# ULTRAFAST DYNAMICS OF IRON(II)-BASED COMPLEXES IN SOLUTION AND SEMICONDUCTOR-CHROMOPHORE ASSEMBLIES

By

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#### ABSTRACT

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The desire to capitalize on the photochemical and photophysical properties of transition metal complexes is the driving force for a number of applications, such as solar energy conversion and photocatalysis. Work in these areas traditionally employ ruthenium-based chromophores that are successful due to the presence of long-lived metal-to-ligand charge transfer (MLCT) states. Unfortunately, ruthenium is a rare metal, prompting the search for a suitable replacement that is earth abundant. Iron represents one such option that also happens to be isoelectronic with ruthenium. However, as a first-row transition metal, the splitting between the ligand field (LF) states is smaller, such that the lowest energy excited state of iron polypyridyl complexes is a metal-centered state rather than MLCT. The fact that the MLCT manifold in Fe(II) polypyridyls undergoes rapid conversion to the lowest energy LF state on the order of 100 fs is also challenging. Despite this, solar cells featuring Fe(II) sensitizers are able to produce a photocurrent, thus, inspiring research into the fundamentals of Fe(II) dye-semiconductor assemblies.

Before studying the electron transfer processes associated with Fe(II) complexes in devices for solar energy conversion, it is important to understand the excited state dynamics inherent to the chromophores themselves, wherein an interesting discovery was made about the influence of solvent for certain relaxation processes along the way. While the solvent environment is known to shape the dynamics associated with a charge transfer excited state (as it involves a redistribution of charge across the molecule), that is not the case for a LF excited state, which entails an electronic rearrangement on the metal center. Work shown here demonstrates that a solvent dependence can indeed exist for LF transitions, with a particular focus on the ground state recovery process in tris(2,2'-bipyridine)iron(II),  $[Fe(bpy)_3]^{2+}$ . Possible reasons behind what could be driving this solvent dependence, such as ion pairing and changes in solvation energy, are considered and assessed via ultrafast time-resolved absorption spectroscopic and computational methods. Work has been done in an effort to understand the physical origin behind this solvent dependence and get a better idea of how and why outer-sphere variables seem to affect these inner-sphere processes.

Although the discovery that the solvent environment modulates LF state lifetimes in iron(II) polypyridyl complexes is noteworthy, MLCT states are more relevant for the purposes of solar energy conversion. And so, other studies of mine have sought to clarify the results of dye-sensitized solar cells incorporating iron polypyridyl sensitizers, starting with cis-bis(cyano)bis(4,4'-dicarboxylic acid-2,2'-bipyridine)iron(II), hereafter referred to as F2CA. Interestingly, the initial report on this dye revealed a band-selective behavior for interfacial electron transfer (IET) where the absorbed photon-to-current conversion efficiency of F2CA on titanium dioxide (TiO<sub>2</sub>) did not match its absorption spectrum, highlighting a discrepancy between the injection efficiency associated with the two absorption bands. To investigate this, ultrafast time-resolved spectroscopic measurements were carried out on F2CA-TiO<sub>2</sub> assemblies as a function of excitation wavelength and also incorporated studies where the additives in the electrolyte of the solar cell were adjusted to either raise or lower the conduction band edge in an effort to study its impact on the injection yield. Synthetic variants of F2CA, which differ by the number of polypyridyl ligands to the number of cyano groups and incorporate either the carboxylate or hydroxamate linker, were also studied in order to identify how these changes affect the IET dynamics. Altogether, these results help to identify which components should be optimized for more efficient Fe(II) dye-sensitized solar cells.

Copyright by JENNIFER NICOLE MILLER 2018 In loving memory of my father. "Your absence has gone through me Like thread through a needle. Everything I do is stitched with its color." -W. S. Merwin

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vii

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To past, present, and future group members, I hope that I've done justice to the world of ultrafast spectroscopy and iron chemistry so that when you read this, you find my tome of use in understanding the what, why, and how of it all. And with that, I give you what I lovingly call 'the data dump'.

# TABLE OF CONTENTS

LIST OF TABLES	xii
LIST OF FIGURES	. xiii
KEY TO SYMBOLS AND ABBREVIATIONS	. xxi
<ol> <li>Introduction to interfacial electron transfer</li></ol>	1 1 1
<ul> <li>1.1.1 Principles of operation</li> <li>1.1.2 Device characterization</li> <li>1.2 Interfacial electron transfer in dye-sensitized solar cells</li> </ul>	2 4 7
1.2.1Experimental techniques used to study injection1.2.1.1Time-resolved emission1.2.1.2Transient absorption spectroscopy	7 8 8
<ul> <li>1.2.1.3 Time-resolved X-ray spectroscopy</li> <li>1.2.1.4 Measuring injection yield rather than injection rate</li> <li>1.3 Studying the injection process in a fully operational DSSC</li> </ul>	9 9 10
1.4 Contents of dissertation REFERENCES	11 13
2 Experimental methods	16 16
2.1.1 Varian Cary 50 UV-visible spectrophotometer 2.1.2 PerkinElmer LAMBDA 1050 UV/Vis/NIR spectrophotometer	18 18
2.2       Outatast time-resolved absorption measurements         2.2.1       Basic principles of ultrafast laser systems         2.2.2       Wile E laser system	19 23 26
<ul> <li>2.2.3 Road Runner laser system.</li> <li>2.2.3.1 One-color measurements: Single OPA</li> </ul>	26 27
<ul> <li>2.2.3.2 Two-color measurements: Two OPAs</li> <li>2.2.3.3 Two-color measurements: Pump OPA and Probe WLC</li> <li>2.2.4 Checks to ensure reliable data</li> </ul>	28 29 30
2.2.4.1       Beam polarizations.         2.2.4.2       Stage alignment.	30 34
<ul> <li>2.2.4.3 Pulse characterization</li> <li>2.2.4.4 Pulse compression</li> <li>2.3 Computational methods</li> </ul>	35 38 41
<ul> <li>2.3.1 Gaussian 09 software</li></ul>	41 42
2.4.1         LabVIEW           2.4.2         Igor Pro	42 43

2.4.3	Solid-G	44
2.4.4	Olex2	45
2.4.5	MATLAB	45
REFEREN	CES	46
3 Outer-	sphere effects on the excited state dynamics of ligand field states in Fe(II) polyp	oyridyl
complexes		50
3.1 I	ntroduction	50
3.2 E	Experimental details	52
3.2.1	Materials	52
3.2.2	Syntheses and characterization	52
3.2.3	Time-resolved transient absorption data	57
3.2.4	Computational methods	58
3.3 F	Results and discussion	59
3.3.1	Effect of solvent on the excited state dynamics of $[Fe(bpy)_3]^{2+}$	59
3.3.2	Modeling changes to the rate of non-radiative decay	65
3.3.3	Precedent for ion pairing between Fe(II) polypyridyls and counterions	71
3.3.4	How solvation changes between LS and HS states	76
3.3.5	A closer look at $[Fe(bpy)_3]^{2+}$ in aqueous solution	87
3.4 0	Conclusions	89
APPENDE	X	91
REFEREN	CES	97
4 Tunin	g injection and device performance of solar cells sensitized by cis-bis(cyano)bi	s(4,4'-
dicarboxyli	ic acid-2,2'-bipyridine)iron(II) via electrolyte additive control	103
4.1 I	ntroduction	103
4.1.1	Iron(II)-based sensitizers	104
4.1.2	Rationalizing band selectivity for injection in F2CA-TiO <sub>2</sub> devices	107
4.1.3	Optimizing the efficiency of Fe(II)-based DSSCs	109
4.2 E	Experimental details	111
4.2.1	Synthesis and characterization	111
4.2.2	Fabrication of solar cells	112
4.2.3	Electrolyte conditions	113
4.2.4	Time-resolved transient absorption data	114
4.3 F	Results and discussion	115
4.3.1	Investigating the effect of electrolyte on solar cell performance	115
4.3	1.1 Anion dependence on electronic absorption spectra of F2CA-TiO <sub>2</sub> films	115
4.3	1.2 Device characterization	117
4.3.2	Excited state dynamics of F2CA in solution	121
4.3.3	Investigating the interfacial electron transfer of F2CA-TiO <sub>2</sub> assemblies	123
4.3.	3.1 Studying band selectivity of F2CA-TiO <sub>2</sub> assemblies in various electrolyte	s.124
4.3	3.2 Probing interfacial electron transfer in the near-IR region	127
4.4 C	Conclusions	130
REFEREN	CES	132

5 Probing interfacial electron transfer dynamics of Fe(II) polypyridyl-sensitized solar cells	as a
function of linker	136
5.1 Introduction	136
5.1.1 Dependence of anchoring group on interfacial electron transfer rate	136
5.1.2 Impact of cyano groups on injection	138
5.2 Experimental details	139
5.3 Results and discussion	140
5.3.1 Investigating effect of anchoring group on device performance	140
5.3.2 Excited state dynamics of dyes in solution	141
5.3.3 Studying interfacial electron transfer of Fe(II) dye-TiO <sub>2</sub> assemblies	144
5.4 Conclusions	149
REFERENCES	150
6 Conclusions and future directions	152
6.1 Dissertation results	152
6.2 Studying interfacial electron transfer in dye-sensitized solar cells	153
6.2.1 Distinguishing between electron transfer and excited state dynamics	153
6.2.2 Probing in the mid-IR to increase signal associated with injected electrons	157
6.3 Optimization of solar cell components for iron(II)-based chromophores	160
6.3.1 Test injection efficiency with new semiconductor surfaces	161
6.3.2 Modifying electrolyte composition	162
6.4 Extending MLCT state lifetimes of Fe(II) complexes	163
6.4.1 Disrupting the vibrational modes involved in the MLCT-to-LF conversion	164
6.4.2 Increasing ligand field strength in Fe(II) complexes: Stabilizing $t_{2\alpha}$ orbitals	167
$643$ Increasing ligand field strength in Fe(II) complexes: Destabilizing $e_{\alpha}^{*}$ orbitals	169
6.5 Closing comments	171
REFERENCES	172

# LIST OF TABLES

Table 3-1.	Properties associated with each solvent <sup>a,b</sup>
Table 3-2.	Relaxation times for $[Fe(bpy)_3]^{2+}$ in acetonitrile for various anions at different concentrations after 550 nm excitation
Table 3-3.	Comparison of relaxation times for $[Fe(bpy)_3]^{2+}$ as counterion is changed
Table 3-4.	DFT Calculations for $[Fe(bpy)_3]^{2+}$ with SMD <sup>a</sup> in various solvents at 20 °C 77
Table 3-5.	DFT Calculations for $[Fe(bpy)_3]^{2+}$ with CPCM <sup>a</sup> in various solvents at 20 °C 78
Table 3-6.	Comparing ligand field strength of Co(III) polypyridyl complexes based on ligand field transition positions from electronic absorption spectra in acetonitrile <sup>a</sup> 81
Table 3-7.	Comparison of relaxation times for $[Fe(R-bpy)_3]^{2+}$ as substituent is changed 81
Table 3-8.	Average bond distances (Å), angles (°), and G values (%) of $[Fe(bpy)_3]^{2+}$ in LS and HS states in alcohol-based solvents from computational results with CPCM 83
Table 3-9.	Average bond distances (Å), angles (°), and G values (%) in selected Fe(II) complexes from computational results under vacuum
Table 3-10.	DFT Calculations for $[Fe(dmb)_3]^{2+}$ with CPCM <sup>a</sup> in various solvents at 20 °C 84
Table 3-11.	DFT Calculations for [Fe(5,5'-dmb) <sub>3</sub> ] <sup>2+</sup> with CPCM <sup>a</sup> in various solvents at 20 °C
Table 3-12.	DFT Calculations for [Fe(dtbbpy) <sub>3</sub> ] <sup>2+</sup> with CPCM <sup>a</sup> in various solvents at 20 °C 85
Table 3A-1.	Lifetimes for [Fe(bpy) <sub>3</sub> ]Br <sub>2</sub> in water/acetonitrile solvent mixtures
Table 4-1.	Electrolyte mixtures used in this work, with all dissolved in acetonitrile 113
Table 4-2.	Parameters from device characterization of F2CA-TiO <sub>2</sub> devices <sup>a</sup>
Table 4-3.	Parameters from device characterization of N3-TiO <sub>2</sub> devices <sup>a</sup> 119
Table 5-1.	Parameters from device characterization of F2X- and F3X-TiO <sub>2</sub> devices <sup>a,b</sup> 141
Table 5-2.	Excited state dynamics of complexes in methanol <sup>a</sup>
Table 5-3.	Qualitative injection yields for F2CA-TiO <sub>2</sub> in various electrolytes <sup>a</sup> 148
Table 6-1.	Summary of frequencies observed for Fe(II) complexes in methanol

