{3+} \rightarrow \text{Dye-S}/\text{TiO}_2 + [\text{Co}^{II}(\text{bpy})_3]^{2+} \quad (4.3)
\]

This reaction was difficult to monitor as the \text{TiO}_2(e^-) and the cobalt compounds absorb light only very weakly in the visible region. Furthermore, the oxidized organic dyes absorb throughout the visible region that makes selective monitoring of reaction 4.3 impossible. An observation wavelength of 740 nm was selected where the \text{TiO}_2(e^-)$s have an extinction coefficient of approximate 1000 M$^{-1}$ cm$^{-1}$. While the oxidized triphenylamine groups absorb light more strongly at this wavelength, the regeneration reaction were sufficiently separated in time that recombination reaction 4.3 could be cleanly observed.
Figure 4.8 Absorption changes monitored at 740 nm after pulsed 532 nm light excitation of Dye-S/TiO$_2$ in 0.5 M LiClO$_4$ and 0.2 M [Co$^{3+}$(bpy)$_3$]$^{2+}$ CH$_3$CN solution. Data were recorded for surface coverages of 7×10$^{-9}$ mol cm$^{-2}$ (black) and 3.5×10$^{-8}$ mol cm$^{-2}$ (red). Data is also shown for a 5.0×10$^{-8}$ mol cm$^{-2}$ Dye-S/TiO$_2$ with chenodeoxycholic acid as coadsorbent (blue). Overlaid in yellow are fits to the KWW function as is described in the text.
Table 4.1 Charge recombination rate constants abstracted from KWW modeling at different surface coverages of Dye-S/TiO$_2$.

<table>
<thead>
<tr>
<th>Surface Coverage of Dye-S/TiO$_2$ (mol·cm$^{-2}$)</th>
<th>$k$ (s$^{-1}$)</th>
<th>$\beta$</th>
<th>$k_{cr}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0×10$^{-9}$</td>
<td>4.0×10$^3$</td>
<td>0.28</td>
<td>3.1×10$^2$</td>
</tr>
<tr>
<td>3.5×10$^{-8}$</td>
<td>4.0×10$^3$</td>
<td>0.28</td>
<td>3.1×10$^2$</td>
</tr>
<tr>
<td>5.0×10$^{-8}$ with CDCA</td>
<td>1.0×10$^3$</td>
<td>0.28</td>
<td>7.8×10$^1$</td>
</tr>
</tbody>
</table>
Shown in Figure 4.8 are representative kinetics monitored at 740 nm after pulsed 532 nm excitation of Dye-S/TiO₂. The first ten microseconds corresponded to the regeneration reaction, Equation 4.2. On longer time scales, the positive absorption was due to TiO₂(e⁻) and provided a means for the study of charge recombination Reaction 4.3. The kinetics were non-exponential and could be well described by a stretched exponential equation, i.e., Kohlrausch-Williams-Watts (KWW) model, Equation 4.4. Average rate constants were calculated at the first moment by Equation 4.5, the values of which are summarized in Table 4.1.

\[ \Delta \text{Abs} = A \exp[-(kt)^\beta] \] (4.4)

\[ k_{cr} = \left[\frac{1}{k\beta} \times \Gamma(1/\beta)\right]^{-1} \] (4.5)

The raw experimental data shows that only minimal differences were observed for the low and high surface coverage thin films. Analysis by the KWW function revealed average rate constants of 310 s⁻¹ that are over a hundred times faster than the corresponding reactions with I₃⁻, 2.3 ± 0.4 s⁻¹. It is puzzling that the recombination rate constants were surface coverage independent within experimental error. Contrary to what was observed, one might have anticipated that at lower surface coverages larger areas of the unsensitized TiO₂ surface would be exposed to the solution where \([\text{Co}^{III}(\text{bpy})_3]^{3+}\) would have a close approach resulting in faster recombination. Although speculative, it may be that under these conditions, there exists a sufficient area of exposed TiO₂ to enable close approach by the oxidized cobalt acceptors. If this were the case, the data would be consistent with the conclusion drawn from the steady state absorption spectra: in the absence of CDCA the dye molecules are aggregated and the average distance between them does not appear to change with the total number of dye molecules present on the surface. This conclusion is also in agreement with a similar data reported for inorganic dye molecules.

The influence of CDCA on charge recombination to the oxidized cobalt mediators was also investigated. Surprisingly, the regeneration step appeared to be slower to the presence of the CDCA co-adsorbent with Dye-S, Figure 4.8. This observation is important and the generality of it with
other organic dye molecules and under other experimental conditions will be the subject of a future publication. On 10 μs and longer time scales, reaction of the injected electron and the oxidized cobalt mediator could be clearly observed. The kinetics were again non-exponential and analysis by the KWW model showed that the average charge recombination rate constant was 4-fold smaller. Indeed the average rate constant was much more comparable to that reported for recombination to I$_3^-$ . This could indeed be attributed to a more uniform blocking layer induced by the CDCA co-adsorbent.
4.4 Conclusions

We have shown that the co-adsorption of CDCA and D-π-A organic dyes has a significant influence on the ground state absorption spectra of sensitized TiO$_2$ thin films. In the absence of CDCA, evidence for aggregation was observed at even the lowest surface coverages. The presence of CDCA also had a significant influence on the unwanted charge recombination reaction between TiO$_2$(e') and oxidized cobalt mediators.
4.5 References


(3) Finklea, H. O. Semiconductor electrodes; Elsevier: Amsterdam, Netherlands, 1988; Vol. 55.


Chapter 5: Direct Spectroscopic Evidence for Constituent Heteroatoms Enhancing Charge Recombination at a TiO₂–Ruthenium Dye Interface

In part a compilation of one publication.¹

This work was collaborative in conjunction with Holly A. Severin‡, Bryan D. Koivisto‡, Kiyoshi C. D. Robson‡, Eduardo Schott§, Ramiro Arratia-Perez‖, Gerald J. Meyer†, and Curtis P. Berlinguette‡,┴

‡Johns Hopkins University, Baltimore, MD, USA

‡University of Calgary, Calgary, Alberta, Canada

┴The University of British Columbia, Vancouver, BC, Canada

§Universidad Bernardo O’Higgins, Santiago, Chile

‖Universidad Andres Bello, Santiago, Chile

5.1 Introduction

Interfacial processes at the titania photoanode in a dye-sensitized solar cell (DSSC) are sensitive to a myriad of factors.²⁻⁴ The electron promoted by light from a dye into titania is ideally collected at the transparent conducting glass substrate and returned to an oxidized dye by a redox mediator that is in intimate contact with the counter electrode.⁵ These injected electrons can, however, also be intercepted by the small concentration of photo-oxidized dyes on the surface⁶⁻⁸ or
by the oxidized form of the redox shuttle (e.g., I$_2$, I$_3$).$^{9,10}$ A lower open-circuit voltage ($V_{oc}$) is often attributed to the latter recombination event, which can be suppressed by bulky, aliphatic substituents tethered to the dye molecules that serve to inhibit redox active species from reaching the surface,$^{11,12}$ but is also intimately related to the regeneration of the photo–oxidized dyes by the electrolyte.$^6$

Resolving the factors that influence recombination and regeneration, which can manifest as lower photovoltages in operational devices, is complicated by the dynamic nature of the cell. Regeneration of dyes by I$_1$, for example, most likely involves the formation of an adduct with the dye.$^{13-15}$ A consequence of this adduct formation is that specific chemical components of the dye may alter interfacial electron transfer kinetics and, in turn, device efficiency—a feature that we recently described for a pair of metal-free triarylamine-based donor–bridge–acceptor molecules that differed only in the identity of two heteroatoms, sulfur and oxygen, comprising the donor unit of the respective dyes (Figure 5.1).$^6$ While this study demonstrated sulfur atoms can have a measurable effect on photovoltages—particularly at the power point or open circuit conditions where competitive recombination pathways play a more prominent role—a seemingly contrarian observation was made earlier by O’Regan and coworkers$^9$ when they showed that sulfur atoms in a common ruthenium-based dye scaffold enhanced recombination with I$_3^-$ or I$_2$. 
Figure 5.1 (a) Series of ruthenium chromophores Ru-X (X = O, S, Se) used in this study. (b) Previously documented dyes used to probe interfacial electron transfer (X = O, S).\textsuperscript{6,9}
We conjecture that the relative positions of the heteroatoms account for these apparent disparities; namely, the organic dyes presented in Figure 5.1 involve a heteroatom change within the donor unit that is positioned away from the surface and ostensibly spatially optimized for reaction with the electrolyte, whereas the ruthenium scaffold positions the sulfur atom closer to the titania surface and away from the anionic NCS⁻ ligands that are a more likely site for regeneration.⁹ This manuscript reports our first steps towards reconciling these experimental discrepancies by examining how heteroatoms, carefully positioned within the donor units of otherwise structurally related ruthenium-based dyes, impact both regeneration and recombination. The unique series of bis(tridentate) cycloruthenated dyes used for this study contain terminal furyl, thiophene and selenophene substituents (Figure 5.1) that offer the opportunity to examine how interfacial electron transfer kinetics are affected for a series of metal-based dyes with uniform optical and electrochemical properties. It is found that changing the chalcogen within the five-membered rings of these terminal substituents does not impact the regeneration step, but transient spectroscopic methods indicate that the more polarizable selenophene unit increases the rate of recombination with I₃⁻ thereby compromising the measured photovoltages.
5.2 Experimental

Preparation of Compounds. All reagents were purchased from Aldrich and used without further purification except for RuCl$_3$·3H$_2$O (Pressure Chemical Company) and trimethyl-4,4’,4”-tricarboxylate-2,2’:6’,2”-terpyridine (L4; Helios Chemical Company, Switzerland). Purification by column chromatography was carried out using silica (Silicycle: Ultrapure Flash Silica). Analytical thin-layer chromatography (TLC) was performed on aluminum-backed sheets pre-coated with silica 60 F254 adsorbent (0.25 mm thick; Merck, Germany) and visualized under UV light. Routine $^1$H and $^{13}$C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker AV 400 instrument at ambient temperatures. Chemical shifts (δ) are reported in parts per million (ppm) from low- to high-field and referenced to residual non-deuterated solvent. Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; t = triplet; m = multiplet. All proton assignments correspond to the generic molecular schemes that are provided (Figure 5.2). Organic precursors selenophene-2-carbaldehyde,$^{16}$ 1-(2-(3-bromophenyl)-2-oxoethyl)pyridinium iodide,$^{17}$ (E)-1-(pyridin-2-yl)-3-(thiophen-2-yl)prop-2-en-1-one (P2),$^{18}$ 2-(furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (P7),$^{19}$ and 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (P8)$^{20}$ were prepared as previously reported.
Figure 5.2 Labelling scheme for $^1$H NMR signal assignments.
(E)-3-(furan-2-yl)-1-(pyridin-2-yl)prop-2-en-1-one (P1). A methanol/water (9:1; 60 mL) solution containing acetylpyridine (4.5 mL, 40 mmol), furan-2-carbaldehyde (3.3 mL, 40 mmol) and potassium hydroxide (2.14 g, 38.2 mmol) was stirred at room temperature overnight and then the solvent was removed \textit{in vacuo}. The oil residue was dissolved in DCM and washed with water/brine (1:1; 2 × 200 mL). The organic fractions were dried with MgSO$_4$, filtered, and dried \textit{in vacuo} to yield a brown oil. Purification by column chromatography [SiO$_2$: DCM/EtOAc, 9:1; R$_f$ = 0.86] yielded 2.6 g (33%) of the product as a yellow oil that solidified upon standing. $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.71 (ddd, 1H, $^3J = 4.7$ Hz, $^4J = 1.6$ Hz, $^5J = 0.9$ Hz, $H_a$), 8.15-8.09 (m, 2H, $H_d$, $H_b$), 7.83 (dt, 1H, $^3J = 7.7$ Hz, $^4J = 1.7$ Hz, $H_c$), 7.67 (d, 1H, $^3J = 15.8$ Hz, $H_e$), 7.51 (d, 1H, $^3J = 1.5$ Hz, $H_f$), 7.44 (ddd, 1H, $^3J = 7.6$ Hz, $^4J = 4.7$ Hz, $^5J = 1.2$ Hz, $H_h$), 6.74 (d, 1H, $^3J = 3.4$ Hz, $H_f$), 6.48 (dd, 1H, $^3J = 3.4$ Hz, $^4J = 1.8$ Hz, $H_g$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 189.3, 154.2, 152.1, 148.9, 145.1, 136.9, 130.6, 126.8, 122.8, 118.8, 116.2, 112.6. HRMS (EI): m/z = 199.0630 [(M$^+$) (calcd for C$_{12}$H$_9$NO$_2^+$; m/z = 199.0633)].

(E)-1-(pyridin-2-yl)-3-(selenophen-2-yl)prop-2-en-1-one (P3). A methanol/water (9:1; 60 mL) solution containing acetylpyridine (2.2 mL, 19.7 mmol), selenophene-2-carbaldehyde (3.12 g, 19.7 mmol) and potassium hydroxide (1.05 g, 29.7 mmol) was stirred at room temperature overnight. Vacuum filtration yielded 1.43 g (27.8%) of the product as a bright yellow powder. $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.71 (ddd, 1H, $^3J = 4.7$ Hz, $^4J = 1.7$ Hz, $^5J = 0.9$ Hz, $H_a$), 8.14 (ddd, 1H, $^3J = 7.9$ Hz, $^4J = 1.0$ Hz, $^5J = 1.0$ Hz, $H_b$), 8.08 (d, 1H, $^3J = 5.6$ Hz, $H_h$), 8.05 (d, 1H, $^3J = 15.5$ Hz, $H_f$), 7.93 (d, 1H, $^3J = 15.5$ Hz, $H_h$), 7.83 (dt, 1H, $^3J = 7.7$ Hz, $^4J = 1.7$ Hz, $H_c$), 7.55 (d, 1H, $^3J = 3.7$ Hz, $H_f$), 7.45 (ddd, 1H, $^3J = 7.6$ Hz, $^4J = 4.7$ Hz, $^5J = 1.2$ Hz, $H_h$), 7.27 (dd, 1H, $^3J = 5.5$ Hz, $^4J = 3.8$ Hz, $H_g$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 189.3, 154.3, 149.0, 147.1, 139.6, 137.2, 135.8, 134.6, 130.9, 127.0, 123.0, 121.2. HRMS (EI): m/z = 262.9860 [(M$^+$) (calcd for C$_{12}$H$_9$NO$_2^80$Se$^+$; m/z = 262.9849)].
6-(3-bromophenyl)-4-(furan-2-yl)-2,2'-bipyridine (P4). A mixture of \( (E)-3-\text{(furan-2-yl)}-1-\text{(pyridin-2-yl)}\text{prop-2-en-1-one (P1)} \) (1.74 g, 8.79 mmol), ammonium acetate (17.8 g, 228 mmol), and 1-(2-(3-bromophenyl)-2-oxoethyl)pyridinium iodide (3.55 g, 8.79 mmol) and formamide (30 mL) was slowly brought to 120 °C under a dinitrogen atmosphere with stirring. The reaction was left at 120 °C overnight and then cooled to room temperature. The precipitate was isolated by vacuum filtration and washed with EtOH. The solid was solubilized in DCM, dried with MgSO\(_4\), filtered, and concentrated before being purified by column chromatography (SiO\(_2\): DCM/EtOAc, 9:1; \( R_f = 0.83 \)) to yield the product as a dark orangey-brown oil (1.87 g, 56.4%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 8.70 \) (d, 1H, \(^3\)J = 5.5 Hz, \( H_a \)), 8.60 (d, 1H, \(^3\)J = 7.9 Hz, \( H_d \)), 8.58 (d, 1H, \(^4\)J = 1.4 Hz, \( H_e \)), 8.33 (t, 1H, \(^4\)J = 1.8 Hz, \( H_j \)), 8.06 (d, 1H, \(^3\)J = 8.9 Hz, \( H_k \)), 7.95 (d, 1H, \(^4\)J = 1.4 Hz, \( H_i \)), 7.84 (td, 1H, \(^3\)J = 7.7 Hz, \(^4\)J = 1.8 Hz, \( H_c \)), 7.56–7.53 (m, 2H, \( H_h, H_m \)), 7.53 (t, 1H, \(^3\)J = 7.9 Hz, \( H_l \)), 7.32 (ddd, 1H, \(^3\)J = 7.4 Hz, \(^3\)J = 4.8 Hz, \(^4\)J = 1.1 Hz, \( H_b \)), 7.04 (d, 1H, \(^3\)J = 3.4 Hz, \( H_f \)), 6.54 (dd, 1H, \(^3\)J = 1.8 Hz, \(^3\)J = 3.4 Hz, \( H_g \)); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 156.5, 156.1, 155.6, 151.9, 150.3, 140.1, 139.6, 137.1, 132.2, 130.4, 130.3, 125.7, 124.2, 123.2, 121.6, 114.6, 114.3, 112.4, 109.4 \); HRMS (EI): \( m/z = 376.0193 \) [(M)\(^+\)] (calcd for C\(_{20}\)H\(_{13}\)N\(_2\)OBr\(^+\): \( m/z = 376.0211 \)).