# LIST OF FIGURES

Figure 1-1.	Cartoon representation of a DSSC
Figure 1-2.	General schematic of the energy levels and device operation of DSSCs under illumination. Processes which increase efficiency are shown in green, while red depicts undesirable processes
Figure 1-3.	Representation of kinetics associated with DSSC processes. Blue arrows represent desirable processes, while black arrows signify loss pathways. The vertical scale characterizes the free energy associated with those states. Timescales are typical of Ru(II) dyes-TiO <sub>2</sub> assemblies with the $\Gamma/I_3$ <sup>-</sup> redox shuttle. Reprinted with permission from Reference 13. Copyright (2011) American Chemical Society
Figure 1-4.	Representative current-voltage curve (red line). Labeled are the short-circuit photocurrent density ( $J_{SC}$ , red circle), the maximum power point ( $P_{max}$ , red triangle) and the open-circuit photovoltage ( $V_{OC}$ , red diamond). The fill factor (ff) is the area of the green shaded region divided by the area of the region outlined by the blue lines.
Figure 2-1.	Generalized Jablonski diagram of photophysical processes involved in relaxation. The energy level of each state is indicated on the vertical axis, while states are grouped by spin multiplicity along the horizontal axis. GS refers to the ground state. ES signifies the excited state. S and S' denote different spin states
Figure 2-2.	Generalized potential energy level diagram displaying effects of pump and probe interactions on a sample during a TA experiment. The pump pulse promotes an electron to an excited state. The probe pulse monitors the excited state absorption. 20
Figure 2-3.	(a) Comparison of the absorption spectra of the ground state (in green) and the excited state (in blue) of a hypothetical molecule. (b) Example of transient absorption data (dashed line) at some delay after photoexcitation
Figure 2-4.	Example of how TA data is two-dimensional, allowing us to select either particular time slices (spectrum boxed in red) or individual wavelengths (spectrum boxed in green)
Figure 2-5.	Layout of Wile E laser system. The green beam represents the pump beam line. The red beam bypassing TOPAS 2 is the probe beam which generates a WLC just before the sample
Figure 2-6.	Layout of Road Runner laser system under 'one-color' conditions
Figure 2-7.	Layout of Road Runner laser system under 'two-color' conditions, where the probe beam comes from the second OPA

Figure 2-8.	Layout of Road Runner laser system under 'two-color' conditions, where a white light continuum is produced as the probe beam
Figure 2-9.	Wave and vector representations of linearly, circularly, and elliptically polarized light
Figure 2-10.	The amount of light transmitted through a polarizer based on the input polarization of linearly polarized light relative to the transmission axis of the polarizer. The intensity of the throughput is normalized to the initial intensity before the polarizer. Data are only plotted along the x-axis up to 180°, after which the data repeat 32
Figure 2-11.	Effect of (a) half-wave and (b) quarter-wave plates on the polarization of linearly polarized light
Figure 2-12.	Example depictions of the laser set-up after the solvent sample for determining pulse durations (left) and instrument response function (right). The double-headed arrows represent the polarization of the beams, with the beam after the polarizer matching its transmission axis. 36
Figure 2-13.	Representative spectra from OKE measurements for acetonitrile (left) and methanol (right) with the corresponding Gaussian fit (black line), following photoexcitation at 480 nm
Figure 2-14.	Broadening of a femtosecond pulse at 800 nm after propagation through 0 mm (black), 1 mm (red), 10 mm (yellow), 20 mm (green), and 50 mm (blue) of N-BK7 material. The dashed lines represent conditions for Road Runner (purple, at an input pulse duration of 35 fs) and Wile E (black, at 130 fs)
Figure 2-15.	Representation of folded prism compressor set-up. In this example, the incoming pulse is compressed and leaves stretched. The opposite can be true if in the incoming pulse has redder wavelengths leading the blue
Figure 2-16.	Illustration of geometrical solid angle ( $\Omega$ ), measured from the spherical surface area (A) and radius (r) of that sphere
Figure 3-1.	Molecular structure for complexes discussed here: (a) $[Fe(bpy)_3]^{2+}$ , (b) $[Fe(dmb)_3]^{2+}$ , (c) $[Fe(5,5'-dmb)_3]^{2+}$ and (d) $[Fe(dtbbpy)_3]^{2+}$
Figure 3-2.	Rates of ground state recovery for $[Fe(bpy)_3]^{2+}$ in different solvents with excitation at 550 nm. The time constants are color-coded based on which counterion was associated with $[Fe(bpy)_3]^{2+}$ in said solvent, which varied for solubility reasons: Br (green) and BAr <sup>F</sup> <sub>4</sub> (blue). 60
Figure 3-3.	Rates of GSR for $[Fe(bpy)_3]^{2+}$ versus static dielectric constants
Figure 3-4.	Comparison of GSR lifetime for $[Fe(bpy)_3]^{2+}$ versus (a) dipole moment, (b) molar volume, (c) optical dielectric constant, (d) polarizability, (e) static dielectric constant, and (f) viscosity for alcohols (red squares), diols (green triangles), and

	nitriles (blue circles). The results for water (black diamonds) are presented in the figures, but not included in any fits
Figure 3-5.	Comparison of the static dielectric constant versus (a) dipole moment, (b) molar volume, (c) optical dielectric constant, (d) polarizability, and (e) viscosity for alcohols (red squares), diols (green triangles), and nitriles (blue circles). The results for water (black diamonds) are presented in the figures, but not included in any fits.
Figure 3-6.	General depiction of the energy separations determining rates of relaxation from the ${}^{5}T_{2}$ excited state to the ${}^{1}A_{1}$ ground state in Fe(II) polypyridyl complexes with a LS ground state. H <sub>ab</sub> represents the matrix element, $\lambda$ is the reorganization energy, and $\Delta G^{0}$ is the free energy. 66
Figure 3-7.	Theoretical findings from the non-radiative decay equation, calculating the (a) matrix element and the (b) change in free energy for $[Fe(bpy)_3]^{2+}$ in water at 20 °C and $\tau_{GSR} = 677.42$ ps
Figure 3-8.	Theoretical findings from the non-radiative decay equation, calculating the (a) matrix element and the (b) change in free energy for $[Fe(bpy)_3]^{2+}$ in dichloromethane at 20 °C and $\tau_{GSR} = 1281.75$ ps
Figure 3-9.	Theoretical findings from the non-radiative decay equation for $H_{ab}$ of ${}^{5}T_{2} \rightarrow {}^{1}A_{1}$ transition in $[Fe(bpy)_{3}]^{2+}$ in water (purple, $\tau_{GSR} = 677.42$ ps) and dichloromethane (green, $\tau_{GSR} = 1281.75$ ps) at suggested values for the (a) change in free energy (-6800 cm <sup>-1</sup> ) and the (b) reorganization energy (6800 cm <sup>-1</sup> )
Figure 3-10.	Theoretical findings from the non-radiative decay equation for $\Delta G^0$ of ${}^5T_2 \rightarrow {}^1A_1$ transition in $[Fe(bpy)_3]^{2+}$ in water (purple, $\tau_{GSR} = 677.42$ ps) and dichloromethane (green, $\tau_{GSR} = 1281.75$ ps) at suggested values for the (a) reorganization energy (6800 cm <sup>-1</sup> ) and the (b) matrix element (170 cm <sup>-1</sup> )
Figure 3-11.	The difference between the calculated (a) $H_{ab}$ values and (b) $\Delta G^0$ values for $[Fe(bpy)_3]^{2+}$ in water ( $\tau_{GSR} = 677.42$ ps) and dichloromethane ( $\tau_{GSR} = 1281.75$ ps) at 20 °C.
Figure 3-12.	Rates of GSR for [Fe(bpy) <sub>3</sub> ]Br <sub>2</sub> in (a) water, (b) dimethyl sulfoxide, (c) methanol, (d) acetonitrile, and (e) 1-butanol at different concentrations after excitation at 550 nm.
Figure 3-13.	Size comparison of each anion as well as $[Fe(bpy)_3]^{2+}$ , for reference. Reproduced from crystal structures with refcodes: ABAJEV (Cl <sup>-</sup> ), AAZDCO (Br <sup>-</sup> ), PAFSIB (I <sup>-</sup> ), AFODIJ (PF <sub>6</sub> <sup>-</sup> ), ABAHUH (BPh <sub>4</sub> <sup>-</sup> ), ABEBEQ (BAr <sup>F</sup> <sub>4</sub> <sup>-</sup> ), and NUZKOI ([Fe(bpy) <sub>3</sub> ] <sup>2+</sup> )
Figure 3-14.	Correlating the estimated change in Gibbs free energy of solvation of $[Fe(bpy)_3]^{2+}$ from SMD calculations to the associated GSR rate for (a) all solvents in this study

Figure 3-17.	The GSR rate for [Fe(bpy) <sub>3</sub> ]Br <sub>2</sub> (red circles), [Fe(dmb) <sub>3</sub> ]Br <sub>2</sub> (yellow squares),
	[Fe(5,5'-dmb) <sub>3</sub> ]Br <sub>2</sub> (green triangles) and [Fe(dtbbpy) <sub>3</sub> ]Br <sub>2</sub> (blue diamonds) in
	alcohol-based solutions. The inset shows data which have been normalized to
	methanol

Figure 3A-7.	Electronic absorption spectrum of [Fe(dmb) <sub>3</sub> ]Br <sub>2</sub> in acetonitrile94
Figure 3A-8.	Electronic absorption spectrum of [Fe(5,5'-dmb) <sub>3</sub> ]Br <sub>2</sub> in acetonitrile
Figure 3A-9.	Electronic absorption spectrum of [Fe(dtbbpy) <sub>3</sub> ]Br <sub>2</sub> in acetonitrile95
Figure 3A-10.	GSR dynamics for $[Fe(dtbbpy)_3]Br_2$ as a function of temperature after excitation at 550 nm in (a) methanol and (b) 1-butanol. Data collected by Monica C. Carey and analyzed by Jennifer N. Miller
Figure 3A-11.	(a) Arrhenius and (b) Eyring plots of GSR dynamics for [Fe(dtbbpy) <sub>3</sub> ]Br <sub>2</sub> in methanol (red squares) and 1-butanol (blue circles) following excitation at 550 nm. Data collected by Monica C. Carey and analyzed by Jennifer N. Miller
Figure 4-1.	Molecular structures of complexes in this chapter: F2CA and N3 104
Figure 4-2.	Results of first iron(II) dye-sensitized solar cell. (a) J-V curve of F2CA on TiO <sub>2</sub> under illumination (top curve) versus in the dark (bottom curve). The electrolyte contained 0.5M lithium iodide, 0.05M iodine, and 0.2M 4- <i>tert</i> -butylpyridine in a mixture of acetonitrile (90% by volume) and 3-methyl-2-oxazolidinone. Device parameters: $J_{SC} = 0.29 \text{ mA/cm}^2$ , $V_{OC} = 360 \text{ mV}$ , ff = 0.75, $P_{in} = 75 \text{ mW/cm}^2$ , $\eta = 0.1\%$ . (b) Comparison of the absorption spectrum (dotted line) and absorbed photon-to-current conversion efficiency spectrum (solid line) of F2CA on TiO <sub>2</sub> . The absorption spectrum was collected with 0.5M lithium iodide in acetonitrile, while the APCE data reflects the same conditions as reported for the J-V curve. Reprinted with permission from Reference 10. Copyright (1998) American Chemical Society. 105
Figure 4-3.	Depiction of energetics and excited state evolution for F2CA and N3 sensitizers relative to anatase TiO <sub>2</sub> . MLCT stands for metal-to-ligand charge transfer, LF is ligand field, and GS represents ground state

- Figure 4-8. Percent change in (a) short-circuit current density, (b) open-circuit voltage, (c) fill factor, and (d) cell efficiency for N3-TiO<sub>2</sub> solar cells (red circles) and F2CA-TiO<sub>2</sub> devices (green triangles) in different electrolyte compositions relative to the values obtained for Li + TBP. 120

- Figure 4-11. TA data representing the qualitative injection yield following excitation into the MLCT<sub>1</sub> band ( $\lambda_{ex} = 600$  nm, red triangles) versus MLCT<sub>2</sub> ( $\lambda_{ex} = 415$  nm, blue squares) as the additives in the electrolyte are changed: (a) Li', (b) Li + DTBP', (c) Li + TBP', (d) TBA', and (e) TBA + TBP'. All data are normalized at t = 6 ps. 125

Figure 5-1.	(Left) Functional groups studied as anchoring groups for $[Fe(bpy-L)_2(CN)_2]$ attached to a TiO <sub>2</sub> surface. (Right) Theoretical internal quantum efficiencies (TIQE) for dye-TiO <sub>2</sub> systems overlaid with their simulated electronic absorption spectra. Reprinted with permission from Reference 7
Figure 5-2.	Dyes studied throughout this chapter. F3COMe, F3HOMe, F2COMe, and F2HOMe were only studied in solution. F3HA and F2HA were only studied as a part of a dye-TiO <sub>2</sub> solar cell
Figure 5-3.	Time-resolved data displaying the ground state recovery dynamics of different Fe(II)-polypyridyl complexes in methanol. F2X complexes were excited at 610 nm. F3X complexes were excited at 550 nm. 142
Figure 5-4.	Electronic absorption spectra for dye-TiO <sub>2</sub> assemblies with the Li + TBP' electrolyte: $F2CA$ -TiO <sub>2</sub> (green trace), and $F3CA$ -TiO <sub>2</sub> (purple trace). The absorption spectra are normalized to the maximum of the lower energy MLCT band. The absorption of bare TiO <sub>2</sub> has been subtracted from each, prior to normalization. 144
Figure 5-5.	TA data representing the qualitative injection yield following excitation into the MLCT <sub>1</sub> band (red triangles) versus MLCT <sub>2</sub> (blue squares) of (a) F2CA- and (b) F3CA-TiO <sub>2</sub> cells with the Li + TBP' electrolyte. All data are normalized at $t = 6$ ps. 145
Figure 5-6.	Electronic absorption spectra of (a) F2HA-TiO <sub>2</sub> and (b) F2HAM-TiO <sub>2</sub> with the following electrolyte: Li' (red trace), Li + DTBP' (yellow trace), and Li + TBP' (green trace). The absorption spectra are normalized to the maximum of the lower energy MLCT band. The absorption of bare TiO <sub>2</sub> has been subtracted from each, prior to normalization.
Figure 5-7.	TA data representing the qualitative injection yield following excitation into the MLCT <sub>1</sub> band (red triangles) versus MLCT <sub>2</sub> (blue squares) of (a) F2HA-TiO <sub>2</sub> and (b) F2HAM-TiO <sub>2</sub> with the Li' electrolyte. All data are normalized at $t = 6$ ps 147
Figure 5-8.	TA data displaying the qualitative injection yield following excitation into the MLCT <sub>1</sub> band (red triangles) versus MLCT <sub>2</sub> (blue squares) of (a) F2HA-TiO <sub>2</sub> and (b) F2HAM-TiO <sub>2</sub> with the Li + DTBP' electrolyte. All data are normalized at $t = 6$ ps. 147
Figure 5-9.	TA data portraying the qualitative injection yield following excitation into the MLCT <sub>1</sub> band (red triangles) versus MLCT <sub>2</sub> (blue squares) of (a) F2HA-TiO <sub>2</sub> and (b) F2HAM-TiO <sub>2</sub> with the Li + TBP' electrolyte. All data are normalized at $t = 6$ ps. 148
Figure 6-1.	F2CA bound to Al <sub>2</sub> O <sub>3</sub> with 0.5M LiBF <sub>4</sub> in acetonitrile after excitation at 525 nm and probing at 570 nm

Figure 6-2.	Example of experimental set-up for generating a mid-IR continuum by focus	sing the
	beams from third-harmonic generation and filtering out shorter wavelengths	. Based
	on figures from references 39 and 40.	159

- Figure 6-4. Single wavelength kinetic trace of F2COMe in methanol (left) with the resulting power spectrum after LPSVD fit of data (right). The left figure displays the following traces: F2COMe (red), methanol (green), exponential fit (black), and the residual (blue). This sample was pumped at 550 nm and probed at 650 nm..... 165

## KEY TO SYMBOLS AND ABBREVIATIONS

- 5,5'-dmb ......5,5'-dimethyl-2,2'-bipyridine
- A.....pre-exponential factor, absorbance
- Al<sub>2</sub>O<sub>3</sub>.....aluminum oxide, alumina
- ALD .....atomic layer deposition
- APCE .....absorbed photon-to-current conversion efficiency
- b.....cuvette path length
- BArF<sub>4</sub>.....tetrakis(3,5-bis(trifluoromethyl)phenyl)borate
- BF<sub>4</sub>.....tetrafluoroborate
- BPh4 .....tetraphenylborate
- bpy.....2,2'-bipyridine
- btz.....1,1'-bis(p-tolyl-4,4'-bis(1,2,3-triazol-5-ylidene))
- c.....concentration
- CA.....carboxylic acid
- CaF<sub>2</sub> .....calcium fluoride
- CD<sub>3</sub>CN .....deuterated acetonitrile
- CH<sub>3</sub>CN .....acetonitrile
- ClO<sub>4</sub> .....perchlorate
- CN.....cyano
- CNC ......2,6-bis(3-methylimidazole-1-ylidine)pyridine
- CPCM ......conductor-like polarizable continuum model
- CT .....charge transfer
- d.....distance between two ion centers
- dcpp.....2,6-bis(2-carboxypyridyl)pyridine

- DFT .....density functional theory
- dmb ......4,4'-di-methyl-2,2'-bipyridine
- dpb.....4,4'-di-phenyl-2,2'-bipyridine
- DSSC .....dye-sensitized solar cell
- dtbbpy ......4,4'-di-*tert*-butyl-2,2'-bipyridine
- DTBP ......2,6-di-tert-butylpyridine
- dvpp......2,6-bis(2-vinylpyridyl)pyridine
- E.....electric field
- e.....elementary electric charge
- ε.....molar absorptivity, extinction coefficient
- $\epsilon_0$  .....vacuum permittivity
- E<sub>a</sub>.....activation energy
- $\epsilon_r$  .....relative permittivity
- ES.....excited state
- ESA .....excited state absorption
- ESI.....electrospray ionization
- F .....ion association
- F2CA.....cis-bis(cyano)bis(4,4'-dicarboxylic acid-2,2'-bipyridine)iron(II)
- F2COMe .....cis-bis(cyano)bis(4,4'-dimethoxycarbonyl-2,2'-bipyridine)iron(II)
- F2HA .....cis-bis(cyano)bis(4,4'-dihydroxamic acid-2,2'-bipyridine)iron(II)
- F2HAM ......cis-bis(cyano)bis(4,4'-di-N-methyl-hydroxamic acid-2,2'-bipyridine)iron(II)
- F2HOMe ......cis-bis(cyano)bis(4,4'-di-N-methoxy-carboxamide-2,2'-bipyridine)iron(II)
- F3CA.....tris(4,4'-dicarboxylic acid-2,2'-bipyridine)iron(II)
- F3COMe .....tris(4,4'-dimethoxycarbonyl-2,2'-bipyridine)iron(II)
- F3HA .....tris(4,4'-di-hydroxamic acid-2,2'-bipyridine)iron(II)

- F3HAM .....tris(4,4'-di-*N*-methyl-hydroxamic acid-2,2'-bipyridine)iron(II)
- F3HOMe .....tris(4,4'-di-*N*-methoxy-carboxamide-2,2'-bipyridine)iron(II)
- ff.....fill factor
- FFT.....fast Fourier-transform
- FL.....fluorescence
- fs.....femtosecond
- FTO .....fluorine-doped tin oxide
- FWHM ......full-width at half-maximum
- g(r) .....radial distribution function
- GS .....ground state
- GSB.....ground state bleach
- GSR.....ground state recovery
- η.....cell efficiency
- $\hbar$ .....reduced Planck constant
- HA.....hydroxamic acid
- H<sub>ab</sub>.....matrix element
- HPCC ......high performance computing center
- HS .....high-spin
- I .....intensity
- I<sub>0</sub>.....initial intensity
- IC.....internal conversion
- iCER.....institute for cyber-enabled research
- IET .....interfacial electron transfer
- In<sub>2</sub>O<sub>3</sub>.....indium oxide
- IPCE.....incident photon-to-current conversion efficiency

- IRF .....instrument response function
- ISC .....intersystem crossing
- IVR.....intermolecular vibrational redistribution
- J-V.....current-voltage
- J<sub>SC</sub>.....short-circuit current density
- k<sub>B</sub>.....Boltzmann constant
- k<sub>nr</sub> .....non-radiative relaxation rate
- L .....linker
- LF....ligand field
- LIESST .....light-induced excited spin state trapping
- LMCT .....ligand-to-metal charge transfer
- LPSVD.....linear predictive singular value decomposition
- LS.....low-spin
- LUMO.....lowest unoccupied molecular orbital
- MLCT .....metal-to-ligand charge transfer
- MMCT .....metal-to-metal charge transfer
- N3.....cis-bis(isothiocyanato)bis(4,4'-dicarboxylic acid-2,2'-bipyridine)ruthenium(II)
- NA.....Avogadro constant
- Nb2O5 .....niobium oxide
- ND.....neutral density
- NH4 .....ammonium
- NHC ......*N*-heterocyclic carbene
- NMR .....nuclear magnetic resonance
- ns.....nanosecond
- OKE .....optical Kerr effect

- OPA .....optical parametric amplifier
- PCM ..... polarizable continuum model
- PF<sub>6</sub>.....hexafluorophosphate
- PH .....phosphorescence
- phen.....1,10-phenanthroline
- ps.....picosecond
- q.....distance after which two ions are no longer ion paired
- r .....radius
- R<sup>2</sup> .....coefficient of determination
- Sb<sub>2</sub>O<sub>3</sub>.....antimony oxide
- SMD.....solvation model based on density
- $SnO_2$ ....tin oxide
- SO<sub>4</sub>.....sulfate
- T .....temperature
- t .....time
- $\tau$ .....lifetime, time constant
- TA .....transient absorption
- TBA.....tetrabutylammonium
- TBP .....4-tert-butylpyridine
- TCSPC .....time-correlated single photon counting
- TDDFT.....time-dependent density functional theory
- TiO<sub>2</sub>.....titanium dioxide, titania
- TIQE .....theoretical internal quantum efficiency
- tpy .....2,2':6',2"-terpyridine
- tren(6-Me-py)3 .....tris(6-methyl-2-pyridylmethyliminoethyl)amine

VCvibrational cooling
V <sub>OC</sub> open-circuit voltage
VRvibrational relaxation
WLCwhite light continuum
XCcross-correlation
zion charge
ZnOzinc oxide
ZrO <sub>2</sub> zirconium dioxide
$\Delta A$ change in absorbance
$\Delta G^0$ Gibbs free energy of a reaction
$\Delta G_{solv}$ Gibbs free energy of solvation
$\Delta V$ change in volume
$\Delta\Delta G_{solv}$ differential solvation energy
$\lambda$ reorganization energy, wavelength
$\lambda_o$ outer-sphere reorganization energy

# **1** Introduction to interfacial electron transfer

### 1.1 Advantages of solar energy

The world energy consumption rate is projected to increase from nearly 18.4 terawatts (TW, equal to 10<sup>12</sup> watts) in 2012 to 27.3 TW in 2040, where fossil fuels are expected to continue to supply more than three-fourths of the world's energy.<sup>1</sup> Given that the rise in atmospheric temperatures can only be accurately modeled if anthropogenic sources of carbon dioxide emission (a byproduct of fossil fuel combustion) are included,<sup>2</sup> there is motivation to make use of carbon-neutral, renewable energy sources. Alternative energy sources to fossil fuels include nuclear, solar, geothermal, hydropower, biomass, and wind.<sup>3</sup> Of these options, solar energy is not only plentiful, but also accessible world-wide. Despite enough sunlight striking the earth's surface in an hour and a half to "power the planet" for one year,<sup>4</sup> the cost-to-efficiency ratio of cells which harvest solar energy does not match that provided by fossil fuels, warranting further research in the area.

### 1.2 Dye-sensitized solar cells

Solar energy conversion makes it possible to transfer energy from the sun directly to electrical energy. In 1991, a report by O'Regan and Grätzel described an innovative alternative to traditional silicon-based systems for capturing solar energy that was based on a dye-sensitized solar cell (DSSC).<sup>5</sup> This cell was composed of a Ru(II) polypyridyl chromophore, also known as a dye or sensitizer, that absorbs within the solar spectrum and was adsorbed to a porous film of nanocrystalline titanium dioxide (TiO<sub>2</sub>) particles through carboxylate anchoring groups. The use of semiconductor nanoparticles significantly increased the surface area available for binding dye molecules compared to earlier DSSCs which employed dye-sensitized single crystals<sup>6,7</sup> and, as a result, greatly improved device performance. While other types of photovoltaic cells are also being

investigated for their light harvesting abilities,<sup>8–10</sup> DSSCs offer an ease of fabrication and chemical stability, calling for further investigation.

Depicted in Figure 1-1, a DSSC represents a sandwich assembly between two transparent conducting oxide (TCO) electrodes, where the anode is covered with dye-adsorbed semiconductor nanoparticles, the counter electrode is platinized, and an electrolyte with a redox mediator transports charge carriers between them. A cell of this type differs from a traditional photovoltaic cell in that the photoexcited dye acts to separate the electrons and holes between the semiconductor and ions in the electrolyte, respectively. While the Grätzel group has reported an efficiency of 13% with a zinc porphyrin dye,<sup>11</sup> the current maximum independently verified efficiency for a DSSC is 11.9% with a ruthenium-based dye, reported by the Sharp corporation<sup>12</sup> and certified by the National Institute of Advanced Industrial Science and Technology (AIST).



Figure 1-1. Cartoon representation of a DSSC.

## 1.1.1 Principles of operation

In a conventional n-type DSSC, a dye sensitizer absorbs a photon of light, producing an excited state that localizes an electron on the periphery of the complex. The excited sensitizer (S\*)

delivers the electron to the conduction band (CB) of a wide band gap semiconductor, resulting in the oxidized form of the dye ( $S^+$ ); this process will be referred to as interfacial electron transfer (IET) or injection, throughout this dissertation. Following injection, the electron percolates through the nanoparticles to the back electrode, where it is collected and sent through an external load as it proceeds to the counter electrode. The circuit is completed as the electron present at the counter electrode regenerates a redox couple (A/A<sup>-</sup>) present in the electrolyte, which serves to reduce the oxidized dye. This sequence of reactions is advantageous as no net chemistry takes place, allowing the solar cell to repeat the cycle ad infinitum.



**Figure 1-2.** General schematic of the energy levels and device operation of DSSCs under illumination. Processes which increase efficiency are shown in green, while red depicts undesirable processes.

Each of these processes is displayed in Figure 1-2 by green arrows. The red arrows represent undesirable processes which decrease the overall power conversion efficiency of the solar cell. After excitation of an electron, injection competes with excited state decay of the dye. Another undesirable process includes dye regeneration by recombination of an electron from the semiconductor rather than reduction occurring by the redox couple. There is also competition for



**Figure 1-3.** Representation of kinetics associated with DSSC processes. Blue arrows represent desirable processes, while black arrows signify loss pathways. The vertical scale characterizes the free energy associated with those states. Timescales are typical of Ru(II) dyes-TiO<sub>2</sub> assemblies with the  $I^{-}/I_{3}^{-}$  redox shuttle. Reprinted with permission from Reference 13. Copyright (2011) American Chemical Society.

reduction of the redox couple between the counter electrode and back electron transfer from an injected electron in the semiconductor. The efficiency of a DSSC is, thus, dependent on the competition of rates between the forward processes and the reverse. The general timescales of these processes in a Ru(II) dye-sensitized solar cell are highlighted in Figure 1-3,<sup>13</sup> also discussed elsewhere.<sup>14,15</sup> As can be seen from the typical time constants, relative to one another, the success of this type of solar cell stems from the effectiveness of two charge separation steps: electron injection from the excited dye to the conduction band of the semiconductor and dye regeneration by the redox shuttle. This serves to show the importance of the chosen dye and the complementary redox shuttle in the electrolyte. Changes to components within the device allow for optimization of these kinetic processes, and the impact these modifications have on cell efficiency parameters can be quantified by experimental methods.