6-(3-bromophenyl)-4-(thiophen-2-yl)-2,2'-bipyridine (P5). A mixture of \( (E)-1-\text{(pyridin-2-yl)}-3-\text{(thiophen-2-yl)}\text{prop-2-en-1-one (P2)} \) (2.00 g, 9.29 mmol), 1-(2-(3-bromophenyl)-2-oxoethyl)pyridinium iodide (3.75 g, 9.29 mmol), and formamide (25 mL) was stirred and slowly heated to 120 °C under a N\(_2\) atmosphere and left under these conditions overnight. The solution was cooled to room temperature and the solvent removed in vacuo. The remaining solids were triturated with EtOH and air-dried. The dark solid was solubilized in DCM, dried with MgSO\(_4\), and solvents removed by rotovap. The product was purified by column chromatography (SiO\(_2\): DCM/\( \text{EtOAc}, 9:1; R_f = 0.95 \)) to yield an oil that solidified upon standing 1.67 g (45.7%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 8.70 \) (dd, 1H, \(^3\)J = 4.7 Hz, \(^4\)J = 0.8 Hz, \( H_a \)), 8.61 (m, 2H, \( H_b, H_d \)), 8.33 (t, 1H, \(^4\)J = 1.8 Hz, \( H_j \)), 8.06 (d, 1H, \(^3\)J = 7.8 Hz, \( H_k \)), 7.87 (d, 1H, \(^4\)J = 1.6 Hz, \( H_i \)), 7.85 (t, 1H, \(^3\)J = 7.8 Hz, \( H_l \)).
Hz, \(^4J = 1.8\) Hz, \(H_a\), 7.69 (dd, 1H, \(^3J = 3.7\) Hz, \(^4J = 1.0\) Hz, \(H_b\)), 7.56 (dq, 1H, \(^3J = 7.9\) Hz, \(^4J = 0.9\) Hz, \(H_m\)), 7.43 (dd, 1H, \(^3J = 5.1\) Hz, \(^4J = 0.9\) Hz, \(H_i\)), 7.37 (t, 1H, \(^3J = 7.9\) Hz, \(H_j\)), 7.33 (dd, 1H, \(^3J = 4.8\) Hz, \(^4J = 0.9\) Hz, \(H_c\)), 7.16 (dd, 1H, \(^3J = 5.0\) Hz, \(^3J = 3.7\) Hz, \(H_g\)). 13C NMR (100 MHz, CDCl\(_3\)):

\[\delta 156.8, 156.0, 155.9, 149.3, 143.7, 141.8, 141.5, 132.3, 130.5, 130.4, 128.6, 127.4, 125.9, 125.8, 124.3, 123.3, 121.7, 116.9, 116.4;\]

HRMS (EI): \(m/z = 393.9945 [(M)^+]\) (calcd for C\(_{20}\)H\(_{13}\)N\(_2\)SBr: \(m/z = 393.9962\)).

6-(3-bromophenyl)-4-(selenophen-2-yl)-2,2'-bipyridine (P6). A stirring mixture of (E)-1-(pyridin-2-yl)-3-(selenophen-2-yl)prop-2-en-1-one (P3) (1.20 g, 4.58 mmol), 1-(2-(3-bromophenyl)-2-oxoethyl)pyridinium iodide (1.85 g, 4.58 mmol), ammonium acetate (9.20 g, 119 mmol), and formamide (25 mL) was brought to 120 °C under a N\(_2\) atmosphere and left overnight. The dark brown reaction mixture was allowed to cool down to room temperature. The resulting solid was removed by vacuum filtration, and purified by column chromatography to yield 1.28 g (63.5%) of the product as a tan solid after drying \(\text{in vacuo}\). 1H NMR (400 MHz, CDCl\(_3\)):

\[\delta = 8.69\) (ddd, 1H, \(^3J = 4.8\) Hz, \(^4J = 1.8\) Hz, \(^5J = 0.9\) Hz, \(H_a\)), 8.56 (ddd, 1H, \(^3J = 8.0\) Hz, \(^4J = 1.0\) Hz, \(^5J = 1.0\) Hz, \(H_a\)), 8.52 (d, 1H, \(^3J = 1.6\) Hz, \(H_a\)), 8.30 (t, 1H, \(^3J = 1.8\) Hz, \(H_i\)), 8.08 (dd, 1H, \(^3J = 5.5\) Hz, \(^4J = 1.0\) Hz, \(H_e\)), 8.01 (ddd, 1H, \(^3J = 7.8\) Hz, \(^4J = 1.6\) Hz, \(^5J = 1.1\) Hz, \(H_i\)), 7.86 – 7.77 (m, 2H, \(H_c, H_d\)), 7.75 (d, 1H, \(^3J = 3.7\) Hz, \(H_i\)), 7.54 (ddd, 1H, \(^3J = 7.9\) Hz, \(^4J = 2.0\) Hz, \(^5J = 1.0\) Hz, \(H_e\)), 7.38 – 7.28 (m, 3H, \(H_g, H_h, H_i\)); 13C NMR (100 MHz, CDCl\(_3\)):

\[\delta = 156.5, 155.8, 155.6, 149.2, 147.9, 145.3, 141.3, 137.0, 132.8, 132.1, 131.0, 130.3, 130.2, 128.1, 125.6, 124.1, 123.2, 121.6, 117.2, 116.7;\]

HRMS (EI): \(m/z = 439.9407 [(M)^+]\) (calcd for C\(_{20}\)H\(_{13}\)N\(_2\)SeBr\(^+\); \(m/z = 439.9427\)).

4,4,5,5-tetramethyl-2-(selenophen-2-yl)-1,3,2-dioxaborolane (P9). n-BuLi (1.6 M in hexanes, 26.2 mL, 42.0 mmol) was added dropwise to a solution of selenophene (5.00 g, 38.2 mmol) in THF (120 mL) at -78 °C. The solution was stirred for 30 min at room temperature. After cooling to -78 °C, 2-isopropoxy-4,4',5,5'-tetramethylidioxaborolan (11.7 g, 62.9 mmol) was added and the reaction mixture was stirred for 20 min at room temperature. The reaction was quenched with
MeOH (5 mL) and the product extracted with Et₂O. The ether layer was washed with brine (2 100 mL), dried with MgSO₄, filtered, and the solvent removed by rotary evaporation. The oil residue was purified by column chromatography (SiO₂: hexanes/EtOAc (9:1); Rf = 0.49) to give the product as a light yellow oil that solidified upon standing (3.54 g, 36.1%). ¹H NMR (400 MHz, CDCl₃): δ = 8.33 (d, 1H, 3J = 5.1 Hz, Hₖ), 7.95 (d, 1H, 3J = 3.4 Hz, Hₚ), 7.43 (dd, 1H, 3J = 5.1 Hz, 3J = 3.7 Hz, Hₒ), 1.32 (s, 12H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ = 139.6, 137.8, 131.0, 84.0, 82.8, 24.8, HRMS (EI): m/z = 258.0327 [(M)⁺] (calcd for C₁₀H₁₅BO₂Se⁺: m/z = 258.0330).

4-(furan-2-yl)-6-(3-(furan-2-yl)phenyl)-2,2'-bipyridine (L1H). 2-(furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (P7) (1.09 g, 5.61 mmol) and 6-(3-bromophenyl)-4-(furan-2-yl)-2,2'-bipyridine (P4) (933 mg, 2.47 mmol) were solubilized in THF/H₂O (9:1, 125 mL) and sparged with N₂ for 10 min. K₂CO₃ (3.44 g, 24.7 mmol) and Pd(PPh₃)₄ (405 mg, 0.35 mmol) were then added and the reaction was left to reflux for 14 h under N₂. The reaction mixture was cooled to room temperature and washed with brine. The organic layer was dried with MgSO₄ and then the solvent was removed in vacuo. The residue was purified by column chromatography (SiO₂: gradient elution DCM/hexanes 8:2 to DCM to DCM/EtOAc 9:1; Rf = 0.13 in 8:2 DCM/hexanes) to yield the product as a yellow oil that solidified upon standing, 715 mg (79.3%). ¹H NMR (400 MHz, CDCl₃): δ = 8.71 (d, 1H, 3J = 4.7 Hz, Hₐ), 8.65 (d, 1H, 3J = 7.9 Hz, Hₕ), 8.62 (s, 1H, Hₖ), 8.46 (s, 1H, Hₗ), 8.07 (d, 1H, 3J = 7.8 Hz, Hₖ), 8.04 (s, 1H, Hₙ), 7.84 (td, 1H, 3J = 7.7 Hz, 3J = 1.4 Hz, Hₒ), 7.74 (d, 1H, 3J = 7.8 Hz, Hₘ), 7.57 (s, 1H, Hₖ), 7.53 – 7.48 (m, 2H, Hₖ, Hₙ), 7.32 (dd, 1H, 3J = 7.4 Hz, 3J = 5.5 Hz, Hₕ), 7.05 (d, 1H, 3J = 3.4 Hz, Hₕ), 6.78 (d, 1H, 3J = 3.3 Hz, Hₕ), 6.55 (dd, 1H, 3J = 3.2 Hz, 3J = 1.7 Hz, Hₖ), 6.50 (dd, 1H, 3J = 3.0 Hz, 3J = 1.8 Hz, Hₕ); ¹³C (100 MHz, CDCl₃): δ = 157.1, 156.4, 156.3, 154.1, 152.1, 149.2, 143.8, 142.4, 140.0, 139.5, 137.1, 131.5, 129.3, 126.3, 124.7, 124.1, 122.6, 121.6, 114.7, 114.0, 112.3, 111.9, 109.2, 105.6; HRMS (EI): m/z = 364.1207 [(M)⁺] (calcd for C₂₄H₁₈N₂O₂⁺: m/z = 364.1212).
4-(thiophen-2-yl)-6-(3-(thiophen-2-yl)phenyl)-2,2′-bipyridine (L2H). 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (P8) (915 mg, 4.35 mmol) and 6-(3-bromophenyl)-4-(thiophen-2-yl)-2,2′-bipyridine (P2) (842 mg, 2.14 mmol) were solubilized in a THF/H₂O (9:1, 125 mL) and sparged with N₂ for 10 min. K₂CO₃ (2.98 g, 21.4 mmol) and Pd(PPh₃)₄ (352 mg, 0.30 mmol) were then added and the reaction left to reflux for 14 h under N₂. The reaction mixture was cooled to room temperature and washed with brine. The product was extracted into ether and the organic layer dried with MgSO₄. Solvents were removed in vacuo and the oil residue purified by column chromatography (SiO₂: gradient elution DCM/hexanes 8:2 to DCM to DCM/EtOAc 9:1; Rf = 0.26 in 8:2 DCM/hexanes) to yield the product as a yellow-brown oil that was further purified by trituration with absolute EtOH to yield 688 mg (81.0%) of a tan solid.

1H NMR (400 MHz, CDCl₃): δ = 8.72 (dd, 1H, 3J = 4.8 Hz, 4J = 0.9 Hz, Hₐ), 8.66 (d, 1H, 3J = 7.1 Hz, Hₐ), 8.63 (d, 1H, 4J = 1.6 Hz, Hₐ), 8.40 (t, 1H, 4J = 1.7 Hz, Hₐ), 8.05 (ddd, 1H, 3J = 7.8 Hz, 4J = 1.6 Hz, 4J = 1.2 Hz, Hₐ), 7.95 (d, 1H, 4J = 1.6 Hz, Hₐ), 7.85 (td, 1H, 3J = 7.6 Hz, 4J = 2.0 Hz, Hₐ), 7.70 (dd, 1H, 3J = 3.7 Hz, 4J = 1.1 Hz, Hₐ), 7.68 (dd, 1H, 4J = 1.8 Hz, 4J = 1.1 Hz, Hₐ), 7.52 (t, 1H, 3J = 7.8 Hz, Hₐ), 7.45-7.42 (m, 2H, Hₐ, Hₐ), 7.35 (dd, 1H, 3J = 4.4 Hz, 4J = 1.2 Hz, Hₐ), 7.32 (dd, 1H, 3J = 4.9 Hz, 4J = 1.2 Hz, Hₐ), 7.16 (dd, 1H, 3J = 5.0 Hz, 3J = 3.7 Hz, Hₐ), 7.12 (dd, 1H, 3J = 5.1 Hz, 3J = 3.6 Hz, Hₐ); 13C NMR (100 MHz, CDCl₃): δ = 157.1, 156.7, 156.2, 149.2, 144.5, 143.5, 141.9, 140.1, 137.1, 135.1, 129.5, 128.5, 128.3, 127.2, 126.9, 126.4, 125.8, 125.2, 124.9, 124.1, 123.7, 121.7, 117.0, 116.1; HRMS (EI): m/z = 396.0746 [(M⁺)⁺] (calcd for C₂₄H₁₆N₂S₂⁺: m/z = 396.0755).

4-(selenophen-2-yl)-6-(3-(selenophen-2-yl)phenyl)-2,2′-bipyridine (L3H). 6-(3-bromophenyl)-4-(selenophen-2-yl)-2,2′-bipyridine (P3) (642 mg, 1.46 mmol) and 4,4,5,5-tetramethyl-2-(selenophen-2-yl)-1,3,2-dioxaborolane (P9) (756 mg, 2.94 mmol) were solubilized in THF/water (9:1, 125 mL) and sparged with N₂ for 10 min. K₂CO₃ (2.02 g, 14.6 mmol) and Pd(PPh₃)₄ (236 mg, 0.204 mmol) were then added and the reaction left to reflux under nitrogen for 14 h. The reaction mixture was then cooled to room temperature and washed with brine. The product was extracted
with Et₂O. The organic layer was dried with MgSO₄, filtered and then the was solvent removed in vacuo. Purification by column chromatography [SiO₂: DCM/EtOAc (9:1); Rf = 0.34] yielded 516 mg (72.1%) of the product as an orange solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.72 (ddd, 1H, ³J = 4.8 Hz, ⁴J = 1.7 Hz, ⁵J = 0.9 Hz, Hₐ), 8.64 (d, 1H, ³J = 8.0 Hz, Hₐ), 8.58 (d, 1H, ⁴J = 1.5 Hz, Hₐ), 8.36 (t, 1H, ³J = 1.7 Hz, Hₐ), 8.10 (d, 1H, ³J = 5.6 Hz, Hₐ), 8.04 (d, 1H, ⁴J = 7.8 Hz, Hₐ), 7.98 (d, 1H, ³J = 5.5 Hz, Hₐ), 7.90 - 7.81 (m, 3H, Hₐ, Hₐ, Hₐ), 7.63 (d, 1H, ⁴J = 7.7 Hz, Hₐ), 7.59 (d, 1H, ³J = 3.7 Hz, Hₐ), 7.50 (t, 1H, ³J = 7.7 Hz, Hₐ), 7.33 (dddd, 1H, ³J = 5.5 Hz, ⁴J = 3.9 Hz, Hₐ), 7.36 (dd, 1H, ³J = 5.4 Hz, ⁴J = 3.8 Hz, ⁵J = 1.0 Hz, Hₐ), 7.33 (dddd, 1H, ³J = 7.4 Hz, ⁴J = 4.8 Hz, ⁵J = 1.0 Hz, Hₐ); ¹³C NMR (100 MHz, CDCl₃): δ = 157.0, 156.6, 156.1, 150.9, 149.2, 148.2, 145.3, 140.1, 137.1, 137.0, 132.7, 131.0, 130.8, 130.5, 129.4, 128.1, 127.4, 126.4, 125.8, 125.3, 124.1, 121.6, 117.5, 116.6. HRMS (EI): m/z = 491.9639 [(M)⁺] (calcd for C₂₄H₁₆N₂80Se₂⁺; m/z = 491.9644).

**General Preparation of Methyl Ester Complexes (Ru-XMe).** To a MeOH:H₂O:THF solution (5:1:1, v/v/v, 210 mL) containing 0.40 mmol of the ligand (e.g., L₁H—L₃H) was added 0.40 mmol Ru(L₄)Cl₃ and N-ethylmorpholine (0.5 mL). Following a 16-h reflux, AgNO₃ (1.20 mmol) was added to the reaction mixture and then left to reflux for an additional 1.5 h. The mixture was then cooled, preabsorbed on silica, and the solvent was removed in vacuo. The product was purified by chromatographic techniques (details specified below). The desired fraction was collected and isolated to yield a dark red fine solid.

[Ru(L₁)(L₄)]NO₃ (Ru-O₂Me). Chromatographic conditions: SiO₂: CH₂Cl₂/MeOH 9:1; Rf = 0.50. Yield = 213 mg (0.23 mmol, 57.2%). ¹H NMR (400 MHz, CDCl₃): δ = 9.14 (s, 2H, Hₐ), 9.08 (s, 1H, Hₐ), 8.96-8.88 (m, 2H, Hₐ, Hₐ), 8.47 (s, 1H, Hₐ), 8.07 (s, 1H, Hₐ), 7.96 (t, 1H, ³J = 6.8 Hz, Hₐ), 7.77-7.62 (m, 6H, Hₐ, Hₐ, Hₐ, Hₐ), 7.33 (s, 1H, Hₐ), 7.17 (d, 1H, ³J = 3.1 Hz, Hₐ), 7.03 (d, 1H, ³J = 5.7 Hz, Hₐ), 6.77-6.70 (m, 2H, Hₐ, Hₐ), 6.40 (d, 1H, ³J = 1.0 Hz, Hₐ), 6.34 (d, 1H, ³J = 0.9 Hz, Hₐ), 5.37 (d, 1H, ³J = 7.5 Hz, Hₐ), 4.18 (s, 3H, Hₐ), 3.92 (s, 6H, Hₐ); HRMS (ESI): m/z = 866.1310 [(M)⁺]
(calcd for C$_{45}$H$_{31}$N$_{5}$O$_{8}$Ru: m/z = 866.1321); Anal. Calcd for C$_{45}$H$_{32}$N$_{6}$O$_{11}$Ru•3H$_{2}$O: C, 54.71; H, 3.88; N, 8.51. Found: C, 54.53; H, 3.82; N, 8.49.

[Ru(L2)(L4)]NO$_{3}$ (Ru-S$_{Me}$). Chromatographic conditions: SiO$_{2}$: CH$_{2}$Cl$_{2}$/MeOH 9:1; R$_{f}$ = 0.36. Yield = 277 mg (0.29 mmol, 72.0%). $^{1}$H NMR (400 MHz, CDCl$_{3}$): $\delta$ = 9.15 (s, 2H, $H_b$), 9.06 - 9.03 (m, 2H, $H_d$, $H_c$), 8.92 (d, 2H, $^{4}J$ = 1.0 Hz, $H_d$), 8.29 (d, 1H, $^{4}J$ = 1.2 Hz, $H_i$), 8.23 (dd, 1H, $^{3}J$ = 3.5 Hz, $^{4}J$ = 0.6 Hz, $H_a$), 7.96 - 7.92 (m, 2H, $H_c$, $H_i$), 7.71 (d, 2H, $^{3}J$ = 5.8 Hz, $H_a$), 7.65 (dd, 2H, $^{3}J$ = 5.9 Hz, $^{4}J$ = 1.6 Hz, $H_b$), 7.55 (d, 1H, $^{3}J$ = 5.0 Hz, $H_b$), 7.32 (dd, 1H, $^{3}J$ = 5.0 Hz, $^{2}J$ = 3.8 Hz, $H_i$), 7.22 (d, 1H, $^{3}J$ = 4.7 Hz, $H_f$), 7.13 (dd, 1H, $^{3}J$ = 5.0 Hz, $^{4}J$ = 0.9 Hz, $H_a$), 7.08 (dd, 1H, $^{3}J$ = 3.6 Hz, $^{4}J$ = 0.9 Hz, $H_b$), 7.06 (d, 1H, $^{3}J$ = 6.4 Hz, $H_m$), 6.95 (dd, 1H, $^{3}J$ = 5.0 Hz, $^{3}J$ = 3.7 Hz, $H_g$), 6.70 (dd, 1H, $^{3}J$ = 7.9 Hz, $^{4}J$ = 1.9 Hz, $H_a$), 5.39 (d, 1H, $^{3}J$ = 7.8 Hz, $H_i$), 4.20 (s, 3H, $H_f$), 3.94 (s, 6H, $H_c$); HRMS (ESI): m/z = 898.0849 [(M$^+$)] (calcd for C$_{45}$H$_{32}$N$_{6}$O$_{6}$RuS$_{3}$: m/z = 898.0865); Anal. Calcd for C$_{45}$H$_{32}$N$_{6}$O$_{6}$RuS$_{2}$•2H$_{2}$O: C, 53.94; H, 3.62; N, 8.39. Found: C, 54.24; H, 3.67; N, 8.09.