#### 1.1.2 Device characterization

The performance of a solar cell is based on its efficiency at converting solar power ( $P_{in}$ ) into electricity ( $P_{max}$ ) under standard sunlight conditions (air mass 1.5 or 1 Sun), where  $P_{in}$  is



**Figure 1-4.** Representative current-voltage curve (red line). Labeled are the short-circuit photocurrent density ( $J_{SC}$ , red circle), the maximum power point ( $P_{max}$ , red triangle) and the open-circuit photovoltage ( $V_{OC}$ , red diamond). The fill factor (ff) is the area of the green shaded region divided by the area of the region outlined by the blue lines.

assumed to be 100 mW cm<sup>-2</sup> on a clear day.<sup>16</sup> Following irradiation, electrons are able to flow through the cell as current, and a potential difference develops between the photoelectrode and the counter electrode. The maximum current that can be produced is known as the short-circuit current and is written as  $I_{SC}$ . Since the photocurrent produced is dependent on the incident light area, the current density, J, is generally reported instead in order to normalize the results between different cells. The maximum voltage, designated as  $V_{OC}$ , occurs when there is no net current since the rate of electron injection and the rate of recombination are equal. This value represents the difference between the quasi Fermi level of the semiconductor and the redox potential of the redox mediator. These two extremes, along with the shape of the current-voltage (J-V) curve, can be used to determine the efficiency ( $\eta$ ) of a solar cell, as shown in the following equation:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{V_{OC} \cdot J_{SC} \cdot ff}{P_{in}}$$
 Equation 1.1

where ff describes the fill factor of the cell.<sup>16</sup> The ff denotes the ideality of diode behavior and is represented by the area of the inner rectangle (green box) divided by the area of the outer rectangle (outlined by blue lines) in Figure 1-4.

The incident photon-to-current conversion efficiency (IPCE) presents another way of evaluating the primary processes in a cell as a function of excitation wavelength. This is expressed by the following equation:

$$IPCE(\lambda) = LHE(\lambda) \cdot \Phi_{inj}(\lambda) \cdot \eta_{coll}(\lambda) \cdot \eta_{reg}(\lambda)$$
 Equation 1.2

where LHE refers to the light harvesting efficiency of the dye,  $\Phi_{inj}$  is the electron injection efficiency,  $\eta_{coll}$  is the charge collection efficiency, and  $\eta_{reg}$  is the efficiency of dye regeneration.<sup>17</sup> Essentially, the IPCE determines the ratio of generated electrons in the external circuit to incident photons at each specific wavelength (i.e. the external quantum efficiency (EQE)).

In order to improve the efficiency of a solar cell, the aim is to maximize  $J_{SC}$  and  $V_{OC}$  while minimizing the over-potentials associated with the electron transfer processes in the DSSC. Ignoring the relaxation rates associated with the sensitizer, the photocurrent could be increased by extending the dye's absorption to redder wavelengths. To do this, the energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the dye must decrease either by destabilizing the HOMO or stabilizing the LUMO. If the HOMO level is destabilized, this act may speed up the recombination of the injected electron in the conduction band of the semiconductor to the oxidized dye, while simultaneously slowing down the dye regeneration process since the driving force for that reaction would be decreased. If the LUMO level is stabilized, this decreases the driving force for transferring the excited electron into the conduction band, and could thus slow down the injection process. In order to boost the photovoltage of a DSSC, the redox couple could be changed such that the redox potential is at a more positive voltage; however, this may decrease the rate of dye regeneration as a result of decreasing the driving force for that process. Alternatively, modulating the conduction band edge of the semiconductor to a more negative potential should increase the  $V_{OC}$  of the cell; however, it may slow down, and thus decrease the yield of, the injection process.

From this discussion, it is easy to see how interrelated different parameters are to one another, such that the modification of one component may improve one aspect, but could also increase deleterious processes to the extent that any improvement is voided. Therefore, actually quantifying the kinetics associated with these individual processes and understanding how changing cell components impact the device's function is of utmost importance for solar cell development. While all are important for favorable device performance, if the initial charge separation step results in a poor injection yield, the processes that follow will never be able to deliver a high-performance device. And so, the remainder of this chapter (and dissertation) will focus on the kinetic competition between interfacial electron transfer to the semiconductor and the excited state decay of the dye, as this represents the limiting factor for devices that will be discussed in later chapters.

## 1.2 Interfacial electron transfer in dye-sensitized solar cells

#### 1.2.1 Experimental techniques used to study injection

The timescales associated with the processes described in Figure 1-3 demonstrate the need for many different experimental methods in order to fully characterize the processes involved in a solar cell. And in fact, it is beneficial to employ multiple methods when analyzing a system, as it allows for better identification of the relevant states and excited species that are present. However, if the focus here is on the dynamics associated with injection, then the equipment and techniques used to identify those time constants need to function on the ultrafast timescale. Time-resolved

spectroscopy represents one such way to measure these dynamics, and the following discussion only highlights a few of the more common techniques.

#### 1.2.1.1 Time-resolved emission

After exciting the dye sensitizer with a laser pulse, the two main pathways available to the excited electron are to either undergo interfacial electron transfer to the semiconductor substrate, or follow a relaxation pathway that dissipates the excess energy either by heat or through the emission of light. And so, time-resolved emission is one area that allows for the study of the excited state of the dye (so long as the molecule does, in fact, emit), but does not provide any information about the electrons in the semiconductor. Techniques that are typically used for this type of experiment include time-correlated single photon counting (TCSPC)<sup>18</sup> or fluorescence up-conversion, <sup>19</sup> where the former is more sensitive but the latter allows for better temporal resolution. In addition to the dye-semiconductor of interest, if control samples are used (with an inert substrate where injection is not possible, such as with zirconium oxide or aluminum oxide films), electron injection dynamics can then be parsed out. For this to be accurate, however, it is important that the densities of absorbed photons be equal between the two samples (i.e. identical absorption at the pump wavelength with the same pump intensity for both experiments).

#### 1.2.1.2 Transient absorption spectroscopy

This method is generally referred to as a pump-probe technique where the pump represents the excitation pulse (typically in the UV or visible region) that promotes an electron to an excited state, and the probe pulse analyzes the sample response at different time delays after excitation. Different signatures can be studied depending on the wavelength of the probe pulse – visible wavelengths tend to examine signals specific to the excited dye or the oxidized dye, while wavelengths in the near-IR to mid-IR more easily detect the electrons in the conduction band of the semiconductor directly.<sup>20</sup> Unfortunately, distinguishing between all of these species is not always straightforward, as absorption bands are broad enough that they tend to overlap. Additionally, any injection dynamics detected do not necessarily correspond to a single, clean time constant due to changing rates of injection as the excited electron relaxes relative to the conduction band density of states. Fitting with a stretched exponential is sometimes used to correct for this.

#### 1.2.1.3 Time-resolved X-ray spectroscopy

This experiment is similar to a pump-probe technique, except an X-ray pulse is used as a probe pulse. This allows for the transient structure to be studied, where absorption of an X-ray photon promotes an electron from a core orbital to either a higher unoccupied level or to the continuum. This technique allows for changes in the oxidation state of the transition metal in the sensitizer to be detected, as well as any changes in metal-ligand bond lengths as a result of injection from the dye to the semiconductor.<sup>21,22</sup>

## 1.2.1.4 Measuring injection yield rather than injection rate

The injection yield represents the number of electrons injected relative to the number of photons absorbed by a molecule. This ratio can be determined by either direct or indirect measurements. In the case of time-resolved emission, an indirect method, the change in intensity between the sample of interest and the signal when the dye is bound to an inert substrate can be used to calculate the injection yield. For such an experiment, it is assumed that the dye packing is comparable between the two samples so that any self-interaction is controlled for. With transient absorption measurements, if the absorption coefficient of the oxidized state and properties specific to the excitation pulse, such as beam size and peak power, are known, then the injection yield can be calculated based on the magnitude of the signal of the oxidized dye. If these conditions are not

met, the injection efficiency can still be established based on the amount of signal that remains once injection is complete; this can be used a qualitative measure for comparison between samples.

If the rate of interfacial electron transfer can be measured directly, the injection yield can be calculated by the following equation:

$$\phi_{inj} = \frac{k_{inj}}{k_{inj} + k_{other}}$$
 Equation 1.3

where  $k_{other}$  refers to any processes specific to the excited state of the dye that may also be present. While the sample of interest will exhibit dynamics for both injection and 'other' relaxation dynamics, the 'other' dynamics can be determined by measuring the signal when bound to an inert substrate. Recall, however, that the injection process is not necessarily a single exponential process, and therefore it is not as simple as it looks in Equation 1.3; to work around this, some use the average lifetime for the injection process instead. Another issue that has been observed when attempting to measure the injection yield by measuring dynamics directly is the fact that trap states present in the inert semiconductor can give false readings regarding a dye's excited state dynamics.

## **1.3** Studying the injection process in a fully operational DSSC

Only recently have the interfacial electron transfer dynamics of a solar cell been studied in complete DSSCs, where it was previously investigated as a dry film or in the presence of an inert electrolyte. Compared to previous results, injection has actually been found to be slower in a complete solar cell.<sup>23</sup> While it is ideal to measure the kinetics as they would be in a functional device, this can have the disadvantage of not being transparent enough for whatever wavelength range the probe is in – for example, the probe wavelength can be absorbed by the electrolyte, the platinum on the counter electrode, or by the conductive glass electrodes. On the other hand, including the redox couple in the cell being studied may result in a more stable cell overall such that it does not need to be translated during the measurement. Another benefit to using a fully
operational DSSC while measuring the interfacial electron transfer dynamics is that that same cell can be studied by IPCE measurements and current-voltage parameters as well, which would allow for a better correlation between the photodynamics being measured and cell efficiency. It could also help to check the effect of aging and/or degradation after being studied by laser spectroscopy. While studying the full cell is beneficial, it is still important to build up the complexity of processes that may be occurring when studying a new dye-semiconductor device.

## **1.4** Contents of dissertation

As highlighted earlier, the most well-studied dye-sensitized solar cells tend to incorporate ruthenium in their sensitizers. Unfortunately, ruthenium is a rare metal which limits its use as a viable, scalable solution for solar energy harvesting in commercial devices. Iron represents an abundant alternative which is isoelectronic with ruthenium(II).<sup>24</sup> In fact, work published in 1998 showed that an iron-based sensitizer is capable of conducting a photocurrent.<sup>25</sup> However, the cell's efficiency was significantly diminished, roughly 100 times less, compared to the ruthenium analog. As it turns out, low-spin iron(II) complexes generally exhibit lowest energy excited states which are ligand field in nature and populated via deactivation from the <sup>3</sup>MLCT state on the 100-fs timescale.<sup>26,27</sup> Research within the McCusker group, and more recently others, has concentrated on modifying the ligands to extend the MLCT lifetime.<sup>28–31</sup> What is known about this class of molecules and future directions will be discussed in greater detail in the following chapters.

**Chapter 2** reviews the experimental methods used to obtain the data presented throughout this dissertation. The instruments themselves are described as well as procedures for data collection and subsequent work up.

**Chapter 3** presents data of solvent effects on a metal-centered process. Dynamics involving charge transfer excited states tend to be particularly responsive to solvent properties due

to the charge redistribution associated with these types of excited states. Conversely, ligand field excited states are not expected to be affected by solvent since they are metal-centered. Given that assumption, a variety of measurements were conducted in an effort to understand the nature of this solvent dependence on the ground state recovery of  $[Fe(bpy)_3]^{2+}$ , where bpy = 2,2'-bipyridine.

**Chapter 4** expands on what is known about the interfacial electron transfer dynamics of the Ferrere molecule, *cis*-bis(cyano)bis(4,4'-dicarboxylic acid-2,2'-bipyridine)iron(II), by modulating the energetics of the solar cell with different electrolyte additives. The initial report on this molecule revealed a band-selective behavior for interfacial electron transfer. To discern the origin of this selectivity, spectroscopic measurements were carried out on this dye in solution and on  $TiO_2$  as a function of excitation wavelength across the distinct absorption features.

**Chapter 5** studies how different binding modes impact the interfacial electron transfer dynamics of  $[Fe(bpy')_n(CN)_{6-2n}]^{(2n-4)}$  (where bpy' varies with linker group and n = 2-3). This series of complexes makes it possible to study the effect of cyano groups on injection and compare experimental results to a computational study of how the linker group influences the interfacial electron transfer rate. As in Chapter 4, the studies build upon each other, progressing from dynamics in solution, to bound, to interfacial electron transfer.

**Chapter 6** concludes this body of work by reflecting on how my research contributes to what is known about Fe(II)-based complexes in solar cells and where things are headed. There are a number of avenues being pursued to improve the efficiency of solar cells incorporating iron sensitizers. Work has predominately focused on modifying the iron complexes themselves in order to hinder charge transfer deactivation, and current methods will be highlighted. Additionally, the overall efficiency is expected to improve when all of the cell components have been optimized for an iron-based sensitizer.

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# **2** Experimental methods

This chapter describes the instruments and techniques employed to gather the data presented in this dissertation, as well as how to analyze said data. These methods comprise static and time-resolved spectroscopic measurements, such as UV-Vis absorption and ultrafast transient absorption spectroscopy. Computational methods will also be discussed. All data were collected with spectrophotometric grade solvents, unless otherwise indicated.

## 2.1 Steady-state absorption measurements

For transition metal complexes, a variety of electronic transitions can be observed in the ultraviolet (UV) and visible spectral regions and are characterized by the types of orbitals involved in the absorption. Transitions may occur between orbitals on the ligand, the metal, or as charge transfer between the two. A transition which promotes an electron from one ligand-based state to another is known as an intraligand transition. A transition that occurs between two states on the metal center is referred to as a d-d transition; it may also be called a ligand field (LF) transition. An absorption that involves the transfer of an electron from a metal-based orbital to a ligand-based one is known as metal-to-ligand charge transfer (MLCT). The inverse is described as ligand-to-metal charge transfer (LMCT). A complex that contains multiple metal centers may also exhibit charge transfer between two metal centers, known as metal-to-metal charge transfer (MMCT). An absorption spectrum can help distinguish between these different transitions, provided there is not significant overlap of absorption bands in the same wavelength region.

Absorbance is the measure of a molecule's ability to absorb light at wavelength  $\lambda$ . This attenuation of light correlates with properties specific to the sample being studied, according to the Beer-Lambert law:

$$A(\lambda) = \log_{10}\left(\frac{I_0(\lambda)}{I(\lambda)}\right) = \varepsilon(\lambda) \cdot b \cdot c$$
 Equation 2.1

where A is the absorbance (and has been referred to as optical density in the past),  $I_0$  and I represent the intensity of light before and after traversing the sample medium, respectively,  $\varepsilon$  is the molar absorptivity (also known as the extinction coefficient, in M<sup>-1</sup>cm<sup>-1</sup>), b is the path length of the cuvette (in cm), and c is the sample concentration (in M). Since concentration and path length are wavelength independent, the molar absorptivity is an indicator of how efficiently a molecule absorbs a given wavelength of light. Values can range from nearly zero to greater than 10,000 M<sup>-1</sup>cm<sup>-1</sup>. Typically, the molar absorptivity values of charge transfer transitions are intense, on the order of  $10^3 - 10^4$  M<sup>-1</sup>cm<sup>-1</sup>. Conversely, weak molar absorptivity values are observed for d-d transitions (typically less than 100 M<sup>-1</sup>cm<sup>-1</sup>).

The significant difference between the molar absorptivity values of charge transfer and d-d transitions arises primarily from two selection rules.<sup>1</sup> The spin selection rule conveys that only transitions between states of the same multiplicity are allowed. Forbidden transitions of this sort may become 'allowed' (with molar absorptivity values around 1  $M^{-1}cm^{-1}$ ) through spin-orbit coupling. In addition to the spin selection rule, the Laporte selection rule is particularly relevant for LF transitions, which states that there must be a change in parity (gerade  $\rightarrow$  ungerade, or vice versa). So, for a molecule with octahedral symmetry, as is common for the complexes described in this dissertation, all d-d transitions are formally Laporte-forbidden. Despite being forbidden, deviation from perfect symmetry and vibronic coupling can disrupt this enough to permit weakly-allowed transitions. Since charge transfer transitions are considered both spin-allowed and symmetry-allowed, they exhibit peaks which are much more intense. These guidelines, in conjunction with other physical measurements, can help interpret the origin of peaks observed in

a molecule's electronic absorption spectrum, knowledge which is necessary in understanding the photophysical processes that follow the absorption of light.

#### 2.1.1 Varian Cary 50 UV-visible spectrophotometer

Ground state electronic absorption spectra were typically measured in a 1-mm path length quartz cell, prior to and following ultrafast time-resolved absorption measurements. Before each use, a wavelength calibration was performed. Typically, the spectrophotometer was set to collect UV-Vis spectra between 200 and 800 nm at 1 nm intervals on the 'fast' scan rate. The instrument was blanked with air, and a solvent scan was taken to allow for baseline correction of the sample spectrum at the wavelength of interest. Since the cell holder was made for 1-cm path length cuvettes, the 1-mm cells were held in place in the holder during the scans. Samples for time-resolved spectroscopic measurements were generally prepared with ground state absorbances between 0.3 and 0.6 at the excitation wavelength to be studied. As for studies involving dye-sensitized solar cells, they were too large for the cell holder, and so each was held against the wall in front of the detector opening in order to minimize movement while collecting the absorption spectrum. After completing these scans, data were saved as comma separated values text files (.csv) and named based on the date and sample studied.

#### 2.1.2 PerkinElmer LAMBDA 1050 UV/Vis/NIR spectrophotometer

Molar absorptivities of the molecule of interest were measured in 1-cm path length quartz cells using serial dilutions of the original solution. As this is a double-beam instrument, a second, matched cell with solvent was used as the reference. Measurements were taken after allowing the lamp to warm up for at least 20 minutes. Unlike the Varian Cary 50 spectrophotometer, this instrument only needs to be calibrated every few months. This spectrophotometer features a 3-detector module which was used for solution-based measurements, and can also be equipped with a 150 mm InGaAs integrating sphere for the collection of transmittance data on solar cells. In the PerkinElmer UV WinLab program, the spectrophotometer was set to collect UV-Vis spectra between 200 and 900 nm at 1 nm intervals. The data were exported and saved as .csv and .sp files to a folder, named based on the date and sample studied.

## 2.2 Ultrafast time-resolved absorption measurements

Absorption of a photon promotes an electron from the ground state to a higher energy level, placing that molecule in an excited state. Following photoexcitation, there are many options as to how this excited state may be deactivated.<sup>2</sup> Light absorption can induce a chemical reaction, such as the redox reaction in interfacial electron transfer described in Chapter 1. Alternatively, physical processes may relax the excited complex to other states through the dissipation of energy. Examples of possible relaxation pathways for excited state evolution are depicted in Figure 2-1.



**Figure 2-1.** Generalized Jablonski diagram of photophysical processes involved in relaxation. The energy level of each state is indicated on the vertical axis, while states are grouped by spin multiplicity along the horizontal axis. GS refers to the ground state. ES signifies the excited state. S and S' denote different spin states.

Relaxation from an excited state can involve radiative and/or non-radiative processes.

Radiative decay refers to processes which emit light, such as fluorescence or phosphorescence.

Fluorescence occurs between two states with matching spin multiplicities, whereas the spin

multiplicities differ in phosphorescence. Non-radiative decay processes shown here include internal conversion, intersystem crossing, and vibrational relaxation. Internal conversion describes relaxation between two electronic states of the same spin multiplicity by transferring heat to the solvent. Intersystem crossing involves an isoenergetic transition from one state to another with a different spin multiplicity. Vibrational relaxation can refer to relaxation within a given state by transferring heat to the surrounding medium (vibrational cooling, VC) or transferring energy to different vibrational modes within the molecule itself (intramolecular vibrational redistribution, IVR). There are rates associated with each of these processes, and being able to detect and distinguish what happens following photoexcitation is very important.



Nuclear Coordinate

**Figure 2-2.** Generalized potential energy level diagram displaying effects of pump and probe interactions on a sample during a TA experiment. The pump pulse promotes an electron to an excited state. The probe pulse monitors the excited state absorption.

One way to analyze the dynamics of processes following excited state absorption is with time-resolved spectroscopy. My studies have employed transient absorption (TA) spectroscopy (described briefly in Chapter 1) for this purpose. In this type of experiment, a pump pulse excites a fraction of the molecules in the sample and is followed by a less intense probe pulse which monitors excited state absorption by recording changes to the transmitted intensity through the sample over time.<sup>3,4</sup> A simplified example of how these pulses interact with the potential energy surfaces of a molecule is illustrated in Figure 2-2.

Signal is reported as the difference between the absorbance of the excited sample and that of the ground state,  $\Delta A$ , at time t and probe wavelength  $\lambda$ . This is expressed as:

$$\Delta A(\lambda, t) = \log_{10}\left(\frac{I_{GS}(\lambda)}{I_{ES}(\lambda, t)}\right) = \sum_{i} [\varepsilon_{i}(\lambda) - \varepsilon_{GS}(\lambda)] \cdot b \cdot c_{GS} \cdot \eta_{i}(t) \quad \text{Equation 2.2}$$

which is an extension of the Beer-Lambert law.<sup>5</sup> Here,  $I_{GS}$  and  $I_{ES}$  represent the intensities of the probe beam through the sample before and after photoexcitation, respectively,  $\varepsilon_i$ - $\varepsilon_{GS}$  represents the difference between the molar absorptivities of transient species i and the ground state at the probe wavelength, b is still the path length of the sample,  $c_{GS}$  is the concentration of the ground state, and  $\eta_i$  denotes the fraction of molecules that are in excited species i at time t.  $\eta$  is dependent on a number of variables, including the incident photon flux and the molar absorptivity of the ground state at the pump wavelength.<sup>6</sup> Equation 2.2 is represented by a summation, as multiple sources may contribute to the signal observed if the absorption bands of different species happen to overlap. An example of a transient absorption spectrum, and how the ground state and excited state components contribute to it, is shown in Figure 2-3.

The sign of  $\Delta A$  provides information about the excited state relative to the ground state. A negative signal may arise if the excited state does not absorb as strongly as the ground state. Here, a decrease in the concentration of molecules in the ground state increases the number of photons reaching the detector, resulting in a negative response referred to as ground state bleach (GSB). Naturally, this only occurs in wavelength regions where the ground state absorbs light. A negative signal may also be the result of stimulated emission (SE), where a photon from the probe pulse induces emission of a second photon from the sample, and both are detected. A positive signal can



**Figure 2-3.** (a) Comparison of the absorption spectra of the ground state (in green) and the excited state (in blue) of a hypothetical molecule. (b) Example of transient absorption data (dashed line) at some delay after photoexcitation.

signify excited state absorption (ESA), where the excited state species absorbs the wavelength of the probe pulse to a greater extent than the ground state. Another possible source for a positive signal refers to product absorption. A reaction (accidental or not) may take place where the product then absorbs some of the light. If the molecule has not already returned to the ground state, a point where the transient absorption signal is zero represents an isosbestic point, where the molar absorptivities of the ground state and the excited state are equal.

TA spectroscopy can be used to study dynamics over a large range of timescales, so while the principles and interpretation of data do not change with timescale, the data collection process might. Measuring the dynamics for interfacial electron transfer and charge transfer deactivation of iron(II) polypyridyl complexes requires ultrafast spectroscopic techniques, where a process is classified as 'ultrafast' if the phenomena is on the order of picoseconds (ps) or less. Since dynamics on these timescales are too fast to be monitored by electronics directly, my time-resolved spectroscopic experiments utilize femtosecond (fs) pulses where the delay between the pump and probe pulses must be varied by physically changing the distance traveled by the pump pulse with a linear stage. When it comes to collecting TA data, the ultrafast laser lab in the McCusker group has two laser systems, dubbed Wile E and Road Runner, which differ both in pulse duration and the maximum possible time delay between the pump and probe pulses. These laser systems allow for data collection from roughly 35 fs up to 13 nanoseconds (ns), a time point which overlaps nicely with the group's ns laser system, should a longer delay be necessary. Both fs laser systems were used to collect the data presented in this dissertation. The basic components which make up these systems will now be described.

#### 2.2.1 Basic principles of ultrafast laser systems

Each laser system described here starts with an oscillator which dictates the pulse duration of the beams. Next, this output must be amplified as it is too weak to be used in spectroscopic studies directly. To prevent damage to optics and gain media from high peak powers during the amplification process, the pulses are temporally 'chirped' in the stretcher to increase the pulse dispersion before entering the regenerative amplifier. Essentially, this results in redder wavelengths traveling ahead of bluer wavelengths. Once in the regenerative amplifier, polarization optics (e.g. Pockels cells) trap the beam in the laser cavity such that it makes several passes through a gain medium until reaching saturation. For both of these systems, the active laser medium is a Ti:Sapphire crystal that has been pumped at a 1 kilohertz (kHz) repetition rate. The amplified pulse is then released to the compressor from the cavity following a polarization switch induced by the Pockels cell. The compressor undoes the work of the stretcher to return a temporally-short pulse, where the redder and bluer wavelengths of the beam once again travel at the same time delay.

Once out of the regenerative amplifier, the laser beam travels through a 70:30 beamsplitter to generate the two pulses necessary for TA spectroscopy, with 70% of the power allocated for the

pump and 30% for the probe. Although one would be ready to conduct TA experiments at this point, options would be limited to studying complexes and excited states which absorb the same wavelength as the regenerative amplifier output, or roughly 800 nm. One way to get around this is with an optical parametric amplifier (OPA), which uses the output from the regenerative amplifier to generate spectrally tunable laser pulses with wavelengths ranging from the UV to infrared (IR). Depending on the desired wavelength, different tuning configurations are necessary.

Within an OPA, the signal beam is produced by mixing a fraction of the 800-nm input with a white light continuum (WLC) in a nonlinear crystal. The idler beam is generated by mixing the signal beam with more of the 800-nm input in a second nonlinear crystal. The signal and idler beams, tuned by the timing of the beams and crystal angles, can be used as is to pump or probe in the near-IR region. For visible wavelengths, either beam is mixed with the remaining pump beam in a *beta*-barium borate (BBO) crystal through a process known as sum-frequency generation. In this case, two photons combine to generate one photon with an angular frequency equal to the sum of the input photons. Second-harmonic generation represents a special case where the two angular frequencies are equal. Fourth-harmonic generation is required to generate the bluest wavelengths, essentially the second-harmonic of the second-harmonic. Although the OPAs in the McCusker group do not currently have these capabilities, mid-IR pulses can be generated through differencefrequencies are taken, rather than the sum. For both ultrafast laser systems, the desired wavelength for the pump beam was tuned with an OPA. This was not always the case with the probe beam.