[Ru(L3)(L4)]NO$_{3}$ (Ru-Se$_{Me}$). Chromatographic conditions: SiO$_{2}$: CH$_{2}$Cl$_{2}$/MeOH 9:1; R$_{f}$ = 0.32. Yield = 327 mg (0.31 mmol, 77.4%). $^{1}$H NMR (400 MHz, CDCl$_{3}$): $\delta$ = 9.15 (s, 2H, $H_b$), 9.05 (d, 1H, $^{3}J$ = 8.2 Hz, $H_b$), 8.98 (d, 1H, $^{4}J$ = 1.4 Hz, $H_c$), 8.92 (d, 2H, $^{4}J$ = 1.0 Hz, $H_d$), 8.37 (dd, 1H, $^{3}J$ = 3.8 Hz, $^{4}J$ = 0.9 Hz, $H_a$), 8.23 (dd, 1H, $^{3}J$ = 5.5 Hz, $^{4}J$ = 0.9 Hz, $H_b$), 8.20 (d, 1H, $^{4}J$ = 1.4 Hz, $H_i$), 7.95 (td, 1H, $^{3}J$ = 7.9 Hz, $^{4}J$ = 1.5 Hz, $H_c$), 7.87 (d, 1H, $^{4}J$ = 1.9 Hz, $H_i$), 7.78 (dd, 1H, $^{3}J$ = 5.5 Hz, $^{4}J$ = 1.0 Hz, $H_d$), 7.71 (d, 2H, $^{3}J$ = 5.9 Hz, $H_a$), 7.50 (dd, 2H, $^{3}J$ = 5.9 Hz, $^{4}J$ = 1.7 Hz, $H_a$), 7.55 (dd, 1H, $^{3}J$ = 5.6 Hz, $^{4}J$ = 3.9 Hz, $H_d$), 7.90 - 7.80 (m, 3H, $H_g$, $H_m$, $H_a$), 7.07 (ddd, 1H, $^{3}J$ = 7.5 Hz, $^{4}J$ = 5.5 Hz, $^{3}J$ = 1.0 Hz, $H_b$), 6.65 (dd, 1H, $^{3}J$ = 7.8 Hz, $^{4}J$ = 1.9 Hz, $H_o$), 5.38 (d, 1H, $^{3}J$ = 7.9 Hz, $H_i$), 4.22 (s, 3H, $H_f$), 3.96 (s, 6H, $H_c$); HRMS (ESI): m/z = 997.9756 [(M$^+$)] (calcd for C$_{45}$H$_{32}$N$_{6}$O$_{6}$RuSe$_{3}$: m/z = 997.9734). Anal. Calcd for C$_{45}$H$_{32}$N$_{6}$O$_{6}$RuSe$_{2}$•3H$_{2}$O: C, 50.15; H, 3.18; N, 7.80. Found: C, 49.99; H, 3.57; N, 7.51.

**General Preparation of Carboxylic Acid Complexes (Ru-X$_{Me}$).** A solution containing 0.13 mmol of ester metal complexes (Ru-X$_{Me}$) in DMF:H$_{2}$O:NEt$_{3}$ (3:1:1, v/v/v, 25 mL) was refluxed for 4h.
The solution was then cooled, and the solvent was removed in vacuo. The product was triturated with DCM and collected via vacuum filtration to yield a dark red fine solid.

[Ru(L1)(L5)]NO₃ (Ru-OH). Yield = 105 mg (0.13 mmol, 98.6%). ¹H NMR (400 MHz, DMSO-<sup>d₆</sup>): δ = 9.44 (s, 2H, Hₐ), 9.19 (s, 2H, H₀), 9.04 (s, 1H, Hₑ), 8.97 (d, 1H, ³J = 8.3 Hz, Hₐ), 8.83 (d, 1H, ⁴J = 0.6 Hz, Hₐ), 8.13 (d, 1H, ³J = 1.5 Hz, Hₐ), 8.02 (t, 1H, ³J = 7.9 Hz, Hₐ), 7.84 (d, 1H, ³J = 3.3 Hz, Hₐ), 7.72 (d, 2H, ³J = 5.9 Hz, Hₐ), 7.61-7.58 (m, 3H, Hₐ, Hₐ), 7.48 (d, 1H, ³J = 4.9 Hz, Hₐ), 7.16 (dd, 1H, ³J = 5.5 Hz, ³J = 1.9 Hz, Hₐ), 6.95 (dd, 1H, ³J = 3.5 Hz, ³J = 1.8 Hz, Hₐ), 6.80 (dd, 1H, ³J = 7.8 Hz, ⁴J = 1.7 Hz, Hₐ), 6.76 (d, 1H, ³J = 3.3 Hz, Hₐ), 6.49 (dd, 1H, ³J = 3.4 Hz, ³J = 1.8 Hz, Hₐ), 5.54 (d, 1H, ³J = 7.9 Hz, Hₐ); HRMS (ESI): m/z = 824.0838 [(M)⁺] (calcd for C₄₂H₂₆N₃O₈Ru: m/z = 824.0838); Anal. Calcd for C₄₂H₂₆N₃O₈Ru•4H₂O: C, 52.34; H, 3.56; N, 8.72. Found: C, 52.15; H, 3.65; N, 8.57.

[Ru(L2)(L5)]NO₃ (Ru-Sₙ). Yield = 109 mg (0.13 mmol, 97.8%). ¹H NMR (400 MHz, DMSO-<sup>d₆</sup>): δ = 9.43 (s, 2H, Hₐ), 9.18 (s, 2H, H₀), 9.03 (d, 1H, ³J = 8.3 Hz, Hₐ), 8.99 (s, 1H, Hₑ), 8.84 (s, 1H, Hₑ), 8.41 (d, 1H, ³J = 2.8 Hz, Hₐ), 8.37 (d, 1H, ⁴J = 1.5 Hz, Hₐ), 8.01 (dt, 1H, ³J = 8.6 Hz, ³J = 1.2 Hz, Hₐ), 7.94 (d, 1H, ³J = 5.1 Hz, Hₐ), 7.70 (d, 2H, ³J = 5.8 Hz, Hₐ), 7.58 (dd, 2H, ³J = 5.8 Hz, ⁴J = 1.2 Hz, Hₐ), 7.49 (dd, 1H, ³J = 5.6 Hz, ⁴J = 0.7 Hz, Hₐ), 7.44 (dd, 1H, ³J = 4.8 Hz, ³J = 3.7 Hz, Hₐ), 7.39 (d, 1H, ³J = 3.4 Hz, Hₐ), 7.34 (d, 1H, ³J = 4.9 Hz, Hₐ), 7.15 (dd, 1H, ³J = 6.8 Hz, ³J = 5.4 Hz, Hₐ), 7.02 (dd, 1H, ³J = 4.9 Hz, ³J = 3.7 Hz, Hₐ), 6.67 (d, 1H, ³J = 7.4 Hz, Hₐ), 5.50 (d, 1H, ³J = 7.8 Hz, Hₐ); HRMS (ESI): m/z = 856.0392 [(M)⁺] (calcd for C₄₂H₂₆N₃O₈RuS₂⁺: m/z = 856.0392); Anal. Calcd for C₄₂H₂₆N₃O₈RuS₂•4H₂O: C, 50.65; H, 3.44; N, 8.44. Found: C, 50.55; H, 3.21; N, 8.42.

[Ru(L3)(L5)]NO₃ (Ru-Seₙ). Yield = 122 mg (0.13 mmol, 98.9%). ¹H NMR (400 MHz, DMSO-<sup>d₆</sup>): δ = 9.47 (s, 2H, Hₐ), 9.23 (s, 2H, H₀), 9.07 (d, 1H, ³J = 8.1 Hz, Hₐ), 8.95 (s, 1H, Hₑ), 8.81 (s, 1H, Hₑ), 8.58 (d, 1H, ³J = 3.6 Hz, Hₐ), 8.55 (d, 1H, ³J = 5.6 Hz, Hₐ), 8.35 (d, 1H, ⁴J = 1.5 Hz, Hₐ), 8.01 (t, 1H, ³J = 7.7 Hz, Hₐ), 7.94 (d, 1H, ³J = 5.6 Hz, Hₐ), 7.71 (d, 2H, ³J = 5.9 Hz, Hₐ), 7.64
(dd, 1H, $^3J = 5.4$ Hz, $^4J = 4.0$ Hz, $H_a$), 7.60 (dd, 2H, $^3J = 5.8$ Hz, $^4J = 1.4$ Hz, $H_b$), 7.52 (d, 1H, $^3J = 3.6$ Hz, $H_a$), 7.49 (d, 1H, $^3J = 5.2$ Hz, $H_a$), 7.23 (dd, 1H, $^3J = 5.3$ Hz, $^4J = 3.9$ Hz, $H_a$), 7.15 (t, 1H, $^3J = 6.5$ Hz, $H_a$), 6.61 (d, 1H, $^3J = 7.7$ Hz, $H_a$), 5.48 (d, 1H, $^3J = 7.8$ Hz, $H_i$); HRMS (ESI): $m/z = 955.9274$ [(M)$^+$] (calcd for $C_{42}H_{26}N_5O_6Ru^80Se_2$; $m/z = 955.9281$). Anal. Calcd for $C_{42}H_{26}N_5O_6RuSe_2•4H_2O$: C, 46.29; H, 3.14; N, 7.71. Found: C, 45.99; H, 2.84; N, 7.56.

**Physical Methods.** Elemental analysis (EA), electrospray ionization mass spectrometry (ESI-MS), matrix-assisted laser desorption/ionization mass spectrometry (MALDI-TOF), and electron impact (EI) mass spectrometry data were collected at the Chemistry Instrumentation Facility of the University of Calgary. Electrochemical measurements on dyes in solution were performed under anaerobic conditions with a Princeton Applied Research VersaStat 3 potentiostat using dry solvents, a glassy carbon working electrode, a platinum counter electrode, a silver pseudoreference electrode, and a 0.1 M NBut$_4$BF$_4$ supporting electrolyte. Electronic spectroscopic data were collected on MeCN solutions using a Cary 5000 UV-vis spectrophotometer (Varian).

**Sensitized TiO$_2$ substrate preparation.** Mesoporous nanocrystalline TiO$_2$ thin films were deposited onto microscope glass slides (for spectroscopic study) or fluorine doped tin oxide (FTO) substrate (for electrochemistry) as previously described$^{21}$. The films were then immersed in methanol solution containing $\sim 1\times 10^{-4}$ M dye molecules and 1 equivalent of tetrabutylammonium hydroxide for $\sim 20$ min to achieve a surface coverage of $\sim 2\times 10^{-8}$ mol/cm$^2$. The sensitized films were then washed with neat methanol and acetonitrile. The films were diagonally positioned in a standard 1cm$^2$ quartz cuvette with electrolyte and purged with argon gas for at least 30 min prior to experimentation.

**Spectroelectrochemistry.** Steady-state UV-vis absorption spectra were obtained on a Varian Cary 50 spectrophotometer at room temperature. A potentiostat (BAS model CV-50W) was employed for measurements in a standard three-electrode configuration with a sensitized TiO$_2$/FTO working electrode, a platinum disk counter electrode and a Ag/AgCl reference electrode (Bioanalytical...
Scientific Instruments, Inc.) in 0.5 M LiClO₄/CH₃CN solution. All potentials were reported versus the normal hydrogen electrode (NHE). The ferrocenium/ferrocene half-wave potential was measured at room temperature before and after each experiment and was used as an external standard to calibrate the reference electrode. Conversion constant of -640 mV from NHE to Fe⁺/Fe was used in acetonitrile at 25 °C.²²

**Transient Absorption Spectroscopy.** Nanosecond transient absorption measurements were acquired with an apparatus similar to that which has been previously described.²¹ Briefly, samples were excited by a frequency doubled Q-switched, pulsed Nd:YAG laser (Quantel USA (BigSky) Brilliant B; 532 nm, 5-6 ns full width at half-maximum (fwhm), 1 Hz, ~10 mm in diameter) directed 45° to the film surface. A 150 W Xenon arc lamp served as the probe beam (Applied Photophysics) that was aligned orthogonally to the excitation light. Detection was achieved with a monochromator (Spex 1702/04) optically coupled to an R928 photomultiplier tube (Hamamatsu). Typically, 30 laser pulses were averaged at each observation wavelength for full spectra generation. Single wavelength kinetic measurement was acquired by 100-200 laser averages. Kinetic data fitting and spectral modeling was performed in Origin 8 and least-squares error minimization was accomplished using the Levenberg-Marquardt iteration method.

**Open Circuit Photovoltage Measurements.** Sensitized TiO₂/FTO substrate was sandwiched against a platinized FTO counter electrode with a vinyl film (Warps, 8 mil Vinyl-Pane) spacer. Electrolyte containing 0.5 M LiI and 0.05 M I₂ dissolved in CH₃CN was employed. Steady-state light excitation was achieved with the 514.5 nm line of an Innova Ar⁺ laser (Coherent). The laser line was expanded by a Thorlabs BE 10X beam expander. Alteration of the incident light irradiance was achieved by using a combination of neutral density filters (Newport). The cell area illuminated was 2.2 cm². Photovoltage was measured with a potentiostat (BASi Epsilon-EC, Bioanalytical). Light soaking was performed to mitigate any hysteresis from the lowest to the highest irradiance.
and then back and forth until the open circuit photovoltage stabilized (< 5 mV) at each irradiance prior to data acquisition. The light soaking process typically took two cycles.

**Computational Methods.** The Gaussian 03 computational package\textsuperscript{23} was used to perform ground-state geometry optimization calculations employing Becke’s three-parameter hybrid exchange functional and the Lee–Yang–Parr nonlocal correlation functional B3LYP\textsuperscript{24-26} and LANL2DZ basis set\textsuperscript{27,28} with an effective core potential for Ru and a 6–31G* basis set was used for Se, S, C, N, O and H atoms.\textsuperscript{29} Time-dependent density functional theory (TDDFT) calculations were also performed using this methodology and the first 60 singlet excited states were calculated. Calculations by the first-principles method were used to obtain accurate excitation energies and oscillator strengths. We modeled the solvent with the polarizable continuum model (PCM) using MeCN as the solvent.\textsuperscript{30}
5.3 Results

5.3.1 Synthesis and Characterization.

A modular synthetic approach provided access to the series of tridentate cyclometalating ligands, $L_1H - L_3H$, on a relatively large scale using established procedures. Pro-ligands $P_4 - P_6$ were each synthesized upon a Kröhnke condensation of 1-(2-(3-bromophenyl)-2-oxoethyl)pyridinium iodide$^{17}$ with $P_1 - P_3$, respectively, to yield the substituted phenyl bipyridine derivatives that were further reacted with Suzuki reagents $P_7 - P_9$ to furnish $L_1H - L_3H$ in high yields. The syntheses of complexes $RuXMe$ ($X = O, S, Se$) followed a previously described protocol$^{31-34}$ involving the reaction of $Ru(L_4)Cl_3$ with $L_1H - L_3H$, respectively. The resultant chromatographically pure methyl ester versions of the complexes were acquired in yields ranging from 52-78% (Scheme 5.2). The isomer containing the substituent para to the anionic carbon was isolated in exclusivity in all cases.

The structural identities of all ligands and complexes were confirmed by a combination of NMR spectroscopy, mass spectrometry, and/or elemental analysis. The $^1H$ NMR spectra for $RuXMe$ reveal that the chalcogen heterocycle resonances ($H_g$, $H_h$, $H_o$, $H_p$) shift progressively downfield for $X = O, S, and Se$, respectively. The relative electron-donating character is attributed to lesser orbital overlap and elongation of the $X-C$ bonds with the larger chalcogen atoms resulting in heterocycles possessing more olefinic character.
Scheme 5.1 Synthesis of Ligands L1H-L3H.\textsuperscript{a}

\textsuperscript{a}Reaction conditions: a) ammonium acetate, formamide, 120 °C, 14 h; b) Pd(PPh\textsubscript{3})\textsubscript{4}, K\textsubscript{2}CO\textsubscript{3}, THF:H\textsubscript{2}O (9:1); 65 °C, 14 h.
Scheme 5.2  Synthesis of Metal Complexes \( \text{Ru-X}_{\text{Me}} \) and \( \text{Ru-X}_{\text{H}} \).\(^a\)

\[ \text{Ru} - \text{MeO}_2\text{C} - \text{CO}_2\text{Me} \quad \text{Ru} - \text{O}_2\text{C} - \text{CO}_2\text{Me} \]

\[ \text{Ru} - \text{X}_{\text{H}} \quad \text{Ru} - \text{X}_{\text{Me}} \]

\(^a\)Reaction conditions: a) MeOH/H\(_2\)O/THF (5:1:1 \(v/v/v\)), \(N\)-ethylmorpholine, 65 °C, \(N_2\), 14 h. b) DMF:NEt\(_3\):H\(_2\)O (3:1:1 \(v/v\)), reflux, 4 h.
The Ru$^{III}$/Ru$^{II}$ reduction potentials for $\text{Ru-X}_{\text{Me}}$ measured by cyclic voltammetry in MeCN (Table 5.1) indicate only a slight sensitivity to terminal substituents. The furyl rings appear to act as weakly electron-donating substituents (corroborated by the NMR data); the thiophene and selenophene units have a nominal effect on the Ru(III) reduction potentials. UV-vis absorption spectra recorded on the complexes dissolved in MeCN also reveal a lack of sensitivity to the identity of the chalcogenides (Figure 5.3). The presence of the five-membered rings benefit light absorption as evidenced by higher extinction coefficients of the major absorption bands relative to a ruthenium complex not containing the substituents. TD-DFT calculations performed on ground-state optimized structures of the respective dyes indicate four metal-to-ligand charge transfer transitions are responsible for the absorption bands in the visible region (Figure 5.3).
Table 5.1 Reduction Potentials of $\text{Ru-X (X = O, S, Se)}$ in Solution and on Mesoporous TiO$_2$.