Equation 2.2 highlights that data from TA spectroscopy is two-dimensional, dependent not only on time, but also wavelength; this is further illustrated in Figure 2-4. And so, there are different methods of collecting time-resolved data, depending on which dimension is being

24



**Figure 2-4.** Example of how TA data is two-dimensional, allowing us to select either particular time slices (spectrum boxed in red) or individual wavelengths (spectrum boxed in green).

emphasized and is subject to the bandwidth of the probe beam. To gather data over a broad spectral window, a WLC was created by focusing 800-nm light into either calcium fluoride (CaF<sub>2</sub>) or sapphire. This continuum is then collected by a spectrometer to measure changes to the spectrum over time. For full spectral traces,  $\Delta A$  is determined from a background spectrum collected at a time point prior to excitation (representing  $I_{GS}(\lambda)$ ) and a spectrum collected at some time delay after that (representing  $I_{ES}(\lambda,t)$ ). Alternatively, the kinetics of a particular process can be studied by a probe beam with a narrow bandwidth, where the probe source is either an OPA or a portion of the WLC selected by a bandpass filter or a monochromator. Here,  $\Delta A$  is calculated from the signals of a photodiode after the sample ( $I_{ES}(\lambda,t)$ ) and a reference photodiode set to read the same voltage as the sample photodiode prior to excitation ( $I_{GS}(\lambda)$ ). Including a reference photodiode allows for improved signal-to-noise of the data collected, as it accounts for shot-to-shot laser instability. For single wavelength measurements, a lock-in amplifier is used to record the difference between the two photodiodes, after which  $I_{ES}(\lambda,t)$  can be extracted during the data work-

up process since the value for  $I_{GS}(\lambda)$  is known. Custom-built LabVIEW programs allow for all time-resolved data to be collected as well as analyzed.

#### 2.2.2 Wile E laser system

This laser system produces pulses that are approximately 130 fs in duration and has been described previously.<sup>7</sup> It has been modified since then to include a 1035-mm stage on the pump line. This stage double passes the pump beam, making it possible to collect data with time delays out to over 13 ns. The source of the probe beam is a WLC, generated by focusing the output from the regenerative amplifier into a  $CaF_2$  window. To prevent damage, the  $CaF_2$  was continuously translated on a linear stage moving perpendicular to the direction of the laser beam. This laser system (in Figure 2-5) was used to study the ground state recovery lifetimes of Fe(II) complexes (discussed in Chapters 3 thru 5) and to check for a pump dependence on the injection yield of Fe(II) dyes adsorbed to titanium dioxide (TiO<sub>2</sub>) with various electrolytes (in Chapters 4 and 5).



**Figure 2-5.** Layout of Wile E laser system. The green beam represents the pump beam line. The red beam bypassing TOPAS 2 is the probe beam which generates a WLC just before the sample.

#### 2.2.3 Road Runner laser system

This laser system produces pulses with a pulse duration of 35 fs. The reader is directed to Chapter 2 of Dr. Eileen Foszcz's dissertation for more specific information regarding its hardware and software.<sup>8</sup> The translation stage on the pump line allows for delays out to roughly 1.3 ns. This

system was used when studying dynamics with lifetimes less than 1 ps, such as the MLCT state lifetimes of Fe(II) polypyridyls and injection dynamics of Fe(II) dye-TiO<sub>2</sub> assemblies (in Chapters 4 and 5). Multiple pump/probe configurations exist on this system for different TA experiments, where the changes are reflected in the probe beam line, as will be discussed below.

# 2.2.3.1 One-color measurements: Single OPA

The configuration in Figure 2-6 is referred to as 'one-color' due to the probe beam deriving from the output of the pump OPA with a beamsplitter. This set-up was used primarily to measure the pulse duration of the pump beam, before transitioning the laser table to a 'two-color' set-up.



Figure 2-6. Layout of Road Runner laser system under 'one-color' conditions.

## 2.2.3.2 Two-color measurements: Two OPAs

In this scenario, both OPAs on the Road Runner laser table are used – one for the pump beam and one for the probe. The beam path for the pump is identical to the 'one-color' condition, while the probe is the same after being directed into the probe translation stage. Utilizing an OPA to produce the probe beam allowed for wavelengths ranging from the visible to the near-IR. This kind of set-up was employed when studying the injection dynamics of Fe(II) dye-TiO<sub>2</sub> assemblies.



**Figure 2-7.** Layout of Road Runner laser system under 'two-color' conditions, where the probe beam comes from the second OPA.

2.2.3.3 Two-color measurements: Pump OPA and Probe WLC

In this 'two-color' situation, the pump wavelength is determined with an OPA, while the probe wavelength is selected from a WLC. This layout allows for quick changes to the probe wavelength simply by changing the micrometer setting on the monochromator. The WLC probe source also makes it possible to collect full spectral data with the SPEX spectrometer. Certain optics on the table must be removed, as compared to the previous set-ups, to generate the WLC.



**Figure 2-8.** Layout of Road Runner laser system under 'two-color' conditions, where a white light continuum is produced as the probe beam.

#### 2.2.4 Checks to ensure reliable data

There are a number of things that need to be considered in order to collect short and accurate kinetics. The following topics apply to both laser systems; however, pulse compression is more essential for optimal function on the Road Runner laser system, as will be discussed.

#### 2.2.4.1 Beam polarizations

One fundamental property of light that needs to be carefully considered for proper data interpretation is polarization. As an electromagnetic wave, light travels along a sinusoidal path, say, along the z-axis. Thus, its electric field can be oriented in any direction in the xy plane. How it is oriented, or polarized, is determined based on the relative amplitudes and phase matching of the electric field along the x- and y-axes,<sup>9</sup> demonstrated by the following equation:

$$\boldsymbol{E}(z,t) = E_x^0 \sin(\omega t - kz + \phi_x) \hat{\boldsymbol{x}} + E_y^0 \sin(\omega t - kz + \phi_y) \hat{\boldsymbol{y}} \qquad \text{Equation 2.3}$$

where the electric field, **E**, at position z and time t is determined by the magnitude of the electric field in the x and y directions ( $E_x^0$  and  $E_y^0$ , respectively), the angular frequency ( $\omega$ ) of the wave, the wavenumber (k) associated with the light, and the absolute phase of the x and y components ( $\phi_x$  and  $\phi_y$ , respectively). Now, natural light sources tend to have a mixture of waves at multiple wavelengths such that the electric vectors are oriented randomly, resulting in what is known as unpolarized light. On the contrary, the pulses from these laser systems are referred to as linearly polarized. This means that the vector components in the x and y direction are in phase with one another ( $\phi_x=\phi_y$ ). When the phases do not match, elliptically polarized light is observed, where the electric field appears to rotate around the z-axis over time. Interestingly, elliptically polarized light can rotate either to the right or to the left, depending on whether the sine of the phase difference ( $\phi_x-\phi_y$ ) is a positive or negative value, respectively. Circularly polarized light represents a

specialized case where the phase difference is  $\pm \pi/2$ , and the amplitudes along the x- and y-axes are identical ( $E_x^0 = E_y^0$ ). Examples of these polarizations are shown in Figure 2-9.



Figure 2-9. Wave and vector representations of linearly, circularly, and elliptically polarized light.

Knowing the polarization of a laser beam is pertinent, not only because an optic's effectiveness can depend on the polarization of light hitting it, but also to be able to interpret data being collected during TA spectroscopy. Specifically, it is necessary to know how the two beams in TA experiments (the pump and the probe) are oriented relative to one another. Different experiments require different relative orientations, but a typical TA set-up will have the difference between the pump and probe beam polarizations set at 54.7 degrees.<sup>10</sup> This particular difference is referred to as magic angle because anisotropic responses are canceled out, leaving only signal due

to population dynamics. Since anisotropic signals can persist to the ps timescale,<sup>11–13</sup> they are extremely important to account for when the molecule of interest exhibits ultrafast dynamics.

The transmission axis of a polarizer allows it to preferentially select the polarization of light that passes through the optic. This is beneficial not only to produce linearly polarized light from unpolarized light, but can also be used to measure the polarization of a laser beam – it may be more aptly referred to as an analyzing polarizer in this situation. Two types of polarizers are featured on the ultrafast laser systems described here. Linear film polarizers, which consist of a dichroic polarizing film located between two N-BK7 windows with anti-reflective coating, absorb light that does not match the transmission axis. Glan-Laser polarizers, prepared from two air-spaced calcite prisms, transmit the component of the beam that is parallel to the transmission axis and reflect the component that is perpendicular. In general, the linear polarizers were used to clean up the beam polarization and maintain linearly polarized light just before the sample, while the Glan-Laser polarizers were used for measuring beam polarizations. As all of these polarizers



**Figure 2-10.** The amount of light transmitted through a polarizer based on the input polarization of linearly polarized light relative to the transmission axis of the polarizer. The intensity of the throughput is normalized to the initial intensity before the polarizer. Data are only plotted along the x-axis up to 180°, after which the data repeat.

have been placed in rotation mounts, they can be rotated as needed. The amount of light transmitted through a polarizer is related to the following equation:

$$I = I_0 \cos^2 \theta \qquad \qquad \text{Equation 2.4}$$

where  $\theta$  represents the angle between the transmission axis of the polarizer and the polarization of light that travels through it. This is referred to as Malus's Law.<sup>14</sup> The results of this are illustrated in Figure 2-10. Essentially, the polarization of linearly polarized light can be measured by rotating the analyzing polarizer to determine the angle at which there is the maximum throughput, as that is where the transmission axis of the polarizer matches the polarization of the beam. Since these polarizers were placed into the rotation mounts by hand, the values read off them may not be true; so, instead, it is the relative difference between the pump and probe beam polarizations that matter.

If a beam's polarization does not match that required for an experiment, a waveplate can be used to adjust it without affecting the intensity of the beam or its trajectory. Due to the damaging effects of high peak power, the beam polarization necessary for the prism compressor set-ups on Road Runner are actually modified by using two mirrors in a periscope instead. Two types of waveplates are found on these laser tables: half-wave ( $\lambda/2$ ) plates and quarter-wave ( $\lambda/4$ ) plates. These work by having a slow axis and a fast axis which are perpendicular to the beam direction, where the slow axis imparts a phase delay of  $\pi$  with a half-wave plate and  $\pi/2$  with a quarter-wave plate. The effects of this on the output polarization can be seen in Figure 2-11. If the beam's polarization matches either the fast or the slow axis, the beam will pass through without any change. For a half-wave plate, the beam polarization is rotated by 2 $\theta$ , where  $\theta$  refers to the number of degrees the polarization is off from the optical axis of the waveplate. For a quarter-wave plate, it is important to note that because of the  $\pi/2$  phase delay to only one of the two axes, if linearly polarized light enters a quarter-wave plate, it may exit as elliptically polarized light (circularly,



**Figure 2-11.** Effect of (a) half-wave and (b) quarter-wave plates on the polarization of linearly polarized light.

if  $\theta$ =45°). This is why a polarizer is found after the quarter-wave plate on the probe beam line for the Wile E laser system, to return it to linearly polarized light. The waveplates on these laser tables are also in rotation mounts, so  $\theta$  can be adjusted as necessary. By using both waveplates and polarizers, the beam polarizations for the pump and probe beams can be assessed and adjusted as needed before collecting spectroscopic data.

## 2.2.4.2 Stage alignment

While both the pump and probe beams are initially aligned up to the sample position by irises on the laser table, the time delay between the pump and the probe pulses is adjusted by moving the pump delay line during data collection. If the pump beam is not directed into and out of the translation stage properly, the beam will drift at the sample position as the stage is moved and changes in the TA signal may result from changes to the pump/probe overlap rather than excited state signal. Therefore, it is important to check the stage alignment by collecting data on a well-studied molecule first to ensure that the kinetics observed for new molecules are accurate. In an ideal situation, the excited state lifetime of the standard will be sufficiently long such that no decay is observed. As that is not always the case, it is important to know what percentage change to observe in order to say with confidence that everything is aligned. This is quantified by:

$$N(t) = N_0 e^{-(t/\tau)}$$
 Equation 2.5

where N(t) is the  $\Delta A$  value at time t, N<sub>0</sub> is the initial signal amount at t=0, and  $\tau$  is the lifetime (or time constant) associated with the excited state. If the experimental value of N(t) at time t does not match the one estimated by Equation 2.5, the alignment is most likely off and no data should be trusted until this is corrected.

## 2.2.4.3 Pulse characterization

There are a number of instances where it is important to know the pulse duration of the beams being utilized. Not only is it helpful in order to identify whether a laser system is optimized properly, but for spectroscopic data, the pulse duration also controls whether it is possible to produce coherence in a sample or observe transitions which occur within the first few hundred fs. Similarly, it is often necessary to measure the instrument response function (IRF) of the laser system to determine its time resolution for fitting purposes, where the IRF is a convolution of the pulse duration and the detector response time. Since both ultrafast laser systems in the McCusker group produce fs pulses, one cannot rely on electronics to measure these parameters in real time. Instead, it is necessary to study the nonlinear optical effects that result from the pump and probe pulses interacting with each other. Two techniques are commonly employed to characterize pulses from these laser systems, based on the optical Kerr effect (OKE) and cross-correlation (XC).

The Kerr effect refers to the phenomenon where an applied electric field is able to induce a change in the refractive index of a medium. Although this was originally discovered by applying an external voltage across solids<sup>15</sup> and liquids,<sup>16</sup> it has since been shown that birefringence can also be induced by the high intensity, electromagnetic field of a laser pulse (thus, the term *optical* Kerr effect).<sup>17</sup> As a result, oscillatory artifacts due to self-phase modulation and cross-phase modulation are seen in TA data when the pump and probe beams spatially and temporally overlap in the sample (when the time delay is zero). While OKE spectroscopy is more generally used as a technique to identify how long the induced birefringence of a sample lasts to study the timescale associated with orientational diffusion,<sup>18</sup> it is also convenient for establishing the pulse durations of the pump and probe beams. An autocorrelator performs the same duty via the cross-correlation of a pulse with itself, and in fact, there is one in the McCusker group's inventory, however, the doubling crystal employed for that set-up limits its use to wavelengths near 800 nm. An OKE experiment does not have those restrictions. As for the data collected from a XC set-up, it does a better job accounting for the IRF of the system in that particular solvent. The difference between pulse characterization by OKE spectroscopy versus XC relies simply on how the transmission axis of the analyzing polarizer relates to the probe beam polarization (see Figure 2-12).



**Figure 2-12.** Example depictions of the laser set-up after the solvent sample for determining pulse durations (left) and instrument response function (right). The double-headed arrows represent the polarization of the beams, with the beam after the polarizer matching its transmission axis.

While conducting these measurements, the cuvette in the sample holder should only contain solvent to simplify the possible signal sources. If the goal is to identify when the solvent response ends in order to determine when to start fitting dynamics specific to the molecule of interest, the same solvent used to dissolve the sample should be employed in the XC measurement, as that measurement is solvent-dependent.<sup>19</sup> Additionally, in this configuration, the analyzing polarizer is optional, given that it should be set to match the polarization of the probe beam (i.e. parallel). To study pulse duration via OKE spectroscopy, an analyzing polarizer should be placed after the sample with the transmission axis set 90° from the polarization of the probe beam. Under



**Figure 2-13.** Representative spectra from OKE measurements for acetonitrile (left) and methanol (right) with the corresponding Gaussian fit (black line), following photoexcitation at 480 nm.

these conditions, no photons should reach the photodiode unless both the pump and probe beams are present in the sample to induce birefringence.

In an ideal scenario, the OKE response can be fit by a Gaussian distribution, as it is a convolution of two Gaussian pulses, peaking when the delay between the pump and probe pulses is zero; however, this is not always the case considering the second half of the measured response is dependent on how quickly the anisotropic signal dissipates. Methanol has been found to provide a cleaner signal response in this regard, and so, is recommended as the solvent of choice for OKE measurements (Figure 2-13). Otherwise, care must be taken to only fit the portion of the data which follows the Gaussian curve, up to a few data points beyond when the maximum absolute signal is observed. From the fit parameters, the pulse duration can be assessed with the following equation:

$$\tau_c = \sqrt{\tau_{pu}^2 + \tau_{pr}^2}$$
 Equation 2.6

where  $\tau_c$  refers to the full width at half maximum (FWHM) calculated from the width of the Gaussian fit,  $\tau_{pu}$  refers to the pulse duration of the pump pulse, and  $\tau_{pr}$  refers to the pulse duration

of the probe pulse. In a one-color experiment, the pump and probe beams are the same wavelength and should pass through the same amount of glass, so they can be treated as equal ( $\tau_{pu} = \tau_{pr}$ ). Therefore, the pulse duration of the beam in a one-color experiment can be solved for directly after obtaining the FWHM from the OKE results. Then, if the pulse duration of one of the pulses has already been determined, the other can be solved for in a two-color experiment.

## 2.2.4.4 Pulse compression

If the IRF of an ultrafast laser system is significantly longer than expected, such that it is not possible to accurately detect the ultrafast dynamics associated with the molecule of interest, the pump and probe pulses may need to be compressed. The reasoning behind this can be explained by the following equation, describing the time-bandwidth product:

## $0.441 \le \Delta \tau \Delta \nu$ Equation 2.7

where 0.441 is specific to Gaussian-shaped pulses,  $\Delta \tau$  refers to the beam's pulse duration, and  $\Delta v$  refers to the spectral bandwidth of the beam. Pulses which exhibit the minimum possible time-bandwidth product, which speaks to the pulse quality, are said to be transform-limited. From this equation, it is easy to see that as the pulse duration of a beam decreases, the bandwidth increases. For instance, a 130-fs pulse exiting the regenerative amplifier on Wile E should have a bandwidth of  $3.39 \times 10^{12} \text{ Hz} - \text{given}$  a center wavelength at 800 nm, that amount of energy would be reflected in a bandwidth of 7.24 nm. Conversely, a transform-limited 35-fs pulse on Road Runner should have a bandwidth of  $1.26 \times 10^{13} \text{ Hz}$ , resulting in 26.88 nm at 800 nm. Interestingly, as the pulse duration decreases and the subsequent bandwidth increases, ultrashort pulses become more sensitive to the effects of group velocity dispersion (GVD). This means that, as a laser pulse travels through optics, such as lenses, the beam may be temporally stretched due to each medium's wavelength-dependent index of refraction. So, the pulse duration registered at the photodiode will



**Figure 2-14.** Broadening of a femtosecond pulse at 800 nm after propagation through 0 mm (black), 1 mm (red), 10 mm (yellow), 20 mm (green), and 50 mm (blue) of N-BK7 material. The dashed lines represent conditions for Road Runner (purple, at an input pulse duration of 35 fs) and Wile E (black, at 130 fs).

be inadvertently longer, as each wavelength travels through the media at slightly different rates. Figure 2-14 demonstrates how the amount of N-BK7 (a common lens material used on these laser tables) that a fs laser pulse travels through impacts the output pulse duration, with vertical lines to highlight how differently the two ultrafast laser systems in the McCusker laser lab are effected. It serves to show that there is a more serious need for pulse compression on the Road Runner system, especially if the dynamics of interest occur on the sub-100 fs timescale.

In order to have transform-limited pulses at the sample, the pulses must be treated to preemptively correct for the stretching that occurs while traveling along the laser table. Since optical materials such as lenses introduce positive chirp, where redder wavelengths lead the blue, a material which introduces an equal and opposite chirp (negative chirp) is desired. This is achieved by directing each beam through a prism compressor such as the one on display in Figure 2-15. This particular set-up refers to a folded prism compressor, where the folding mirror



**Figure 2-15.** Representation of folded prism compressor set-up. In this example, the incoming pulse is compressed and leaves stretched. The opposite can be true if in the incoming pulse has redder wavelengths leading the blue.

allows for the beam to travel back through the original prisms at a slight vertical displacement, thus, bypassing the need for four separate Brewster prisms. Essentially, the first prism introduces angular dispersion, the second collimates the beam, and the folding mirror sends the beam back through the two prisms to undo the spatial separation. Overall, this has the effect of making redder wavelengths travel through more glass, slowing them.

Changing the distance between the two prisms adjusts how much negative chirp is introduced, and since angular dispersion is wavelength-dependent, that distance will need to be adjusted every time the beam wavelength is switched. Based on information provided by Newport Corporation,<sup>20</sup> a worksheet was generated to solve for this distance based on material properties specific to LaKL21 prisms (the kind used on the Road Runner laser table). Overall, four parameters are needed to reliably estimate the distance desired between the apex of the first prism and the apex of the second: the center wavelength of the pulse, the bandwidth associated with the laser beam, the 1/e<sup>2</sup> beam diameter, and the uncompressed pulse duration. The first two parameters can be determined by measuring and fitting a UV-Vis spectrum of the beam in Igor Pro. The beam diameter can be determined with an iris, a power meter, and a caliper, by measuring the power as a function of the iris aperture size. The uncompressed pulse duration can be established by collecting an OKE measurement (for example, as a one-color experiment) without the prism

compressor in the beam path. From here, the optimal prism spacing can be set (with the prisms at Brewster's angle), the laser pulse can be aligned into and out of the folded prism compressor, and a new OKE measurement can be collected to test how compressed the pulse is. Adjustments can be made until a satisfactory pulse duration is reached, after which spectroscopic measurements can be done on the molecule of interest.

## 2.3 Computational methods

Density functional theory (DFT) was used in order to get a better understanding of what could be driving trends observed in experimental results. Specifically, these calculations were performed to understand how different solvent environments may influence the energetics of different LF states for a handful of Fe(II) complexes (discussed in Chapter 3).

#### 2.3.1 Gaussian 09 software

Theoretical calculations were carried out using the Gaussian 09 software package<sup>21</sup> through the High Performance Computing Center (HPCC) of the Institute for Cyber-Enabled Research (iCER) at Michigan State University. The initial geometries of select Fe(II) complexes came from their crystal structures, downloaded from the Cambridge Structural Database.<sup>22</sup> Following the advice of Dr. Daniel Ashley and Professor Elena Jakubikova (at North Carolina State University), the geometries of Fe(II) complexes were optimized at the spin-unrestricted B3LYP<sup>23-25</sup> level, using the SDD effective core potential and associated basis set<sup>26</sup> for the Fe metal center, the 6-31G(d) basis set<sup>27,28</sup> for C and N atoms, and the 6-31G(d,p) basis set<sup>27,28</sup> for H atoms without symmetry restrictions. This is comparable to their own calculations of Fe(II) complexes.<sup>29–31</sup> Geometry optimizations and frequency calculations were carried out under vacuum and in solution, as imposed by the conductor-like polarizable continuum model (CPCM).<sup>32,33</sup>

## 2.4 **Programs for data analysis**

A number of programs were necessary to analyze the experimental and computational data described throughout this body of work. In the following section, I will discuss their general function and the information obtained from them.

#### 2.4.1 LabVIEW

The laboratory virtual instrument engineering workbench, or LabVIEW, platform (National Instruments, Inc., Austin, TX, USA) was used to collect the ultrafast TA data discussed in this dissertation. One of the changes to this programming implemented during my time here as compared to previous group members is that one scan now represents the data collected while moving the pump delay line in a single direction, whereas it previously referred to the average of data collected both in the forward direction and then back to the starting position. This modification was done to prevent any inconsistencies in the stage positions between the two directions.

In addition to the custom LabVIEW programs used to collect time-resolved spectroscopic data, other programs were developed with LabVIEW software to convert that raw data to  $\Delta A$  values. For single wavelength data, the parameters needed to work up raw files include the stage position which corresponds with zero time delay between the pump and probes pulses,  $I_{GS}(\lambda)$  (as read from the signal photodiode prior to photoexcitation), and the sensitivity setting for the lock-in amplifier. There is also an option to enter how many of the initial data points one would like to average for a baseline correction. For full spectral data, although the results were already in units of change in absorbance, a LabVIEW program was created to prepare that data for graphing. This program requires input regarding the stage position associated with zero time delay, the first pixel with data (in case the spectra were truncated), and spectrometer-specific information to convert pixels to wavelength.

Another change that has been made since the last dissertation<sup>8</sup> to discuss the McCusker group ultrafast laser lab refers to how single wavelength data is collected, and, as a result of those changes, how it is worked up. Part of how a lock-in amplifier works is by employing phase-sensitive detection to weed out noise.<sup>34</sup> This entails generating a reference sine wave, which should be in-phase with the actual signal response being detected and amplified. Any change in phase between these two sine waves means that the amount of signal that exits through the main output channel is not the maximum possible. The majority goes to channel X, as the 'in-phase' component, while the remaining part goes to channel Y, the 'quadrature' component. If the data from both channels are simultaneously collected and saved, they can be mathematically recombined to generate R, which corresponds to the signal amplitude and is not dependent on phase. And so, the work-up program was modified to incorporate data from both X and Y channels to calculate R, but is otherwise unchanged from previous versions.

### 2.4.2 Igor Pro

This software (WaveMetrics, Inc., Lake Oswego, OR, USA) was used for both graphing and data analysis purposes. The Gaussian function was used to determine the FWHM associated with data from XC and OKE measurements. This program was also used to fit single wavelength traces with built-in mono- and bi-exponential functions. It was used to graph two-dimensional plots from full spectral data measurements as well. The multipeak fitting analysis package was used to deconvolve peaks found in the electronic absorption spectra of Fe(II) complexes. For data which exhibited coherence, the residuals that remained after subtracting out the population dynamics were worked up with the fast Fourier-transform (FFT) analysis procedure to estimate the frequencies associated with the oscillations in the TA data. The results for all of these analyses are found throughout the dissertation.

# 2.4.3 Solid-G

The Solid-G program is used to compute ligand solid angles, equivalent cone angles, and overlap between ligands in organometallic compounds.<sup>35</sup> A 'solid angle', measured in steradians, refers to a two-dimensional angle in a three-dimensional sphere, calculated from the area of a surface on the sphere divided by the square of the sphere's radius. An example of this is portrayed in Figure 2-16. The Solid-G program takes these angles and converts them to percentages in order to describe how much of a metal center in a transition metal complex is shielded by the ligands around it. This percentage is referred to as the G-parameter and is calculated by:

$$G = 100 \frac{\Omega}{4\pi} = 100 \frac{A}{4\pi r^2}$$
 Equation 2.8

where  $\Omega$  refers to the solid angle, A is the surface area, and r is the radius of the sphere. While this program can be used to investigate the congestion around a metal center that results in potentially unfavorable interligand contact, its primary purpose here was to estimate how much of the metal center was left exposed and how that percentage changed between the LF states in different Fe(II) complexes. See Chapter 3 for more information.



**Figure 2-16.** Illustration of geometrical solid angle ( $\Omega$ ), measured from the spherical surface area (A) and radius (r) of that sphere.

#### 2.4.4 Olex2

Although traditionally used to solve and analyze crystallographic data, the Olex2 program<sup>36</sup> was used to calculate the molecular volume and molecular surface area of different structures – both from crystal structures and computationally-optimized structures. The results obtained from this program are included in Chapter 3.

## 2.4.5 MATLAB

MATLAB (short for matrix laboratory) is a product by Mathworks, Inc. (Natick, MA, USA) used for numerical computing. A MATLAB script written by Dr. Andrey Demidov and Professor Paul Champion at Northeastern University (since updated by J. Dan Roscioli of the Beck group and Bryan C. Paulus of the McCusker group, both at Michigan State University) based on linear predictive singular value decomposition (LPSVD)<sup>37</sup> was used to analyze data exhibiting coherence in order to resolve the oscillations present in the data, similar to the FFT results obtained from Igor Pro discussed earlier. Unlike Igor Pro, this technique is able to extract the damping times and phases associated with the detected frequencies. The reader is directed to Appendix E of Chapter 2 in Dr. Eileen Foszcz's dissertation<sup>8</sup> for details on how to operate this program. The results from this procedure can be found in Chapter 6.