<table>
<thead>
<tr>
<th>sample</th>
<th>$E_{1/2}$, Ru(III)/Ru(II) (V vs NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ru-X}_\text{Me}^a$</td>
<td>$\text{Ru-X}/\text{TiO}_2^b$</td>
</tr>
<tr>
<td>$\text{Ru-O}$</td>
<td>1.014</td>
</tr>
<tr>
<td>$\text{Ru-S}$</td>
<td>1.024</td>
</tr>
<tr>
<td>$\text{Ru-Se}$</td>
<td>1.027</td>
</tr>
<tr>
<td>1$^c$</td>
<td>1.028</td>
</tr>
</tbody>
</table>

$^a$Data collected using 0.1M NBu$_4$BF$_4$ MeCN solutions at 100 mV/s and referenced to a $[\text{Fc}]^+$/[Fc]$^+$ internal standard followed by conversion to NHE; $[\text{Fc}]^+$/[Fc]$^+$ = +640 mV vs NHE in MeCN. Data collected using 0.5 M LiClO$_4$ as the electrolyte in MeCN solutions. $^b$Benchmark complex: [Ru(pbpy)(L4)](NO$_3$).
Figure 5.3 Experimental UV-vis absorption spectrum overlaid with calculated transitions represented by vertical bars (only the transitions with contributions >30% are shown). Details of calculated transitions (theoretical wavelength in nm, oscillator strength, % contribution to transition): a) **Ru-O(Me)₃**: 1, HOMO → LUMO (714, 0.024, 93%); 2, HOMO → LUMO+1 (587, 0.009, 64%); 3, HOMO-1 → LUMO and HOMO → LUMO+1 (513, 0.172, 51% and 31%); 4, HOMO → LUMO+5 and HOMO-2 → LUMO+2 (416, 0.199, 46% and 30%). b) **Ru-S(Me)₃**: 1, HOMO → LUMO (890, 0.026, 94%); 2, HOMO → LUMO+1 (575, 0.019, 53%); 3, HOMO-1 → LUMO and HOMO → LUMO+1 (502, 0.179, 39% and 38%); 4, HOMO-1 → LUMO+3 and HOMO → LUMO+5 (420, 0.216, 42% and 41%). c) **Ru-Se(Me)₃**: 1, HOMO → LUMO (691, 0.026, 94%); 2, HOMO → LUMO+1 (575, 0.019, 54%); 3, HOMO-1 → LUMO and HOMO → LUMO+1 (503, 0.193, 41% and 39%); 4, HOMO → LUMO+3 and HOMO → LUMO+5 (421, 0.248, 50% and 40%).
5.3.2 Interfacial Charge Recombination in the Absence of Iodide.

The respective dyes were immobilized on TiO₂ to interrogate the electron transfer processes at the interface. Nanosecond transient absorption spectroscopy was used to quantify the interfacial electron transfer reactions from TiO₂(e⁻) to the oxidized sensitizers (Ru^{III}X/TiO₂(e⁻) → Ru^{II}X/TiO₂). Absorption difference spectra are shown in Figure 5.4 for this reaction after pulsed 532 nm laser excitation in 0.5 M LiClO₄/CH₃CN.
Figure 5.4 Absorption difference spectra measured at the indicated delay times after pulsed 532 nm excitation (laser fluence, 0.5 mJ/cm²) of (a) Ru-O/TiO₂ thin film; (b) Ru-S/TiO₂ thin film; and (c) Ru-Se/TiO₂ thin film immersed in 0.5 M LiClO₄/CH₃CN. (black squares: 45 ns; red circles: 100 ns; blue triangles: 500 ns; magenta reverse triangles: 5 μs; green diamonds: 50 μs; blue solid traces: ground state absorption spectra with y-axis on the right; orange solid curves: simulations based on the difference spectra of Ru³⁺-X/TiO₂ and Ru²⁺-X/TiO₂ by spectroelectrochemistry)
The immediate appearance of the oxidized dye spectra indicated that the electron injection to TiO$_2$ acceptor states was ultrafast ($k_{\text{inj}} > 10^8$ s$^{-1}$). Normalizable spectra at all delay times and maintenance of sharp isosbestic points at approximately 400 nm and 720 nm confirmed one charge separated state, i.e. Ru$^{\text{III}}$-X/TiO$_2$(e$^-$). Figure 5.5 shows single wavelength absorption changes that correspond to charge recombination between TiO$_2$(e$^-$) and the oxidized sensitizer. A probe wavelength of 583 nm was selected because it allowed for observation of the oxidized sensitizer without complications that arise from the shift of the ground state absorption induced by the injected TiO$_2$(e$^-$)$^35$ (Figure A5.2). The kinetics were nonexponential but were satisfactorily modeled by Kohlrausch-Williams-Watts (KWW) function$^{36,37}$, eq 1, with a common $\beta$ value of 0.16. Average rate constants ($k_{\text{cr}}$) were calculated as the first moment by using eq 2. The rate constants were within experimental error the same for all these compounds and hence are summarized as one, $k_{\text{cr}} = (2.5 \pm 0.6) \times 10^2$ s$^{-1}$.

\[ \Delta\text{Abs} = A \exp[-(kt)^{\beta}] \]  

(1)

\[ k_{\text{cr}} = \left[ \frac{1}{k\beta} \times \Gamma\left(\frac{1}{\beta}\right) \right]^{-1} \]  

(2)
Figure 5.5 Absorption changes measured after pulsed laser excitation of the sensitized film in 0.5 M LiClO$_4$/CH$_3$CN. ($\lambda_{exc}$, 532 nm; probe, 583 nm; laser fluence, 0.5 mJ/cm$^2$; ground state absorption at 532 nm, $\approx$ 0.22). Overlaid in yellow are the best fits to KWW kinetic model.
5.3.3 Sensitizer Regeneration by Iodide.

The regeneration of Ru\textsuperscript{III}-X/TiO\textsubscript{2}(e\textsuperscript{−}) by iodide was investigated with nanosecond transient absorption. A pulsed 532-nm laser was used to generate the interfacial charge separated state, Ru\textsuperscript{III}-X/TiO\textsubscript{2}(e\textsuperscript{−}), in an electrolyte solution containing specific quantities of iodide. The time required for regeneration by iodide was tracked by monitoring the spectral changes at 583 nm (Figure A5.1), where it represented only recovery of the ground state sensitizer molecules as a function of time. The sensitizer regeneration kinetics have been previous modeled by single exponential\textsuperscript{38}, biexponential\textsuperscript{6,39} or KWW\textsuperscript{40} functions, but none of them were able to satisfactorily model the data herein. Triexponential function (eq 3) was found to be adequate and an average observed regeneration rate constant ($\bar{k}_{obs}$) can be obtained by eq 4. The observed regeneration rate constants, $\bar{k}_{abs}$, were linear with respect to iodide concentration (Figure 5.6), and the linear fitting of the data indicates that the second-order rate constants ($k_{reg}$) for dye regeneration are effectively the same (Table 5.2).

$$\Delta Abs(t) = A_0 + A_1 \exp(-k_1t) + A_2 \exp(-k_2t) + A_3 \exp(-k_3t)$$  \hspace{1cm} (3)

$$\bar{k}_{obs} = \frac{A_1/k_1^3 + A_2/k_2^3 + A_3/k_3^3}{A_1/k_1^2 + A_2/k_2^2 + A_3/k_3^2}$$  \hspace{1cm} (4)
Figure 5.6 Plot of observed regeneration rate constants ($\bar{k}_{\text{obs}}$) of Ru-O/TiO$_2$ (black squares), Ru-S/TiO$_2$ (red circles), and Ru-Se/TiO$_2$ (green triangles) versus titrated iodide ($I^-$) concentrations.
Table 5.2 Second-Order Regeneration Rate Constants ($k_{\text{reg}}$) for Ru-X/TiO$_2$ by I in CH$_3$CN.

<table>
<thead>
<tr>
<th></th>
<th>Ru-O/TiO$_2$</th>
<th>Ru-S/TiO$_2$</th>
<th>Ru-Se/TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{reg}}$ ($\text{M}^{-1} \text{s}^{-1}$)</td>
<td>$4.7 \pm 0.3 \times 10^5$</td>
<td>$4.1 \pm 0.5 \times 10^5$</td>
<td>$4.7 \pm 0.2 \times 10^5$</td>
</tr>
</tbody>
</table>
5.3.4 **Interfacial Charge Recombination in the Presence of Iodide.**

The open-circuit voltages \( (V_{oc}) \) for the sensitized films were measured as a function of incident steady-state monochromatic 514.5-nm light irradiance in the presence of 0.5 M LiI and 0.05 M I\(_2\) in CH\(_3\)CN electrolyte (Figure 5.7). The \( V_{oc} \) values showed a linear response with respect to the logarithmic incident light flux described by the diode equation.\(^{41-43}\) A 59 mV increase of \( V_{oc} \) per decade increase of the incident light irradiance was also predicted if the ideality factor was one. Indeed, the solar cell that contained **Ru-Se/TiO\(_2\)** under our experimental condition showed a \( V_{oc} \) response of 59 mV/dec of logarithmic irradiance with reproducibility. Solar cells incorporating **Ru-O/TiO\(_2\)** or **Ru-S/TiO\(_2\)** showed slopes of 81 mV/dec or 75 mV/dec respectively. The slopes corresponded to ideality factors of 1.37 or 1.27.
Figure 5.7 Plot of open circuit voltage as a function of incident steady state monochromatic light ($\lambda_{\text{exc}}$, 514.5 nm) for Ru-O/TiO$_2$, Ru-S/TiO$_2$, and Ru-Se/TiO$_2$ measured in solar cells containing 0.5 M LiI and 0.05 M I$_2$ dissolved in CH$_3$CN. The inset shows the ground state absorption spectra of the three sensitizers anchored on TiO$_2$/FTO substrate for the measurement.
The strikingly low photovoltages for the selenophenyl derivative prompted us to measure any differences in the acceptor states of TiO$_2$ for the series of sensitized substrates, but none were found according to the congruent density of states for the series determined by monitoring the spectral changes of the TiO$_2$(e$^-$) as a function of applied potential (Figure A5.2-Figure A5.3). The disappearance of photo-chemically generated I$_3^-$ was monitored by transient absorption at 375 nm, Figure 5.8, where I$_3^-$ absorbed strongly ($\varepsilon \sim 19,000$ M$^{-1}$ cm$^{-1}$)$^{44}$. Triiodide was assumed to be consumed by TiO$_2$(e$^-$) by one electron reduction to form one equivalent of diiodide (I$_2^-$) and I$^-$.\textsuperscript{15,45} This recombination reaction occurred in the millisecond to second time scale with kinetics that were best modeled by KWW function (eq 1). Note that in order to increase the recombination rate, excess electrons were introduced into the TiO$_2$ thin film with a potentiostat. The negative applied potential corresponded to approximately 20-25 electrons per TiO$_2$ nanocrystallite based on spectroelectrochemical data shown in Figure A5.3. The average recombination rate constants ($\bar{k}_{cr}'$) were calculated by eq 2. The rate constants and $\beta'$ are summarized in Table 5.3. To ensure that the results were general to many TiO$_2$(e$^-$) concentrations, the recombination studies were completed at three different bias conditions (Figure A5.4).
Figure 5.8 Absorption changes measured after pulsed laser excitation of the sensitized films in 0.4 M LiI + 0.1 M LiClO₄/CH₃CN. (λ_{exc}, 532 nm; probe, 375 nm; laser fluence, 2.8 mJ/cm²; ground state absorptions at 532 nm, ≈ 0.26). The sensitized films were electrochemically biased to -240 mV vs NHE. Overlaid in yellow are the best fits to KWW kinetic model.
Table 5.3 Rate constants for charge recombination between TiO$_2$(e$^-$) and I$_3^-$ for Ru-X/TiO$_2^a$.

<table>
<thead>
<tr>
<th></th>
<th>Ru-O/TiO$_2$</th>
<th>Ru-S/TiO$_2$</th>
<th>Ru-Se/TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{k}_{cr}$ (s$^{-1}$)</td>
<td>1.94</td>
<td>2.18</td>
<td>10.8</td>
</tr>
<tr>
<td>$\beta'$</td>
<td>0.68</td>
<td>0.68</td>
<td>0.22</td>
</tr>
</tbody>
</table>

$^a$Data were fit to eq 5.1 and eq 5.2.
5.4 Discussion

The most common ruthenium-based dyes in the literature are derivatives of N3 and therefore contain a chalcogen atom in the donor portion of the molecule.\textsuperscript{3,5} It has been asserted that the most likely site of adduct formation with the electrolyte species is at or near the thiocyanato ligands.\textsuperscript{46} This claim resonates with our previous analysis of organic dyes that show faster rates of dye regeneration when sulfur atoms reside within the donor unit instead of oxygen atoms.\textsuperscript{6} Projecting these collective observations to ruthenium dyes related to N3 supports the notion that the sulfur atoms of the thiocyanato groups play a beneficial role in interacting with the electrolyte and mediating dye regeneration. However, there exists no direct spectroscopic proof for this in the literature because the direct measurement of dye-electrolyte interactions, where the heteroatoms in the donor units of ruthenium dyes are systematically modified, has not yet been demonstrated. A study that modifies the chalcogen of the thiocyanato ligand is a synthetically challenging endeavor, and perhaps more importantly, the disparities of the energies of the frontier molecular orbitals for the series would likely preclude an accurate determination of relative dye generation and charge recombination kinetics.

The three ruthenium dyes investigated in this study sidestep said challenges, as each member of the series contains nearly energetically degenerate frontier molecular orbitals despite differing in the identity of two X atoms, one of which compromises the donor portion of the molecule. It is within the donor fragment of the molecule that the HOMO resides (Figure A5.5) and thus the most likely site of adduct formation with the electrolyte. The optical properties for the three complexes are effectively superimposable and the HOMO energies are almost the same for the series, both in solution and on titania. These features therefore enable the opportunity to measure charge-transfer kinetics for a series of ruthenium dyes, with different atoms in the donor unit, where absorptivities and redox parameters are held effectively at parity.
A key structural feature enabling this particular study is the replacement of the thiocyanato ligands with a cyclometalating ligand. Because the aryl ring of this chelating anionic ligand acts as a strong donor, the HOMO is delocalized over the metal, the aryl ring, and terminal substituents attached to the aryl ring. The Ru(III) reduction potential is typically sensitive to substituents attached to the aryl ring—particularly those para to the carbanion—but the electrochemical properties of Ru-X indicate that the identity of the chalcogen in the five-membered aromatic rings does not significantly affect the electron density at the metal center. (The five-membered ring attached to the less electron-rich pyridine ring of the chelating ligand compromises the HOMO-2 level and is therefore not expected to influence the metal-based reduction potentials.) Optical profiles were also found to be the same for the Ru—X series, with the bands in the visible region arising from transitions from the metal-aryl-substituent portion of the molecule to the tridentate ligand bearing the anchoring groups. This scenario satisfies a key aspect of sensitization in that the donor unit resides away from the semiconductor surface—a feature that benefits dye regeneration—and the excited-state electron density is between the surface and the ruthenium center to enable facile electron injection.

Attachment of each of the dyes to anatase mesoporous titania leads to minor but expected changes in optical and electrochemical properties reflecting the slight differences in electron donating character of the anchoring ligand upon absorption to the surface. The ground state absorption spectra for Ru-X/TiO$_2$ recorded in MeCN had the same response to lithium cations and were not affected by changes in concentration of iodide or triiodide within experimental uncertainty (Figure A5.6-Figure A5.8). Quantitative electron injection into the sensitized thin films was observed for each member of the series at rates of $>10^8$ s$^{-1}$ and the rates of dye regeneration by the TiO$_2$(e$^-$) were found to be the same for the series. Spectroelectrochemistry also revealed that the electrochemical reduction of the titania was insensitive to the identity of the surface anchored dye molecules (Figure A5.2). These collective features set the stage for studying the interaction of
Ru\textsuperscript{III}-X/TiO\textsubscript{2} with the iodide electrolyte without needing to account for differences in light absorption and energy levels of the dye-semiconductor.

There were no observable ground state absorption changes when either iodide or triiodide was titrated into the reaction vessel containing Ru-X/TiO\textsubscript{2} (Figure A5.7-Figure A5.8). The generation of the interfacial charge-separated state, Ru\textsuperscript{III}-X/TiO\textsubscript{2}(e\textsuperscript{–}), in an electrolyte solution containing specific quantities of iodide revealed regeneration rate constants, $\tilde{k}_{obs}$, that were within experimental error the same (Figure 5.6 and Table 5.2). However, the reaction of Ru\textsuperscript{III}-X/TiO\textsubscript{2}(e\textsuperscript{–}) with triiodide to form I\textsubscript{3}– and I\textsuperscript{–} revealed a clear sensitivity to X. This reaction was found to occur with an average recombination rate constant ($\tilde{k}_{r}$) of 1.94 s\textsuperscript{–1} for Ru\textsuperscript{III}-O/TiO\textsubscript{2}(e\textsuperscript{–}) and 2.18 s\textsuperscript{–1} for Ru\textsuperscript{III}-S/TiO\textsubscript{2}(e\textsuperscript{–}), but was 10.8 s\textsuperscript{–1} for the reaction of Ru\textsuperscript{III}-Se/TiO\textsubscript{2}(e\textsuperscript{–}) with triiodide. This finding suggests that the selenium atoms play a role in mediating the interaction of I\textsubscript{3}– with the semiconductor surface, a feature that is corroborated by the distinctively lower photovoltages for Ru-Se/TiO\textsubscript{2} relative to the other members of the series.

These collective data indicate that modifying the chalcogen atom in the series of dyes does not impact the regeneration of the oxidized dye by the electrolyte. This finding is not aligned with our examination of organic dyes that showed dye regeneration was sensitive to atoms in the donor unit.\textsuperscript{6} This disparity is attributed to the different basicities of the chalcogens of Ru-X/TiO\textsubscript{2} relative to those in the organic dyes presented in Figure 5.1. Another factor to consider is that Ru-X/TiO\textsubscript{2} contains a chalcogen atom that is not attached to the aryl ring, thereby offering a second binding site not within the donor fragment of the dye that could preclude resolution of the regeneration step. Future studies will address this issue by excluding substituents attached to the pyridine ring of the chelating ligand.

The data clearly show that the chalcogen atoms do effect the interaction between the surface and the electrolyte, a finding that resonates with an earlier study by O’Regan and coworkers indicating that the higher affinity for iodine to bind to $sp^3$-hybridized chalcogen atoms leads to
faster recombination rates. While we had not anticipated that positioning the chalcogens within the donor unit would affect recombination, the molecular structures of Ru-X do allow for the chalcogen to reside close to the semiconductor surface. This proximity could therefore enhance adduct formation close to the semiconductor surface thereby enabling more facile recombination with TiO$_2$(e$^-$) and compromising the photovoltages. This finding calls attention to the need to position atoms capable of interacting with the oxidized iodide species in the electrolyte away from the surfaces.
5.5 Conclusions

The Ru—X cycloruthenated sensitizers reported here provided a means to interrogate the influence of chalcogen atoms on interfacial electron transfer events that occur following light-induced electron injection into titania. It was spectrosopically determined in titration experiments that the reaction between triiodide and TiO$_2$(e$^-$) was approximately five-fold faster in the case of Ru-Se/TiO$_2$ relative to the dyes containing furyl and thiophene substituents. This feature and the correspondingly lower measured photovoltage is ascribed to the heterocycle fostering adduct formation with oxidized iodide near the semiconductor surface. Differences in reaction rates for dye regeneration were not observed for the series despite a variance in atom identity in the donor fragment of the molecule. We conjecture that the congruency in dye regeneration rates for the series is due to the basicities of the heterocycles being too similar and/or the presence of the heterocycle not attached to the aryl ring precluding resolution of regeneration at the donor unit.
Figure A5.1 Absorption changes measured after pulsed laser excitation of the sensitized film in the presence of the indicated concentrations of LiI, (a) Ru-O/TiO$_2$, (b) Ru-S/TiO$_2$, and (c) Ru-Se/TiO$_2$. ($\lambda_{\text{exc}}$, 532 nm; probe, 583 nm; laser fluence, 0.5 mJ/cm$^2$). Overlaid in yellow are the best fits to triexponential kinetic model.
Figure A5.2  Difference absorption spectra of (a) Ru-O/TiO₂, (b) Ru-S/TiO₂, and (c) Ru-Se/TiO₂ measured at the indicated applied potentials in 0.5 M LiClO₄/CH₃CN solution.
Figure A5.3 Absorbance change measured at 900 nm as a function of applied potential.
Figure A5.4  Absorption changes measured after pulsed laser excitation of a) Ru-O/TiO$_2$, b) Ru-S/TiO$_2$, and c) Ru-Se/TiO$_2$ sensitized films in 0.4 M LiI + 0.1 M LiClO$_4$/CH$_3$CN. ($\lambda_{exc}$, 532 nm; probe, 375 nm; laser fluence, 2.8 mJ/cm$^2$; ground state absorptions at 532 nm, $\approx$ 0.26). The sensitized films were electrochemically biased to the indicated potentials vs NHE. Overlaid in yellow are the best fits to KWW kinetic model. Panel d shows the average rate constants measured at each of the three bias conditions.
Figure A5.5  DFT-calculated HOMO molecular orbitals for complexes Ru$^{II}$-X$_{Me}$ and HOMO molecular orbitals for complexes Ru$^{III}$-X$_{Me}$. 
Figure A5.6 Lithium cation effect shown by LiClO₄ titration; (a) Ru-O/TiO₂, (b) Ru-S/TiO₂, and (c) Ru-Se/TiO₂ are the ground state UV-vis absorption change. (d), (e), and (f) are the corresponding delta absorption change using the ground state absorption of the slides immersed in neat CH₃CN as the baseline.
Figure A5.7 UV-vis absorption spectra of (a) Ru-O/TiO$_2$ (b) Ru-S/TiO$_2$ (c) Ru-Se/TiO$_2$ slides in 0.5 M LiClO$_4$/CH$_3$CN with the indicated tetrabutylammonium iodide (TBAI) concentrations. All the absorption spectra have been corrected for the occurrence of triiodide absorption in the titration solutions.
Figure A5.8  UV-vis absorption spectra of (a) Ru-O/TiO₂ (b) Ru-S/TiO₂ (c) Ru-Se/TiO₂ slides in 0.3 M LiClO₄/CH₃CN with the indicated tetrabutylammonium triiodide (TBAI₃) concentrations. All the absorption spectra have been corrected for triiodide absorption in the titration solutions.
5.7 References


Chapter 6: Panchromatic Light Harvesting and Hot Electron Injection by Ru(II) Dipyrrinates on TiO$_2$ Surface

_in part a compilation of one publication._

This work was collaborative in conjunction with Guocan Li$^\dagger$, Chongyue Yi$^\dagger$, Kenneth L. Knappenberger, Jr.$^\dagger$, Gerald J. Meyer$^\ddagger$, Serge I. Gorelsky$^\S$, Michael Shatruk$^\dagger$

$^\dagger$Florida State University, Tallahassee, FL, USA

$^\ddagger$Johns Hopkins University, Baltimore, MD, USA

$^\S$University of Ottawa, Ottawa, ON, Canada.

6.1 Introduction

The growing energy demand of mankind and depletion of fossil fuels stipulate the need for environmentally friendly and sustainable energy technologies. In this vein, solar energy has been the focus of extensive research efforts for many years. In particular, dye-sensitized solar cells (DSSCs) have been explored as a promising technology to provide robust energy-conversion solutions adaptable to various rigid and flexible substrates.$^{2-5}$ The key component in the DSSC device is the dye that harvests sunlight, injects electrons into wide-band-gap semiconductor (usually TiO$_2$), and then oxidizes a redox mediator present in electrolyte solution.$^{6}$ Ru-polypyridyl complexes incorporating thiocyanate ligands, such as [Ru(H$_2$dc bpy)$_2$(NCS)$_2$] (N3; dbpy = 4,4′-
dicarboxylato-2,2′-bipyridine),\(^7\) \((\text{Bu}_4\text{N})_2[\text{Ru(Hdebp}y)_2(\text{NCS})_2]\) (N719),\(^8\) and \((\text{Bu}_4\text{N})_3[\text{Ru(Htetpy})(\text{NCS})_3]\) (N749, tetpy = \(2,2′:6′,2′′\)-terpyridyl-4,4′,4′′-tricarboxylate),\(^9\) are among the most widely used DSSC dyes due to their strong absorptivity in the visible range and favorable redox potentials that facilitate the charge injection.\(^{10}\) A number of recent studies, however, have focused on developing alternative NCS-free Ru dyes\(^{11-15}\) to address stability problems associated with the lability of the NCS\(^−\) ligands.\(^{16}\) In particular, chelating ligands such as phenylpyridine,\(^{17}\) phenyl-bipyridine\(^{18}\) and pyridine-pyrazole,\(^{19}\) have been shown to act as effective alternatives to the monodentate NCS\(^−\).

We have recently reported a detailed investigation of Ru complexes with chelating dipyrrinates and demonstrated their viability as DSSC sensitizers.\(^{20,21}\) Dipyrrins themselves are strongly absorbing molecules that are well known as precursors to porphyrins and components of widely used BODIPY complexes.\(^{22}\) Their Ru complexes exhibit two strong (and complementary) absorption bands in the visible range.\(^{23,24}\) The higher-energy band has been attributed to a combination of intramolecular ligand-to-ligand charge-transfer and dipyrrin \(\pi-\pi^*\) transitions, herein referred to as ligand-localized transitions (LLT), while the lower-energy band was assigned as metal-to-ligand charge-transfer (MLCT) transitions. Thus, one can expect that these complexes will act as panchromatic DSSC sensitizers with excellent light-harvesting properties. Increasing the molar absorptivity of the sensitizer should allow the use of thinner layers of mesoporous TiO\(_2\) or other morphologies, such as nanowires, that have inherently low surface areas. This advance, in turn, will facilitate the exploration of fast outer-sphere redox mediators, such as Co\(^{III}/\text{Co}^{II}\) and Fe\(^{III}/\text{Fe}\) (Fe = ferrocene), as alternatives to the ubiquitous I\(_3^−/\text{I}^−\) redox couple.

Thus far, the efficiency of the DSSC prepared with Ru-dipyrrinate dyes turned out to be quite low, despite their excellent absorptivity.\(^{20}\) Nevertheless, we achieved appreciable photocurrent densities, which suggest thermodynamically favorable electron injection from the excited state(s) of the dye into TiO\(_2\). Further studies are necessary to understand the fundamental
mechanism underlying the excitation and electron-injection processes in these dyes and improve their DSSC performance.

Herein we report detailed optical and electron-injection studies of Ru dipyrrinates, [Ru(bpy)$_2$(3-TDP)](PF$_6$) (1), [Ru(H$_2$dcbpy)(Hdcbpy)(3-TDP)] (2), and [Ru(H$_2$dcbpy)-(Hdcbpy)(TPADP)] (3) (bpy = 2,2′-bipyridine; 3-TDP = 3-thienyl-dipyrrinate; TPADP = triphenylamino-dipyrrinate) (Scheme 6.1). Complexes 1 and 2 bear a 3-thienyl substituent at the meso-position of dipyrrin (DP), while 3 contains a triphenylamine (TPA) substituent at the same position. Time-resolved spectroscopic studies in solution and investigation of dyes on TiO$_2$ surface, supplemented by DFT calculations, elucidate the influence of substituents on the dipyrrinate and bipyridine ligands on the light-harvesting properties and excited-state dynamics of these complexes and identify pathways to the successful implementation of Ru-dipyrrinate dyes in the DSSC.
Scheme 6.1 Molecular structures of Ru(II) dipyrrinates studied in this work.
6.2 Experimental

Physical Measurements. $^1$H NMR spectra were measured on Bruker 600 MHz spectrometer. Chemical shifts were referenced to the signals of residual protons in deuterated solvents (7.26 ppm in CDCl$_3$ and 3.31 ppm in CD$_3$OD).$^{25}$ Electrospray ionization mass spectra (ESI-MS) were acquired on a Beckman Coulter System Gold HPLC BioEssential with Binary Gradient 125S pump and a UV/Vis 166 analytical detector. Electronic absorption (UV-Vis) spectra were collected in the 250-800 nm range on a Varian Cary 50 spectrophotometer. Steady-state photoluminescence (PL) spectrum was obtained with a Spex Fluorolog fluorimeter consisting of a single excitation monochromator (1681) optically coupled to a 450 W Xe arc lamp. Detection was achieved by a double detection monochromator (1682) with a GaAs photomultiplier tube (Hamamatsu). For 77 K PL measurement, argon pre-purged solution sample was put into an NMR tube and immersed in liquid nitrogen in a cold finger. The PL response was detected at a right angle to the excitation beam.

Electrochemistry. Cyclic voltammograms (CV) were recorded on a CH Instruments 600D electrochemical analyzer at the sweep rate of 0.100 V·s$^{-1}$, with 0.100 M (Bu$_4$N)PF$_6$ electrolyte solution, Pt working electrode, and Ag$^+$(0.010 M AgNO$_3$)/Ag reference electrode. All the potentials initially were referenced to the standard Fe$^+/Fc$ couple (Fc = ferrocene). Fe$^+$ was added as an internal standard upon completion of each CV experiment. The redox potentials reported in this work have been converted to the normal hydrogen electrode (NHE), assuming that the Fe$^+/Fc$ couple has a redox potential of +0.630 V vs. NHE in acetonitrile.$^{26}$

Syntheses. All reactions were performed in an inert N$_2$ atmosphere using standard Schlenk techniques, unless noted otherwise. All reagents were purchased from Aldrich, except for pyrrole (Alfa Aesar), and they were used as received, except for pyrrole which was distilled prior to use. 5-(2-thienyl)-4,6-dipyrromethane,$^{27}$ 4,4'-bis(methoxycarbonyl)-2,2'-bipyridine (demb)$^{28}$ [(p-
cymene)RuCl$_2$)$_2$, N,N-(diphenylamino)benzaldehyde, [Ru(bpy)$_2$(3-TDP)]PF$_6$ (1), and [Ru(dcmb)$_2$(3-TDP)]PF$_6$ (2a) were prepared according to reported procedures. Anhydrous commercial solvents were additionally purified by passing through a double-stage drying/purification system (Glass Contour Inc.).

$[\text{Ru}($H$_2$dcbp)$(\text{Hdcbp})(3\text{-TDP})] \quad (2)$. A solution containing [Ru(dcmb)$_2$(3-TDP)]PF$_6$ (41 mg, 0.040 mmol), 3 mL of Et$_3$N, 3 mL of H$_2$O, and 9 mL of DMF was heated at reflux for 18 h. After cooling down to r.t., the solvent was evaporated to dryness under reduced pressure, and 30 mL of CH$_2$Cl$_2$ was added to dissolve the unreacted starting material which was removed by filtration subsequently. The obtained filter cake was washed with diethyl ether (3×10 mL) and dried under vacuum to afford 28 mg of black solid. Yield = 85%. $^1$H NMR (CD$_3$OD, 600 MHz), $\delta$, ppm: 9.02 (d, $J = 5.4$ Hz, 4H), 8.08 (d, $J = 5.9$ Hz, 2H), 7.96 (d, $J = 5.8$ Hz, 2H), 7.89 (dd, $J = 5.9$, 1.7 Hz, 2H), 7.79 (dd, $J = 5.8$, 1.7 Hz, 2H), 7.55 (dd, $J = 3.0$, 1.3 Hz, 1H), 7.51 (dd, $J = 5.0$, 3.0 Hz, 1H), 7.25 (dd, $J = 5.0$, 1.2 Hz, 1H), 6.78 (dd, $J = 4.4$, 1.3 Hz, 2H), 6.39 (t, $J = 1.5$ Hz, 2H), 6.30 (dd, $J = 4.4$, 1.5 Hz, 2H). $HR$-ESI-MS: $m/z$ = 815.05070 (calcd. for $[\text{Ru}($H$_2$dcbp)$]$(3-TDP)]$^+$: 815.04981).

Elem. analysis: calcd. for RuSO$_{12}$N$_6$C$_{37}$H$_{32}$ (1·4H$_2$O), %: C, 50.17 (49.84); H, 3.64 (3.75); N, 9.49 (9.71).

**TPA-dipyrrromethane.** Freshly distilled pyrrole (6 mL) was added to 1.00 g (3.66 mmol) of N,N-(diphenylamino)benzaldehyde in a 50-mL Schlenk flask. The solution was degassed for 15 min, and 84 μL of trifluoroacetic acid (TFA) was added. The mixture was stirred at r.t. for 2 h, and then 0.5 mL of Et$_3$N was added to quench the reaction. After addition of 30 mL of CH$_2$Cl$_2$, the mixture was washed with water (3×30 mL). The organic phase was collected and dried over anhydrous MgSO$_4$. The solvent and excess pyrrole were removed under reduced pressure, and the crude product was charged on a silica gel column (4 cm × 18 cm). Using CH$_2$Cl$_2$:hexanes (1:1, v/v) as eluent, the first colorless band was collected and evaporated to dryness under vacuum to produce 1.20 g of brownish oil. Yield = 84%. $^1$H NMR (CDCl$_3$, 600 MHz), $\delta$, ppm: 7.93 (s, 2H), 7.29-7.20
(m, 4H), 7.12-7.05 (m, 6H), 7.05-6.97 (m, 4H), 6.74-6.66 (m, 2H), 6.22-6.13 (m, 2H), 5.95 (s, 2H), 5.42 (s, 1H). $^{13}$C NMR (CDCl$_3$, 151 MHz), $\delta$, ppm: 147.89, 146.78, 136.26, 132.82, 129.37, 129.25, 124.40, 124.05, 122.93, 117.32, 108.58, 107.29, 77.16, 43.57.

[(p-cymene)Ru(TPADP)Cl]. A solution of p-chloranil (260 mg, 1.06 mmol) in 10 mL of anhydrous THF was added dropwise to a solution of TPA-dipyrromethane (400 mg, 1.03 mmol) in 10 mL of anhydrous THF. The mixture was stirred for 6 h at r.t. The solvent was removed under reduced pressure, and the crude product was added to a 100 mL Schlenk flask containing 315 mg (0.520 mmol) of [(p-cymene)$_2$RuCl$_2$]$_2$. After addition of 1 mL of Et$_3$N and 30 mL of anhydrous MeCN, the mixture was heated at reflux for 12 h. The reaction was cooled down to r.t., filtered through Celite, and the filtrate was evaporated to dryness under reduced pressure. The crude product was loaded on a silica gel column (2.5 cm × 20 cm) and washed with CH$_2$Cl$_2$:MeOH eluent (50:1, v/v). A bright-red band was collected and evaporated to dryness to afford 345 mg of red powder. Yield = 51%. $^1$H NMR (CDCl$_3$, 600 MHz), $\delta$, ppm: 8.03-7.99 (m, 2H), 7.33-7.25 (m, 6H), 7.20-7.18 (m, 4H), 7.14-7.07 (m, 4H), 6.76 (dd, 2H, $J$ = 4.3, 1.3 Hz), 6.50 (dd, 2H, $J$ = 4.3, 1.4 Hz), 5.24-5.26 (m, 4H), 2.43 (hept, 1H, $J$ = 6.9 Hz), 2.22 (s, 3H), 1.07 (d, 6H, $J$ = 7.0 Hz). $^{13}$C NMR (CDCl$_3$, 151 MHz), $\delta$, ppm:154.7, 148.4, 147.6, 146.8, 135.2, 131.7, 131.1, 129.5, 125.1, 123.5, 121.3, 118.3, 102.2, 100.4, 85.0, 84.7, 30.7, 29.7, 22.2, 18.7. HR-ESI-MS: m/z = 622.17974 (calcd. for [(p-cymene)Ru (TPADP)]$:^+$: 622.17962).

[Ru(dcmB)$_2$(TPADP)]PF$_6$ (3a). A mixture of [(p-cymene)Ru(TPADP)Cl] (190 mg, 0.29 mmol), dcmB (236 mg, 0.87 mmol), AgNO$_3$ (53 mg, 0.31 mmol), and 30 mL of anhydrous MeOH was heated at reflux for 16 h in the dark. After cooling to r.t., the reaction mixture was concentrated to ~5 mL under reduced pressure and filtered through a fine porosity frit to remove the excess of dcmB and the AgCl byproduct. To the filtrate was added a solution of NH$_4$PF$_6$ (110 mg, 0.67 mmol) in 2 mL of MeOH, and the mixture was stirred vigorously for 1 h to complete the anion exchange. The precipitated product was recovered by filtration, washed with diethyl ether (3×10 mL), and dried
under vacuum to afford 206 g of 3a as black powder. Yield = 61%. \(^1^H \text{NMR} \text{ (CDCl}_3, 600 \text{ MHz}), \delta, \text{ppm:} 8.90 \text{ (d, } 2H, J = 1.6 \text{ Hz)}, 8.88 \text{ (d, } 2H, J = 1.6 \text{ Hz)}, 8.01-7.96 \text{ (m, } 4H), 7.93-7.86 \text{ (m, } 4H), 7.33-7.28 \text{ (m, } 4H), 7.25-7.21 \text{ (m, } 2H), 7.19-7.15 \text{ (m, } 4H), 7.10-7.05 \text{ (m, } 4H), 6.81 \text{ (dd, } 2H, J = 4.4, 1.5 \text{ Hz)}, 6.30 \text{ (dd, } 2H, J = 4.4, 1.5 \text{ Hz)}, 6.26-6.24 \text{ (m, } 2H), 4.04 \text{ (s, } 6H), 4.01 \text{ (s, } 6H). \(^{13}\text{C NMR} \text{ (CDCl}_3, 151 \text{ MHz}), \delta, \text{ppm:} 164.2, 158.3, 157.5, 152.6, 152.4, 148.7, 148.3, 147.5, 137.6, 137.0, 136.2, 133.2, 132.6, 131.9, 131.7, 129.6, 126.8, 125.9, 125.2, 123.8, 123.2, 122.8, 121.1, 118.7, 77.2, 53.6. \text{HR-ESI-MS:} m/z = 1032.22912 \text{ (calcd. for } \text{[Ru(dcmb)}_2\text{ (TPADP)]}^+: 1032.22948). \text{ Elem. analysis: calcd. (found) for RuPF}_6\text{O}_8\text{N}_7\text{C}_{55}\text{H}_{45} \text{(3a} \cdot 0.5\text{H}_2\text{O)}, \%: \text{C, 55.70 (55.44); H, 3.82 (3.88); N, 8.27 (8.39).}

[Ru(bpy)}_2\text{(TPADP)}\text{(PF}_6\text{)} \text{(3b). Complex 3b was prepared in the same fashion as 3a using bpy instead of dcmb as starting material. Yield = 64%. }\(^1^H \text{NMR} \text{ (CDCl}_3, 600 \text{ MHz}), \delta, \text{ppm:} 8.33 \text{ (dd, } 4H, J = 7.9, 3.6 \text{ Hz)}, 7.89-7.85 \text{ (m, } 6H), 7.70 \text{ (d, } 2H, J = 5.4 \text{ Hz)}, 7.31-7.27 \text{ (m, } 10H), 7.17 \text{ (d, } 4H, J = 8.0 \text{ Hz)}, 7.09-7.06 \text{ (m, } 4H), 6.79 \text{ (d, } 2H, J = 4.2 \text{ Hz)}, 6.38 \text{ (s, } 2H), 6.32 \text{ (d, } 2H, J = 4.4 \text{ Hz). }^{13}\text{C NMR} \text{ (CDCl}_3, 151 \text{ MHz}), \delta, \text{ppm:} 158.1, 157.4, 151.9, 150.9, 148.9, 148.3, 147.5, 136.2, 136.1, 135.6, 131.8, 129.5, 126.9, 126.3, 125.0, 123.6, 123.4, 121.4, 118.2. \text{HR-ESI-MS:} m/z = 800.20780 \text{ (calcd. for } \text{[Ru(bpy)}_2\text{(TPADP)]}^+: 800.20757).}

[Ru(H}_2\text{dcbpy)}\text{(Hdcbpy)(TPADP)} \text{(3). This complex was prepared starting from 3a (40 mg, 0.034 mmol), in the manner similar to that described for the preparation of 2. Yield = 80% (26 mg). }\(^1^H \text{NMR} \text{ (CD}_3\text{OD, 600 \text{ MHz}), } \delta, \text{ppm:} 9.06-9.01 \text{ (m, } 4H), 8.11 \text{ (d, } 2H, J = 5.8 \text{ Hz)}, 7.98 \text{ (d, } 2H, J = 5.9 \text{ Hz)}, 7.90 \text{ (dd, } 2H, J = 5.9, 1.7 \text{ Hz)}, 7.81 \text{ (dd, } 2H, J = 5.9, 1.7 \text{ Hz)}, 7.34-7.26 \text{ (m, } 6H), 7.16-7.12 \text{ (m, } 4H), 7.11-7.03 \text{ (m, } 4H), 6.74 \text{ (dd, } 2H, J = 4.4, 1.1 \text{ Hz)}, 6.41-6.37 \text{ (m, } 2H), 6.31 \text{ (dd, } 2H, J = 4.4, 1.5 \text{ Hz). } \text{HR-ESI-MS:} m/z = 976.17041 \text{ (calcd. for } \text{[Ru(H}_2\text{dcbpy)}_2\text{(TPADP)]}^+: 976.16688). \text{ Elem. analysis: calcd. (found) for RuO}_{11}\text{N}_7\text{C}_{51}\text{H}_{41} (2\cdot3\text{H}_2\text{O)}, \%: \text{C, 59.53 (59.26); H, 4.02 (3.83); N, 9.53 (9.39).}
**Theoretical Calculations.** Density functional theory (DFT) calculations were performed with the Gaussian 09 package,\textsuperscript{31} using the B3LYP hybrid functional\textsuperscript{32,33} and the DZVP basis set\textsuperscript{34} for Ru and the TZVP basis set\textsuperscript{35} for the other elements, within spin-restricted molecular orbital (MO) model. The starting geometry for complex 1 was taken from the refined crystal structure parameters.\textsuperscript{21} Calculations for complexes 2 and 3 were performed by adding carboxylic acid functionalities (–COOH) to bpy ligands of 1, as well as the TPA substituent in the case of 3. All geometries were optimized in the ground state, without symmetry restraints, using the polarizable continuum model of solvation (PCM) with acetonitrile as a solvent to include solute-solvent interaction effects. Time-dependent (TD) DFT calculations in solution (using the same PCM model) were carried out on the optimized geometries. The UV-Vis spectra were simulated with the SWizard program, revision 4.6,\textsuperscript{36,37} using the Gaussian functions with the half-bandwidths, $\Delta_1/2$, of 3000 cm$^{-1}$. Atomic/fragment contributions to the molecular orbitals were calculated using the AOMix software.\textsuperscript{36,38}

**Solution-Phase Transient Absorption Spectroscopy.** Femtosecond time-resolved transient absorption (TA) pump-probe experiments were performed using a 1-kHz regeneratively amplified Ti:Sapphire laser system that delivered 800-μJ pulse energies centered at 800 nm. The duration of the amplified pulse was typically ~90 fs, and the pulse was characterized by frequency-resolved optical gating pulse diagnostics. The amplified laser output was frequency doubled to generate 400-nm light (200 μJ/pulse), which was attenuated and used as the excitation pump pulse. Excitation pulse energies used here ranged from 300 nJ/pulse to 1.0 μJ/pulse. A small portion (4%) of the fundamental laser output was passed through a sapphire plate to generate the continuum probe pulse that typically extended from 450 nm to 850 nm. The pump-probe time delay was controlled using a retroreflecting mirror mounted on a motorized linear translation stage (Newport). Both pulses were spatially overlapped in the sample-laser interaction region. Differential absorption of the probe was measured as a function of the time delay between the pump and probe by mechanically
chopping the pump pulse at 500 Hz. Here, the probe was spectrally dispersed on a silicon diode array to generate a wavelength-resolved differential absorption spectrum that spanned from 450 nm to 800 nm. Data were acquired for 2 s at each pump-probe delay. The instrument response time (~150 fs) was determined from the non-resonant response of the pump and probe pulses in solvent. The full dynamic range of the measurements extended from 10 ps before to 3.2 ns after time zero. Data fitting used in this work was similar to previously published methods. Temporal integration of bleach and excited state absorption peaks measured in the TA spectrum provided electronic relaxation kinetic traces. The transient data were fit with an in-house program that uses an iterative least-squares approach. The best fits were obtained using either single- or multi-exponential decay function, which accounted for relaxation time constants:

\[ S(t) = G(t) \sum A_n \exp \left( -\frac{t}{\tau_n} \right), \]

where \( G(t) \) is a Gaussian function that accounts for the instrument response, \( t \) is the pump-probe delay time, \( A_n \) is the amplitude coefficient that describes the relative contribution from the \( n \)th relaxation component to the total time-dependent signal, and \( \tau_n \) is the corresponding time constant.

**Studies of Dyes on TiO\(_2\) Surface**

**Substrate Preparation.** Mesoporous nanocrystalline TiO\(_2\) thin films were prepared as previously described. Briefly, TiO\(_2\) was prepared by acid hydrolysis of Ti(i-OPr)\(_4\) (Aldrich, 97%) using a sol-gel technique. The TiO\(_2\) was cast onto the transparent FTO (fluorine-doped tin oxide) conductive substrate (Hartford Glass 15 \( \Omega/cm^2 \)) by a doctor blade (~5 \( \mu \)m thick; Scotch tape\textsuperscript{TM} was employed as the spacer) and annealed at 450\(^\circ\)C for 30 minutes under constant oxygen flow. The films obtained were immersed in 40 mM TiCl\(_4\) aqueous solution at 70\(^\circ\)C for 30 minutes and rinsed with de-ionized water. The TiO\(_2\) thin films were sintered again under the same conditions as described above. The films as prepared were immersed in an EtOH solution of the dye (~3\( \times \)10\(^{-4}\) M)
for time periods of hours to days, then rinsed with EtOH and MeCN, and diagonally positioned in a standard 1 cm² quartz cuvette containing 0.5 M solution of LiClO₄ in MeCN. The electrolyte solutions were purged with Ar gas for at least 30 min prior to experiments.

**Spectroelectrochemistry.** Spectroelectrochemistry was carried out in a standard three-electrode cell with a TiO₂ thin-film working electrode, a Pt disk counter electrode, and an Ag/AgCl reference electrode (Bioanalytical Scientific Instruments, Inc.) in a 0.5 M solution of LiClO₄ in MeCN, at variable concentrations of tert-butylpyridine (TBP). UV-visible absorption measurements were obtained on a Varian Cary 50 spectrophotometer at room temperature. A potentiostat (BAS model CV-50W) was employed, and the applied potential was held until a steady state absorption that was invariant in time was achieved. The typical waiting time was 2 to 3 min. The Fc⁺/Fc half-wave potential was measured at room temperature before and after each experiment and used as an external standard to calibrate the reference electrode. All reported potentials have been converted to the NHE scale as described above.

**Nanosecond Transient Absorption Spectroscopy.** Nanosecond TA measurements were obtained with an apparatus similar to the one previously described. The samples were excited by a Q-switched, pulsed Nd:YAG laser (Quantel USA (BigSky) Brilliant B; 5-6 ns full width at half-maximum, 1 Hz, ~10 mm in diameter) at 532 nm (frequency doubled) or 416 nm (H₂ Raman shifter with 355 nm laser light) directed at 45° to the film surface. A Glan-Taylor polarizer was employed in the laser path to attenuate the pulse fluence. A 150 W Xenon arc lamp coupled to a 1/4 m monochromator (Spectral Energy, Corp. GM 252) served as the probe beam (Applied Photophysics) that was aligned orthogonally to the excitation light. For detection at sub-100 μs time scales the lamp was pulsed. Detection was achieved with a monochromator (Spex 1702/04) optically coupled to an R928 photomultiplier tube (Hamamatsu). Transient data were acquired on a computer-interfaced digital oscilloscope (LeCroy 9450, Dual 350 MHz) with 2.5 ns resolution terminated at 50 Ω for sub-100 μs; for longer time scales, the signal was terminated with a 10 kΩ resistor and
bandwidth limited at 80 MHz. Approximately 150-250 laser pulses were typically averaged for each single wavelength measurement to achieve satisfactory signal-to-noise ratios. Kinetic data fitting and spectral modeling were performed in Origin 8, and least-squares error minimization was accomplished using the Levenberg-Marquardt iteration method.

**Incident Photon to Current Efficiency (IPCE).** A two-electrode cell was employed with sensitized TiO$_2$/FTO as the working electrode and Pt wire as the counter electrode. The working electrode was illuminated through the backside of the FTO slide using a 150 W Xenon arc lamp (Spectra-Physics) coupled to a 1/4 m monochromator (Oriel Cornerstone). The light intensity was calibrated by a photodiode (UDT 260) at each measured wavelength. The photocurrent was measured by a Keithley 617 electrometer.
Scheme 6.2 Synthesis of complexes 1-3: (a) [(p-cymene)RuCl$_2$]$_2$, Et$_3$N, MeCN, reflux, 12 h; (b) bpy, AgNO$_3$, NH$_4$PF$_6$, MeOH, reflux, 16 h; (c) dcmb, AgNO$_3$, NH$_4$PF$_6$, MeOH, reflux, 16 h; (d) Et$_3$N:H$_2$O:DMF = 1:1:3 (v/v/v), reflux, 18 h.
6.3 Results and Discussion

6.3.1 Synthesis.

The synthetic procedures are shown in Scheme 6.2. Dipyrrromethanes were converted to the corresponding dipyrrins by oxidation with \( p \)-chloranil. Without further purification, the crude product was reacted with a dinuclear precursor \([(p\text{-cymene})\text{RuCl}_2]_2\) to form the neutral mononuclear complex \([(p\text{-cymene})\text{Ru}(R\text{-DP})\text{Cl}] (R\text{-DP} = 3\text{-TDP or TPADP})\), at which point the product purification was performed. Complexes 1, 2a, and 3a were obtained by refluxing \([(p\text{-cymene})\text{Ru}(R\text{-DP})\text{Cl}]\) with bpy or dcmb in MeOH in the presence of AgNO\(_3\). Ester derivative 2a and 3a were hydrolyzed to form 2 and 3 by refluxing with Et\(_3\)N in a H\(_2\)O-DMF solvent mixture for 18 h.

6.3.2 Electronic Structure.

To establish the electronic structure of the complexes and aid in the subsequent assignment of optical transitions and electrochemical events, we performed DFT calculations using the B3LYP hybrid functional and TZVP basis set (DZVP for Ru). The energy diagram and selected MOs of 1, 2, and 3 are shown in Figure 6.1.

In 1, the highest occupied molecular orbital (HOMO), HOMO–1, and HOMO–3 are primarily based on the Ru \( d \)-orbitals, with a small contribution from the dipyrrinato or bpy \( \pi \)-orbitals, while the HOMO–2 is purely dipyrrinato-based (see Table A6.1 in the Supporting Information). The lowest unoccupied molecular orbital (LUMO) and LUMO+1 correspond to a mixture of dipyrrinato and bpy \( \pi^* \)-orbitals, while the LUMO+2 and LUMO+3 reside mostly on bpy. The Ru contribution to these four LUMOs ranges from 0.7% for the LUMO to 5.9% for the LUMO+2, indicating a rather weak Ru-to-ligand back-donation in this complex (Table A6.1).
The addition of electron-withdrawing carboxylic substituents in 2 changes the order of frontier orbital energies by stabilizing the Ru \( d \)-orbitals and dcbpy \( \pi^* \)-orbitals. As a result, the dipyrrinato-centered \( \pi \)-orbital becomes the HOMO. The mixing between \( \pi^* \)-orbitals of dcbpy and dipyrrinate is also eliminated, giving rise to bpy-centered LUMO/LUMO+1 and dipyrrinato-centered LUMO+2. The Ru contribution to these three orbitals is 6.5\%, 5.4\%, and 1.5\%, respectively (Table A6.1). Thus, Ru-to-ligand back-donation in 2 remains weak.

In 3, the HOMO resides on the TPA moiety, while the order and nature of other frontier MOs are similar to those observed in 2, suggesting that the meso-substituent interacts only weakly with the dipyrrin unit. The latter finding is explained by the lack of co-planarity between the two aromatic fragments.\(^{21}\)
Figure 6.1 Selected frontier molecular orbitals of 1, 2, and 3. Isosurface contour values are 0.05 a.u. H atoms are omitted for clarity except for the ones on carboxylic acid groups. Color scheme: Ru = green, S = yellow, O = pink, N = blue, C = gray, H = cyan.
6.3.3 Optical Spectroscopy.

The absorption spectra of 1, 2, and 3 are similar (Figure 6.2) and exhibit three major bands around 300 nm, 450 nm, and beyond 500 nm. The latter band in the spectra of 2 and 3 is red-shifted by 24 nm relative to the analogous band in the spectrum of 1. The absorption spectra simulated from the TD-DFT calculations reproduce the main features of the experimental spectra quite well (Figure 6.3), and thus can be used for the assignment of the observed absorption bands (see Table A6.2 in Supporting Information for the complete list of assigned excitations).
Figure 6.2 Optical absorption spectra of 1 in MeCN and of 2 and 3 in MeOH at room temperature.
Figure 6.3 Experimental (solid line) and simulated (dashed line) absorption spectra of 1 (blue), 2 (red), and 3 (purple). The gray bars indicate the energy and oscillator strength of electronic excitations. The asterisk marks the excitation in the simulated spectrum that corresponds to the 400-nm absorption in the experimental spectrum (see the “Transient Absorption” section for further details).
The lower-energy absorption band in Ru(II) polypyridyl complexes can be empirically assigned as the metal-to-ligand charge transfer (MLCT) transition. Indeed, the TD-DFT calculations confirm that the lower-energy band in each complex corresponds to excitations from the Ru $d$-orbitals to the set of three (in 1) or two (in 2 and 3) ligand-centered $\pi^*$-orbitals (Figure 6.1). Since the stabilization of the bpy-centered $\pi^*$-orbitals upon addition of the carboxylic groups exceeds the stabilization of the Ru $d$-orbitals, the MLCT transitions in 2 and 3 have lower energy, hence longer wavelengths. The low-energy band in 3 also contains an admixture of an intraligand charge-transfer (ILCT) excitation from the TPA-centered HOMO to the dipyrrinate-centered LUMO+2. In the case of 2, the calculated oscillator strength for the excitation from the 3-TDP-centered HOMO to the dc bpy-centered LUMO/LUMO+1 is low, and this transition does not contribute significantly to the optical absorption spectrum.

The intermediate-energy absorption band appears at about the same energy in all three complexes, with the maximum around 460 nm, although the band in 2, and especially in 3, is broadened relative to the one observed in 1. Nevertheless, in all complexes, this band mainly arises from the ligand-to-ligand (LLT) excitations from the dipyrrinato-centered $\pi$-orbitals to bpy or dipyrrinato-centered $\pi^*$-orbitals (Table A6.2). Although the DFT calculations suggest that there is some mixing of LLT and MLCT transitions, they do support the notion that the intermediate-energy band around 460 nm is predominantly composed of LLT excitations and the low-energy band at 540 nm corresponds to MLCT excitations.

At room temperature, no measurable photoluminescence signal could be detected in solutions of all three complexes. Nevertheless, at 77 K, a significant photoluminescence was observed from a solution of 3 in EtOH:MeOH glass (4:1 v/v), with the maximum at 760 nm (Figure A6.1).

6.3.4 Electrochemistry.
The cyclic voltammogram (CV) of 1 reveals a quasi-reversible process at $E_{1/2} = 0.90$ V, attributed to the Ru$^{III/II}$ redox couple, and three quasi-reversible ligand-based redox processes at $-1.16$, $-1.45$, and $-1.77$ V (Figure 6.4). Similar to 1, only one oxidation was observed for 2 at 1.07 V, while the CV of 3 exhibited two successive quasi-reversible processes at $E_{1/2} = 1.05$ V and 1.26 V in DMF electrolyte. The reductions of 2 and 3 were not well resolved. Therefore, the electrochemical behavior of their ester derivatives, 2a and 3a, was examined. In comparison to 1, both 2a and 3a were more resistant to oxidation and more susceptible to reduction (Table 6.1). Such behavior is in accord with the electron-withdrawing nature of the ester substituents, which stabilize both Ru $d$-orbitals and bpy $\pi^*$-orbitals. Similar to 3, complex 3a exhibits two redox events at $E_{1/2} = 1.12$ V and 1.27 V in MeCN solution. To assign these oxidation processes, a CV of the ligand, TPADP, was acquired in MeCN, and one quasi-reversible oxidation at 1.26 V was observed. In addition, a model complex 3b was prepared, in which the dcbpy ligands were replaced by unsubstituted bpy ligands. In this complex, the second oxidation potential remained unchanged while the first oxidation potential was shifted to much lower value of 0.90 V (Figure A6.2). This is in agreement with the assignment of the first process to the Ru$^{III/II}$ redox couple, as the absence of the electron-withdrawing ester substituents makes the Ru center more prone to oxidation. In turn, taking into account the coincidence of the second redox potential in 3a and 3b and the aforementioned lack of electronic communication between the TPA and dipyrrinate fragments, this redox process can be assigned as the TPA-centered oxidation.
Figure 6.4 Cyclic voltammograms of 1 (black), 2a (red), and 3a (blue) recorded in 0.100 M solutions of (Bu$_4$N)PF$_6$ in MeCN, CH$_2$Cl$_2$, and MeCN, respectively.
Table 6.1  Electrochemical properties of complexes 1-3, 2a, and 3a (the potentials are referenced to NHE).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Half-wave potentials, V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E_{1/2}^{+/0}$</td>
</tr>
<tr>
<td>1</td>
<td>MeCN</td>
<td>0.90</td>
</tr>
<tr>
<td>2a</td>
<td>CH$_2$Cl$_2$</td>
<td>1.21</td>
</tr>
<tr>
<td>3a</td>
<td>MeCN</td>
<td>1.12, 1.27</td>
</tr>
<tr>
<td>3b</td>
<td>MeCN</td>
<td>0.90, 1.27</td>
</tr>
<tr>
<td>2</td>
<td>DMF</td>
<td>1.07</td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
<td>1.05, 1.26</td>
</tr>
</tbody>
</table>
The excited-state redox potential for 3 was calculated through a free-energy cycle as
\[ E_{1/2}(3^{\text{+*}}) = E_{1/2}(3^{*0}) - \Delta G_{\text{ES}} \]
where the latter term corresponds to the free energy stored in the excited state. The value \( \Delta G_{\text{ES}} = 1.72 \text{ eV} \) was abstracted from an intersection of the tangent line drawn on the high-energy side of the 77-K photoluminescence spectrum with the horizontal wavelength axis (Figure A6.1). Using this value and the electrochemical data for 3, the value of \( E_{1/2}(3^{\text{+*}}) \) was calculated to be –0.67 V vs. NHE. Despite our inability to detect photoluminescence from 2, we anticipate that it has a similar excited-state redox potential based on the similarity of electrochemical and optical properties of 2 and 3.

### 6.3.5 Solution-Phase Transient Absorption Spectroscopy.

To study the excited-state dynamics, we carried out ultrafast pump-probe experiments on 1, 2a, and 3a in MeCN solutions. The experiments were conducted by exciting sample solution using a 400-nm laser pulse and probing the time-dependent response using a broad bandwidth continuum pulse. Generally, the differential transient absorption spectra of the samples exhibited two major bleach components, one below and the other above 500 nm.

In the case of 1, excitation by 400-nm light generated ground-state bleaches at 470 nm and 520 nm (Figure 6.5a), which corresponded to the ground-state linear absorption bands observed at 462 nm and 516 nm, respectively. The recovery of the transient bleach signal at 520 nm was best fit using a single-exponential rate law, which yielded a time constant of 4.5 ns. The bleach recovery kinetics of the signal at 470 nm were non-exponential, and required the inclusion of a faster (25 ps) component (Figure 6.5c). The major recovery channel for the 470-nm bleach was characterized by a time constant of 4(1) ns. The pre-exponential constants of 0.03 and 0.97, respectively, indicate that the slower process made the most significant contribution to the total amplitude of the time-resolved TA signal. In addition, a positive transient signal was observed at 650 nm, indicating excited-state absorption. Placing the results of TA experiments in the context of electronic structure
calculations, one can establish that the 400-nm pump resulted in a HOMO–3 → LUMO+3 excitation (Table A6.2) to the bpy-based π*-orbital (Figure 6.1). This excited state, most likely, undergoes internal conversion to the next bpy-based π*-orbital, LUMO+2, followed by vibrational relaxation that delocalizes the electron density over all three ligands in nearly degenerate LUMO and LUMO+1. We attribute the 25-ps component in the transient signal to this vibrational relaxation.

Excitation of complexes 2a and 3a using 400-nm light also resulted in bleaches at 450 nm and 550 nm (Figure 6.5b), corresponding to the LLT and MLCT absorption bands at 460 nm and 540 nm, respectively. Time-resolved TA measurements, however, revealed significant differences for complexes 2a and 3a as compared to 1. In the case of 3a, the transient signal monitored at 540 nm exhibited an initial growth with a time constant τ = 2(1) ps, while the signal monitored at 460 nm exhibited an initial recovery at τ = 9(3) ps (Figure 6.5d). A similar initial growth of the 540-nm signal (τ = 6(2) ps) was observed in the TA spectrum of 2a. (Unfortunately, we could not follow the evolution of the signal around 460 nm in 2a, due to a low signal-to-noise ratio, and therefore only complex 3a will be discussed below.) Both 460-nm and 540-nm transient signals observed for 3a also showed a longer decay component with a characteristic lifetime of ~13 ns that were within experimental error the same at these observation wavelengths. These states were also independently measured for 3 by nanosecond absorption spectroscopy with a lifetime of 13 ns at –30°C in ethanol (Figure A6.3).
Figure 6.5  Transient absorption spectra (a, b) and kinetic traces monitored at two different wavelengths (c, d) for MeCN solutions of 1 (a, c) and 3a (b, d), under 400 nm pulsed laser excitation. Overlaid in red on the experimental data are the best fits to the function described by equation 6.1.
The differences in the excited-state dynamics of 3a and 1 can be rationalized by considering the results of electronic structure calculations and assignments of absorption bands in the spectra of these complexes. In contrast to 1, the LUMO and LUMO+1 in 3a are localized $\pi^*$-orbitals of dcmb and do not exhibit any DP-based character. The 400-nm laser pulse results in promotion of electrons to the dcmb-centered LUMO and LUMO+1 in 3a, which leads to bleaching of both LLT and MLCT bands. In other words, the bleaches observed at 460 nm and 540 nm correspond to transitions from the (dcmb/dcmb)-Ru$^{\text{II}}$-DP-TPA ground state to (dcmb/dcmb$^*$)-Ru$^{\text{II}}$-DP$^*$-TPA (LLT) and (dcmb/dcmb$^*$)-Ru$^{\text{II}}$-DP-TPA (MLCT) excited states, respectively (Scheme 6.3). Importantly, the 540-nm band in 3a also includes a large contribution from the (dcmb/dcmb$^*$)-Ru$^{\text{II}}$-DP-TPA$^+$ charge-separated LLT (CS-LLT) state (Table A6.2). Considering these excited states, we attribute the initial growth of the 540-nm bleach to the vibrational relaxation process, which decreases the contributions from the Ru→dcmb (MLCT) and TPA→dcmb (CS-LLT) transitions with the concomitant increase in the LLT-type DP→dcmb and DP→DP transitions. Hence, a growth of the 540-nm bleach at the expense of the 460-nm bleach is observed, suggesting energy redistribution from the excitation manifold generated by the LLT absorption to the excited states generated by the MLCT/CS-LLT absorption.
Scheme 6.3 An energy level diagram illustrating excited state dynamics of 3a.
6.3.6 Behavior on TiO$_2$ Surface.

Recently, we have reported the first use of Ru dipyrrinates as DSSC sensitizers.\textsuperscript{20} We observed that substantial current densities ($J_{sc} > 10$ mA cm$^{-2}$) could be achieved, but only if the electrolyte contained a large ($\sim$1 M) concentration of Li$^+$ ions. Nevertheless, the open-circuit voltage remained low ($V_{oc} \sim 0.30$ V). Addition of \textit{t}-butylpyridine (TBP), which is a common DSSC electrolyte additive for improving $V_{oc}$, not only failed to produce the desired change in $V_{oc}$, but also led to a dramatic decrease in $J_{sc}$. To understand the origins of such behavior, in the current work we investigated the electron-injection behavior of complexes 2 and 3 deposited on the TiO$_2$ surface.

Dyes 2 and 3 were found to bind strongly to mesoporous nanocrystalline TiO$_2$ thin films. A surface coverage of $\sim$1$\times$$10^{-7}$ mol cm$^{-2}$ was obtained after keeping the films for 24 hours in a $\sim$3$\times$$10^{-4}$ M solution of the dye in EtOH. The films were subsequently immersed into MeCN, and their ground-state absorption spectra were found to be similar to those recorded for free complexes 2 and 3 in solution, although some broadening of the absorption bands was observed. The addition of 0.5 M LiClO$_4$ causes a bathochromic shift of the MLCT band as compared to the spectra recorded on the films immersed in neat MeCN (Figure A6.4). In contrast, the addition of TBP resulted in a hypsochromic shift of the MLCT band that offset the bathochromic shift induced by the LiClO$_4$ solution (Figure 6.6). The hypsochromic shift increased from 170 cm$^{-1}$ to 300 cm$^{-1}$ when the TBP concentration was increased from 0.1 M to 0.5 M. The addition of TBP, however, did not induce a measureable shift of the ligand-based absorption band at intermediate energies, but did slightly increase the absorptivity of this band.
Figure 6.6 Ground-state optical absorption spectra of 2 (a) and 3 (b) on TiO$_2$ surface immersed in a 0.5 M MeCN solution of LiClO$_4$ at variable TBP concentrations.
The incident photon-to-current efficiency (IPCE) measurements were performed for $2/TiO_2$ and $3/TiO_2$ under variable excitation wavelengths, with the dye-covered thin films immersed in 0.5 M LiI/0.05 M I$_2$ acetonitrile solution as electrolyte. The IPCE spectra exhibit two maxima that corresponded to the intermediate-energy LLT band and lower-energy MLCT band (Figure 6.7), with the maximum observable IPCE values of ~40% for $2$ and ~50% for $3$. The addition of 0.1 M and 0.5 M TBP led to a dramatic decrease in IPCE by more than 50% and 70%, respectively (Table 6.2).

Shown in Figure 6.7 are the absorptance spectra of $2/TiO_2$ and $3/TiO_2$ that represent the fraction of incident light absorbed by the sensitized thin films used in these experiments. The fine structure in the absorptance spectra at long wavelengths was attributed to the interference by the thin film. The absorptance at wavelengths below 600 nm was essentially 1 for both sensitizers, indicating quantitative light-harvesting. Therefore, if the injection and the collection yields were quantitative, the photocurrent action spectra would be structureless over this wavelength range and would only be attenuated by reflection losses and the weak absorption of the FTO substrate and the electrolyte. If quantitative injection occurred from the Franck-Condon excited state, the action spectra would also be structureless. Nevertheless, well-defined bands were observed (Figure 6.7), the energies of which coincide with the absorption maxima of the dyes on the TiO$_2$ film (Figure 6.6). Interestingly, the 470 nm absorption band was less sensitive to the presence of TBP than was the lower energy MLCT band. For example, in the case of $3/TiO_2$, the addition of 0.5 M TBP decreased the photocurrent measured at 470 nm by 70% while that at 550 nm was decreased by 77% (Table 6.2).
Figure 6.7 The incident photon-to-current efficiency of 2 (a) and 3 (b) in dye sensitized solar cells with 0.5 M LiI/0.05 M I$_2$ acetonitrile and the 0 M (black), 0.1 M (red), and 0.5 M (blue) TBP. Also shown in olive green is the absorptance spectrum of the sensitized thin film.
Table 6.2 IPCE and comparative actinometry of dyes 2 and 3 on TiO$_2$ surface.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Concentration</th>
<th>IPCE$^a$</th>
<th>Electron injection yield$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>of TBP</td>
<td>470 nm</td>
</tr>
<tr>
<td></td>
<td>0 M</td>
<td>0.44 (1)</td>
<td>0.38 (1)</td>
</tr>
<tr>
<td>2</td>
<td>0.1 M</td>
<td>0.17 (0.39)</td>
<td>0.11 (0.29)</td>
</tr>
<tr>
<td></td>
<td>0.5 M</td>
<td>0.10 (0.23)</td>
<td>0.07 (0.18)</td>
</tr>
<tr>
<td></td>
<td>0 M</td>
<td>0.54 (1)</td>
<td>0.48 (1)</td>
</tr>
<tr>
<td>3</td>
<td>0.1 M</td>
<td>0.26 (0.48)</td>
<td>0.18 (0.38)</td>
</tr>
<tr>
<td></td>
<td>0.5 M</td>
<td>0.16 (0.30)</td>
<td>0.11 (0.23)</td>
</tr>
</tbody>
</table>

$^a$ The values were measured as the maxima of the IPCE curves that appear at 470 nm and 550 nm. Shown in parentheses is the ratio of the specific IPCE value to the value measured in the absence of TBP.

$^b$ The wavelengths correspond to the pulsed laser excitations.
To gain further insight into the effect of TBP additive on the photocurrent action, comparative actinometry measurements of \(2/\text{TiO}_2\) and \(3/\text{TiO}_2\) were performed in the absence of LiI/I\(_2\) redox mediator. The transient actinometry measurements were performed with a 542 nm observation wavelength that corresponds to an isosbestic point in the presence and absence of TBP (Figure 6.6) and a 65 ns delay time to exclude possible excited state contributions (Figure A6.3 and S4). Dyes 2 and 3 thus served as actinometers, and their relative injection yields were taken to be 1 in the absence of TBP. The addition of TBP was found to decrease the injection yield under both 416 nm and 532 nm excitations (Figure 6.8 and Table 6.2). The decreased injection yields are correlated with the appearance of a fast component that is due to the excited state, Figure 6.8. Importantly, the injection yield achieved with 416 nm excitation was higher than that measured with 532 nm excitation at both TBP concentrations. Similar to the photocurrent action spectra, TBP had a more significant influence on the injection yields when 532 nm excitation was utilized relative to 416 nm. For example, with \(3/\text{TiO}_2\) the addition of 0.5 M TBP decreased the injection yield by 72% with 532 nm excitation and by only 67% with 416 nm excitation (Table 6.2).
Figure 6.8 Absorption changes monitored at 542 nm for 2 and 3 anchored to TiO2 surface after pulsed-laser excitations with 532 nm (a and b) and 416 nm (c and d) light. Overlaid on this data are the best fits to the KWW function. The inset displays the first 0.5 microseconds of data, with dashed lines showing the amplitudes assigned to charge-separated states, which were used to measure the relative injection yield.
Kinetics of the absorption signal at 542 nm were non-exponential at all TBP concentrations but could be well fitted to the Kahlraush-William-Watts (KWW) function (Equation 2):

\[ \Delta Abs = A \exp[-(kt)^\beta]. \]  

(2)

The best fits (yellow curves in Figure 6.8) were obtained with the value of \( \beta \) between 0.08 and 0.35. Higher \( \beta \) values were abstracted from data obtained when TBP was present in the solution.

To rationalize the changes in the IPCE and injection yield, spectroelectrochemistry was utilized to investigate the net effect of TBP on the reduction of TiO\(_2\) in the absence of the dye. Application of a negative external bias to a mesoporous nanocrystalline TiO\(_2\) thin film immersed in a 0.5 M LiClO\(_4\)/MeCN solution in a standard three-electrode configuration resulted in the well-known absorption spectrum that has been attributed to reduction of TiO\(_2\) acceptor states, abbreviated TiO\(_2\)(e\(^-\)) herein.\(^{42,43}\) The characteristic featureless absorption spectrum was observed across the entire visible to near-IR region (Figure A6.5) and its magnitude at 800 nm was monitored as a function of the applied potential (Figure 6.9a). The presence of 0.1 M TBP shifted the absorption onset to more negative potentials by approximately 0.2 V, while 0.5 M TBP induced an additional 0.05 V shift. These absorption data were converted to chemical capacitance as was previously described.\(^{44}\) Superimposing the excited-state reduction potential of 3 on the capacitance data clearly shows that the excited state overlap with the TiO\(_2\) acceptor states decreases as TBP concentration increases. As indicated by the dotted line in Figure 6.9b, the capacitance decreased by a factor of 2 upon addition of TBP. This drop in capacitance of TiO\(_2\) explains the decrease in the IPCE and injection yield observed in the presence of TBP (Table 6.2).\(^{45,46}\)
Figure 6.9 (a) Absorption of dye-free TiO$_2$ thin-film electrode measured at 800 nm as a function of applied potential (vs. NHE) at variable concentrations of TBP. (b) The data from (a) recast as chemical capacitance. Superimposed on these data are the ground- and excited-state redox potentials of dye 3.
The IPCE and comparative actinometry clearly demonstrate the decrease in the electron injection yield upon addition of TBP (Figure 6.7 and Figure 6.8). Notably, both measurements indicate that the suppression of electron injection into TiO$_2$ is consistently larger for the 532 nm excitation than for the 416 nm excitation at the same TBP concentration (Table 6.2). These observations suggest more efficient excited state injection from the 460-nm absorption, which could be explained by electron injection from the upper excited states. This so-called hot injection was also previously demonstrated for some other dyes. Nevertheless, it must be noted that vibrational relaxation, which is described by a time constant of 2 ps in solution of 3, can kinetically compete with the hot electron-injection process. The overall consequence is that the electron injection yield decreases at all excitation wavelengths upon TBP addition, but less so for the higher-energy excitations. The acceptor states shift in energy towards the vacuum level upon the addition of TBP (Figure 6.9b). This results in a smaller overlap of the excited state with the TiO$_2$ acceptor levels that in turn decreases the electron injection yield.
6.4 Conclusions

The electrochemical and photophysical characteristics of Ru dipyrrinates 2 and 3 render them viable candidates for DSSC sensitization. The TD-DFT calculations indicate the preferential localization of the excited electron of the anchoring H$_2$dcbpy ligands, which results in a favorable scenario for photoinduced electron injection into TiO$_2$. Nevertheless, as was demonstrated in our earlier contribution, the performance of Ru dipyrrinates as DSSC sensitizers is subpar to their excellent light-harvesting properties. The studies of the excited-state and electron-transfer dynamics reveal that these excited states are weak photoreductants that do not transfer electrons to TiO$_2$ efficiently under many experimental conditions. This was particularly evident when tert-butyl pyridine (TBP) was present and the injection yields measured spectroscopically or inferred from photocurrent action spectra decreased markedly. Importantly, the injection yields with ligand-localized excitation were less sensitive to the TBP concentration than the yields obtained with the lower energy MLCT excitation. This suggests that dyes 2 and 3 are capable of hot injection from upper ligand-localized excited states.

The most obvious target for improving the performance of Ru(II) dipyrrinates as DSSC dyes is to make them stronger photoreductants. This goal can be achieved by introducing electron-donating substituents into the pyrrolic rings of the dipyrrinate ligand or by substituting one of the anchoring H$_2$dcbpy ligand with a bpy that contains electron-donating groups. We are currently exploring both of these approaches, and the properties and DSSC performance of the modified Ru dipyrrinate dyes will be reported in due course.
### 6.5 Appendix

Table A6.1 Energies\textsuperscript{a} and compositions\textsuperscript{b} of selected frontier MOs of 1, 2, and 3.

<table>
<thead>
<tr>
<th>Molecular orbitals</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Energy (eV)</td>
<td>Ru</td>
<td>3-TDP</td>
</tr>
<tr>
<td>LUMO+3</td>
<td>2.75</td>
<td>1.1</td>
<td>2.0</td>
</tr>
<tr>
<td>LUMO+2</td>
<td>2.03</td>
<td>5.9</td>
<td>0.2</td>
</tr>
<tr>
<td>LUMO+1</td>
<td>1.99</td>
<td>3.5</td>
<td>66.1</td>
</tr>
<tr>
<td>LUMO</td>
<td>1.98</td>
<td>0.7</td>
<td>30.4</td>
</tr>
<tr>
<td>HOMO</td>
<td>–1.13</td>
<td>72.6</td>
<td>19.1</td>
</tr>
<tr>
<td>HOMO–1</td>
<td>–1.19</td>
<td>68.1</td>
<td>22.7</td>
</tr>
<tr>
<td>HOMO–2</td>
<td>–1.25</td>
<td>0.7</td>
<td>98.9</td>
</tr>
<tr>
<td>HOMO–3</td>
<td>–1.43</td>
<td>78.4</td>
<td>5.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All energies have been converted to the NHE scale assuming that the NHE potential is –4.5 V vs. vacuum level. \textsuperscript{b} The percent contribution of the constituent moieties to each molecular orbital is shown.
Table A6.2 Assignment of electronic transitions for 1, 2, and 3 from TD-DFT calculations in solvent.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>$f^b$</th>
<th>Assignment</th>
<th>Wavelength (nm)</th>
<th>$f^b$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>523</td>
<td>0.016</td>
<td>HOMO-1→LUMO+2 (89%)</td>
<td>591</td>
<td>0.031</td>
<td>HOMO-2→LUMO+1 (87%)</td>
</tr>
<tr>
<td>515</td>
<td>0.012</td>
<td>HOMO-1→LUMO (84%)</td>
<td>514</td>
<td>0.137</td>
<td>HOMO-3→LUMO (88%)</td>
</tr>
<tr>
<td>497</td>
<td>0.068</td>
<td>HOMO-1→LUMO+1 (76%)</td>
<td>486</td>
<td>0.061</td>
<td>HOMO-3→LUMO+1 (64%)</td>
</tr>
<tr>
<td>476</td>
<td>0.022</td>
<td>HOMO-3→LUMO+1 (92%)</td>
<td>459</td>
<td>0.046</td>
<td>HOMO-2→LUMO+2 (77%)</td>
</tr>
<tr>
<td>468</td>
<td>0.070</td>
<td>HOMO-3→LUMO (91%)</td>
<td>447</td>
<td>0.035</td>
<td>HOMO-1→LUMO+3 (68%)</td>
</tr>
<tr>
<td>441</td>
<td>0.018</td>
<td>HOMO-3→LUMO+2 (76%)</td>
<td>437</td>
<td>0.126</td>
<td>HOMO-2→LUMO+4 (81%)</td>
</tr>
<tr>
<td>405</td>
<td>0.389</td>
<td>HOMO-2→LUMO+1 (63%)</td>
<td>427</td>
<td>0.029</td>
<td>HOMO-3→LUMO+2 (86%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-2→LUMO (30%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>395</td>
<td>0.014</td>
<td>HOMO→LUMO+3 (97%)</td>
<td>419</td>
<td>0.099</td>
<td>HOMO→LUMO+2 (45%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>361</td>
<td>0.012</td>
<td>HOMO-3→LUMO+3 (77%)</td>
<td>412</td>
<td>0.025</td>
<td>HOMO-1→LUMO+5 (93%)</td>
</tr>
<tr>
<td>357</td>
<td>0.014</td>
<td>HOMO→LUMO+6 (62%)</td>
<td>401</td>
<td>0.029</td>
<td>HOMO-2→LUMO+5 (73%)</td>
</tr>
<tr>
<td>355</td>
<td>0.031</td>
<td>HOMO-2→LUMO+3 (87%)</td>
<td>394</td>
<td>0.023</td>
<td>HOMO-3→LUMO+3 (87%)</td>
</tr>
<tr>
<td>351</td>
<td>0.091</td>
<td>HOMO-1→LUMO+5 (33%)</td>
<td>390</td>
<td>0.298</td>
<td>HOMO→LUMO+5 (46%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO→LUMO+6 (29%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>348</td>
<td>0.054</td>
<td>HOMO-4→LUMO+1 (59%)</td>
<td>386</td>
<td>0.030</td>
<td>HOMO-2→LUMO+6 (89%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-4→LUMO (28%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>385</td>
<td>0.057</td>
<td>HOMO-3→LUMO+4 (49%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>355</td>
<td>0.062</td>
<td>HOMO-4→LUMO+2 (50%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>348</td>
<td>0.054</td>
<td>HOMO-4→LUMO+1 (59%)</td>
<td>386</td>
<td>0.030</td>
<td>HOMO-2→LUMO+6 (89%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-4→LUMO (28%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>385</td>
<td>0.057</td>
<td>HOMO-3→LUMO+4 (49%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>355</td>
<td>0.062</td>
<td>HOMO-4→LUMO+2 (50%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wavelength (nm)</td>
<td>$f^b$</td>
<td>Assignment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>---------</td>
<td>-----------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>590</td>
<td>0.029</td>
<td>HOMO-3→LUMO+1 (82%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>516</td>
<td>0.111</td>
<td>HOMO→LUMO+2 (97%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>513</td>
<td>0.137</td>
<td>HOMO-4→LUMO (88%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>485</td>
<td>0.049</td>
<td>HOMO-4→LUMO+1 (64%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>456</td>
<td>0.057</td>
<td>HOMO-3→LUMO+2 (74%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>449</td>
<td>0.036</td>
<td>HOMO-2→LUMO+3 (64%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>439</td>
<td>0.123</td>
<td>HOMO-3→LUMO+4 (81%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>424</td>
<td>0.042</td>
<td>HOMO-4→LUMO+2 (75%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>419</td>
<td>0.056</td>
<td>HOMO-1→LUMO+5 (38%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-1→LUMO+2 (33%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-4→LUMO+2 (21%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>403</td>
<td>0.033</td>
<td>HOMO-3→LUMO+5 (71%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-4→LUMO+4 (25%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>389</td>
<td>0.144</td>
<td>HOMO-3→LUMO+6 (59%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-1→LUMO+5 (20%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>387</td>
<td>0.202</td>
<td>HOMO-3→LUMO+6 (39%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-1→LUMO+5 (28%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-1→LUMO+2 (22%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>386</td>
<td>0.059</td>
<td>HOMO-4→LUMO+4 (50%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>351</td>
<td>0.044</td>
<td>HOMO-7→LUMO (35%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-6→LUMO (29%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>342</td>
<td>0.010</td>
<td>HOMO-6→LUMO+1 (33%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-7→LUMO+1 (32%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>337</td>
<td>0.031</td>
<td>HOMO-9→LUMO+1 (74%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-8→LUMO+1 (15%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>0.040</td>
<td>HOMO-9→LUMO (58%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HOMO-8→LUMO (11%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>332</td>
<td>0.021</td>
<td>HOMO→LUMO+7 (96%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Transitions in the visible and near-UV region (10,000–30,000 cm$^{-1}$). Excitation contributions greater than $10\%$ are shown, smaller contributions are omitted.

$^b$ $f$ = oscillator strength.
Figure A6.1 Photoluminescence spectrum of 3 in EtOH/MeOH (4:1 v/v) solution at 77 K.
Figure A6.2 Cyclic voltammogram of $\text{3b}$ recorded in 0.100 M solutions of (Bu$_4$N)PF$_6$ in MeCN.

$\text{[Ru(bpy)_2(TPADP)](PF_6)} (\text{3b})$
Figure A6.3  Difference absorption spectrum of 3 dissolved in neat EtOH under –30°C at the indicated delay time after 532 nm laser excitation. (Absorbance of 3 at 532 nm is 0.1). Inset: the absorbance change monitored at 460 nm.
Figure A6.4  Ground-state absorption spectra of 2 (a) and 3 (b) on TiO$_2$ surface immersed in neat MeCN (green curve) or in a 0.5 M solution of LiClO$_4$ in MeCN (black curve).
Figure A6.5  Absorbance of a TiO$_2$ thin film at the indicated applied potentials (vs. NHE) in 0.5 M LiClO$_4$/MeCN.
6.6 References


Han, L. Langmuir 2011, 27, 14522.


2000, 104, 4256.

Curriculum Vitae

Ke Hu
Born February 10, 1988 in Shanghai, China

Education

<table>
<thead>
<tr>
<th>Institution</th>
<th>Degree</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Johns Hopkins University, Baltimore, MD</td>
<td>Ph.D. in Chemistry</td>
<td>August 2014 (Expected)</td>
</tr>
<tr>
<td>Johns Hopkins University, Baltimore, MD</td>
<td>M.A. in Chemistry (GPA: 4.00/4.00)</td>
<td>April 2012</td>
</tr>
<tr>
<td>Fudan University, Shanghai, China</td>
<td>B.S. in Chemistry (GPA: 3.71/4.00)</td>
<td>June 2010</td>
</tr>
</tbody>
</table>

Professional Experience

Research

- Graduate Research Assistant (Advisor: Professor Gerald J. Meyer), Department of Chemistry, Johns Hopkins University, Baltimore, MD (September, 2010 – present)
  - Electrochemical and photophysical characterizations of electron transfer reactions of a series of ruthenium–triarylamine bichromic compounds at the TiO$_2$ interfaces
  - Method development and computational simulation (Monte Carlo) for characterizing cross-surface intermolecular electron transfer reactions
  - Kinetic characterization of iodide oxidation and triiodide reduction reactions at sensitized TiO$_2$ interfaces in dye-sensitized solar cells
  - Iodide oxidation using ligand-to-metal charge transfer excited states for metal iodide inorganic compounds in solution and in solid state

- Undergraduate Research Assistant (Advisor: Professor Tao Yi), Department of Chemistry & Laboratory of Advanced Materials, Fudan University, Shanghai, China (January, 2010 – June, 2010)
  - Synthetic exploration of functionalized diarylethene light switch as tumor sensor based on targeted G-quadruplex

- Undergraduate Research Assistant (Advisor: Professor Zhengwen Fu), Department of Chemistry & Laser Chemistry Institute, Fudan University, Shanghai, China (January,
Pulsed laser deposition method for fabrication of electroactive thin films and their electrochemical measurements in the application of thin film lithium-ion batteries

Teaching
- Teaching Assistant, Department of Chemistry, Johns Hopkins University, Baltimore, MD (2010 – 2012)
  - Introductory Chemistry I (Fall 2010, Fall 2011) and II (Spring 2011)
  - Physical Chemistry Lab II (Spring 2012)

Publications


Professional Presentations
1) Molecular Control of Photoinduced Hole Transfer Processes at Sensitized TiO$_2$ Interfaces. 
_The 246$^{th}$ ACS National Meeting, Indianapolis, IN_, September 8 – 12, 2013 (oral presentation)

2) Influence of two atoms change of the molecular sensitizers on dye regeneration in dye-sensitized solar cells. _The 246$^{th}$ ACS National Meeting, Indianapolis, IN_, September 8 – 12, 2013 (poster presentation)

3) Molecular Control of Photoinduced Hole Transfer Processes at Sensitized TiO$_2$ Interface. 
_Gordon Research Conference, Photochemistry, Stonehill College, Easton, MA_, July 14 – 19, 2013 (poster presentation)

4) Molecular Control of Photoinduced Charge Separation at Sensitized TiO$_2$ Interface. _Gordon Research Conference, Electron Donor–Acceptor Interactions, Salve Regina University, Newport, RI_, August 5 – 10, 2012 (poster presentation)


6) Synthetic Exploration of Diarylethene as Tumor Sensor Based on Targeted G-quadruplex. _B.S. Thesis Defense Seminar, Fudan University, Shanghai, China_, June 24, 2010 (oral presentation)

7) Integration of Radio Frequency Non-Contact Charging to Thin Film Batteries, _11$^{th}$ National Undergraduate Curricular Academic Science and Technology Works Contest, Beijing University of Aeronautics & Astronautics, Beijing, China_, October 26 – 31, 2009 (poster presentation)

**Honors & Awards**

- Gordon Research Conference – Photochemistry Best Poster Award (July, 2013)
- The 246$^{th}$ ACS National Meeting Division of Inorganic Chemistry Student Travel Award (September, 2013)
- Harry and Cleio Greer Fellowship – awarded to a senior graduate student for his/her excellent academic performance in chemistry, _Johns Hopkins University_ (June, 2013 – May, 2014)
- The 11$^{th}$ National Undergraduate Curricular Academic Science and Technology Works Contest, _Beijing University of Aeronautics & Astronautics, Beijing_ – 2$^{nd}$ Prize (October, 2009)
- China National Scholarship, _Fudan University_ – top award to the top 2% undergraduate
students in their departments for their excellent curricular and academic performances (2008 – 2009)

- Dow Chemical Scholarship, *Fudan University* – awarded to undergraduate students for their excellent curricular and academic performances in chemical sciences (2007 – 2008)
- China National Petroleum Tarim Oilfield Scholarship, *Fudan University* – awarded to undergraduate students for his/her excellent curricular and academic performances in chemical sciences (2006 – 2007)

**Laboratory Skills**

- Thin Film Fabrication: doctor-blading, spin-coating, pulsed laser deposition
- Electrochemistry: cyclic voltammetry, differential pulse voltammetry, spectroelectrochemistry
- Photoelectrochemistry: IPCE, I-V measurements
- Spectroscopy: UV-vis, fluorescence, nano-second transient absorption, FT-IR, NMR
- Materials Characterization: powder XRD, SEM, TEM
- Computer Simulation: Monte Carlo
- Scientific Software: Origin, Mathematica

**Professional Membership**

- American Chemical Society member (December, 2012 – present)

**Public Service**

- Volunteer of the 41st World Expo, Shanghai, China (April, 2010 – May, 2010)
- Volunteer of the 12th Special Olympics World Summer Games, Shanghai, China (October, 2007)