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# **3** Outer-sphere effects on the excited state dynamics of ligand field states in Fe(II) polypyridyl complexes

# 3.1 Introduction

To understand how a reaction proceeds in solution, it is important to consider how the solvent environment may influence the dynamics of that process. Even under static conditions, it is clear that the solvent environment can affect the physical properties of a molecule.<sup>1</sup> Many studies have demonstrated the impact of intermolecular effects on absorption and fluorescence properties, where the interactions between the solute and the solvent can shift the energies of the potential energy surfaces of reactants and products in relation to those in the gas phase.<sup>2</sup> Solvation can induce structural modifications, electrostatic interactions, polarization effects, or even aggregation of the solute molecules. The band position, band shape, and intensity of peaks for the molecule of interest can vary with solvent, as highlighted in electronic spectra which depict transitions associated with a rearrangement of charge. Even the dipole moment of a transition can vary with changes in solvent, revealing that the solvent environment can modify the electronic distribution of that transition. Despite the wealth of knowledge already obtained on the impact of solvation, there is still a lot of work to be done when it comes to understanding the effect of solvent under non-equilibrium conditions.

There is interest in understanding how solvent responses may couple to and influence reactions.<sup>3–5</sup> This response can be significant for charge transfer processes where there is a redistribution of charge on the solute molecule that the solvent medium responds to. To start, when a polar solute is dissolved in a polar solvent, the solvent molecules will be arranged in such a way as to be in equilibrium with the ground state charge distribution of the solute molecule. If, for example, the solute molecule then undergoes a metal-to-ligand charge transfer (MLCT) following irradiation, an electron will be shifted to a new location on the solute molecule. Since this charge

transfer is instantaneous compared to any solvent response, the solvent molecules will still be oriented as they were prior to the excitation of the solute molecule. As a result of this change, the solvent environment may then reorganize to stabilize the new charge distribution. While understanding the time dependence of this solvation process alone is interesting, previous work also suggests that the solvent response can influence the relaxation dynamics of solute molecules.<sup>6</sup>

While charge transfer excited states are known to be particularly responsive to solvent properties, ligand field (LF) excited states, which correspond to electronic structure rearrangements that are largely localized on the metal center, are traditionally thought to be relatively insensitive to solvent due to the ability of the ligand environment to shield the metal from the surrounding medium.<sup>7</sup> While studying iron-based complexes, a previous group member, Dr. Allison Brown, noticed a surprising solvent dependence on the  ${}^{5}T_{2} \rightarrow {}^{1}A_{1}$  relaxation process, a LF transition, in tris(2,2'-bipyridine)iron(II), [Fe(bpy)<sub>3</sub>]<sup>2+,8</sup> This raises interesting questions as to the nature of this solvent dependence, which I hope to answer with the complexes found in Figure 3-1.



a: R = R' = H b: R = CH<sub>3</sub>; R' = H c: R = H; R' = CH<sub>3</sub> d: R = C(CH<sub>3</sub>)<sub>3</sub>; R' = H

**Figure 3-1.** Molecular structure for complexes discussed here: (a)  $[Fe(bpy)_3]^{2+}$ , (b)  $[Fe(dmb)_3]^{2+}$ , (c)  $[Fe(5,5'-dmb)_3]^{2+}$  and (d)  $[Fe(dtbbpy)_3]^{2+}$ .

# **3.2** Experimental details

#### 3.2.1 Materials

Reagents were all commercially available and purchased from Alfa Aesar, Jade Scientific, Oakwood Chemical, Sigma-Aldrich, Spectrum Chemical, and Strem Chemicals. Solvents for spectroscopic measurements were used as received: 1-butanol (Jade Scientific, JS-B6000), 1,3-propanediol (Alfa Aesar, A10829), 1,4-butanediol (Sigma-Aldrich, 493732), 1,5-pentanediol (Fluka Analytical, 76892), 2-propanol (Sigma-Aldrich, 278475), acetonitrile (Sigma-Aldrich, 34851), butyronitrile (Alfa Aesar, L02999), dichloromethane (Jade Scientific, JS-D2735), diethyl ether (Sigma-Aldrich, 673811), dimethyl sulfoxide (EMD, MX1458-3), ethanol (KOPTEC, V1016), ethylene glycol (CCI, 2165CM), hexanenitrile (Aldrich, 166650), methanol (Jade Scientific, JS-M3650), propionitrile (Alfa Aesar, A13203), propylene carbonate (Sigma-Aldrich, 310328), tetrahydrofuran (Fisher Chemical, T427), and water (Sigma-Aldrich, 270733).

#### 3.2.2 Syntheses and characterization

All of the following complexes were prepared under an inert atmosphere with deoxygenated solvents either in a nitrogen-filled glovebox or by standard Schlenk techniques. Samples were prepared based on routes reported in the literature.<sup>9,10</sup> In general, 1 equivalent of the Fe(II) source was dissolved in nitrogen-sparged water and transferred via cannula to a flask containing 3.1 equivalents of the ligand dissolved in air-free methanol, resulting in a red-colored solution. 10 equivalents of the anion source, dissolved in bubble-degassed water, were then cannula-transferred to the reaction flask, after which the reaction mixture was allowed to stir for 2 hours. Any modifications to this procedure are noted in the appropriate section. Steps taken to purify the product are described individually. Extinction coefficients for the molecules discussed here were determined in matched 1-cm path length quartz cells on the PerkinElmer Lambda 1050

spectrophotometer from serial dilutions of the original solution (see Appendix 3.A for spectra). The composition and purity for all molecules were tested by nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, and elemental analysis. <sup>1</sup>H NMR spectroscopic data were collected with Agilent DD2 500 MHz NMR spectrometers at the MSU Max T. Rogers NMR facility. Samples were analyzed by Sara L. Adelman and Jonathan T. Yarranton at the MSU Mass Spectrometry and Metabolomics Core facility with a Waters Xevo G2-XS QTof instrument. Elemental analyses were run by the analytical facilities in the MSU chemistry department with a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer.

*Tris*(2,2'-*bipyridine*)*iron*(*II*) *chloride*, [*Fe*(*bpy*)<sub>3</sub>]*Cl*<sub>2</sub>. This complex was prepared by a previous group member, Dr. Amanda L. Smeigh, in a nitrogen-filled glovebox by mixing FeCl<sub>2</sub>·2H<sub>2</sub>O and 2,2'-bipyridine in methanol. No water was used in this reaction. The solution was allowed to stir for 10 minutes at room temperature. After evaporating the solvent under a stream of nitrogen, the product was recrystallized via diethyl ether vapor diffusion into a saturated acetonitrile solution of the complex. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta$  8.57 (d, 6H, *J* = 8 Hz), 8.10 (m, 6H), 7.40 (m, 12H). TOF-MS [ESI, *m/z*]: 262.07 [C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>Fe]<sup>2+</sup>. Elemental Analysis for C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>FeCl<sub>2</sub>·2H<sub>2</sub>O, Calculated: C, 57.07%; H, 4.47%; N, 13.31%. Found: C, 57.15%; H, 4.33%; N, 13.32%. UV-Vis (CH<sub>3</sub>CN)  $\lambda$  (nm) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 298 (55600), 350 (5700), 521 (6900).

*Tris*(2,2'-*bipyridine*)*iron*(*II*) *bromide*, [*Fe*(*bpy*)<sub>3</sub>]*Br*<sub>2</sub>. This complex was prepared on a Schlenk line, under air-free conditions. Ferrous ammonium sulfate hexahydrate (or  $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O)$ , 2,2'-bipyridine, and NaBr were the starting materials for this reaction. Following 2 hours of stirring, the solvent was removed from the reaction mixture by a rotary evaporator. The crude product was dissolved in acetonitrile and filtered. The filtrate was then recrystallized by diethyl ether vapor diffusion into a saturated acetonitrile solution of the complex.

The last two steps were repeated. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta 8.55$  (d, 6H, J = 8 Hz), 8.11 (m, 6H), 7.39 (m, 12H). TOF-MS [ESI, m/z]: 262.07 [C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>Fe]<sup>2+</sup>. Elemental Analysis for C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>FeBr<sub>2</sub>·3H<sub>2</sub>O, Calculated: C, 48.81%; H, 4.10%; N, 11.38%. Found: C, 48.79%; H, 4.04%; N, 11.80%. UV-Vis (CH<sub>3</sub>CN)  $\lambda$ (nm) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 299 (60200), 350 (5800), 520 (7800).

*Tris*(2,2'-*bipyridine*)*iron*(*II*) *iodide,* [*Fe*(*bpy*)<sub>3</sub>]*I*<sub>2</sub>. This complex was prepared on a Schlenk line, under air-free conditions. (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, 2,2'-bipyridine, and NaI made up the reactants. Some of the crude product from this reaction formed a precipitate which was filtered. Under vacuum filtration, the precipitate was rinsed with acetone and diethyl ether. The product was then dissolved in acetonitrile, filtered, and recrystallized twice by diethyl ether vapor diffusion. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta$  8.53 (d, 6H, *J* = 8 Hz), 8.10 (m, 6H), 7.39 (m, 12H). TOF-MS [ESI, *m/z*]: 262.07 [C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>Fe]<sup>2+</sup>. Elemental Analysis for C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>FeI<sub>2</sub>·2H<sub>2</sub>O, Calculated: C, 44.25%; H, 3.47%; N, 10.32%. Found: C, 45.52%; H, 3.53%; N, 10.36%. UV-Vis (CH<sub>3</sub>CN)  $\lambda$ (nm) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 298 (64900), 351 (6500), 520 (8400).

*Tris*(2,2'-*bipyridine*)*iron*(*II*) *hexafluorophosphate*, [*Fe*(*bpy*)<sub>3</sub>](*PF*<sub>6</sub>)<sub>2</sub>. This complex was prepared on a Schlenk line, under air-free conditions. The reaction mixture contained (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, 2,2'-bipyridine, and NH<sub>4</sub>PF<sub>6</sub>. The product precipitated out upon the addition of NH<sub>4</sub>PF<sub>6</sub>. The solid product was filtered and rinsed with water, then diethyl ether. The product was then dissolved in acetonitrile, filtered, and recrystallized twice by diethyl ether vapor diffusion. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta$  8.51 (d, 6H, *J* = 8 Hz), 8.10 (m, 6H), 7.38 (m, 12H). TOF-MS [ESI, *m*/*z*]: 262.07 [C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>Fe]<sup>2+</sup>. Elemental Analysis for C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>FeP<sub>2</sub>F<sub>12</sub>, Calculated: C, 44.25%; H, 2.97%; N, 10.32%. Found: C, 44.23%; H, 3.03%; N, 10.32%. UV-Vis (CH<sub>3</sub>CN)  $\lambda$ (nm) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 299 (69500), 351 (6700), 520 (9100).

*Tris*(2,2'-*bipyridine*)*iron*(*II*) *tetraphenylborate*, *[Fe(bpy)<sub>3</sub>](BPh<sub>4</sub>)*<sub>2</sub>. This complex was prepared on a Schlenk line, under air-free conditions. It was prepared from FeCl<sub>2</sub>·2H<sub>2</sub>O, 2,2'- bipyridine, and NaBPh<sub>4</sub>. The product formed a precipitate which was filtered and rinsed with water and diethyl ether. The product was then dissolved in acetone, filtered, and recrystallized twice by diethyl ether vapor diffusion. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta$  8.49 (d, 6H, *J* = 8Hz), 8.08 (td, 6H, *J* = 7.5, 2 Hz), 7.37 (m, 12H), 7.26 (m, 16H), 6.98 (t, 16H, *J* = 7.3), 6.83 (t, 8H, *J* = 7.3). TOF-MS [ESI, *m*/*z* (rel. int.)]: 262.07 (100) [C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>Fe]<sup>2+</sup>, 843.31 (13) {[C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>Fe](C<sub>24</sub>H<sub>20</sub>B)}<sup>+</sup>. Elemental Analysis for C<sub>78</sub>H<sub>64</sub>N<sub>6</sub>FeB<sub>2</sub>·H<sub>2</sub>O, Calculated: C, 79.34%; H, 5.63%; N, 7.12%. Found: C, 79.48%; H, 5.85%; N, 6.90%. UV-Vis (CH<sub>3</sub>CN)  $\lambda$ (nm) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 299 (68200), 351 (6600), 520 (8900).

# *Tris(2,2'-bipyridine)iron(II) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,*

[*Fe(bpy)*<sub>3</sub>](*BAr<sup>F</sup>*<sub>4</sub>)<sub>2</sub>. This complex was prepared on a Schlenk line, under air-free conditions, starting from (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, 2,2'-bipyridine, and 2.10 equivalents of NaBAr<sup>F</sup><sub>4</sub>. The product precipitated from the solution and was subsequently filtered. Under vacuum filtration, the product was dissolved in diethyl ether and filtered. The product was precipitated out of the filtrate by adding acetone. The last two steps were repeated. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta$  8.50 (d, 6H, J = 7.5 Hz), 8.10 (m, 6H), 7.69 (m, 16H), 7.66 (s, 8H), 7.38 (m, 12H). TOF-MS [ESI, *m/z* (rel. int.)]: 262.07 (100) [C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>Fe]<sup>2+</sup>, 1387.22 (40) {[C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>Fe](C<sub>32</sub>H<sub>12</sub>BF<sub>24</sub>)}<sup>+</sup>. Elemental Analysis for C<sub>94</sub>H<sub>48</sub>N<sub>6</sub>FeB<sub>2</sub>F<sub>48</sub>·2H<sub>2</sub>O, Calculated: C, 49.37%; H, 2.29%; N, 3.67%. Found: C, 50.21%; H, 2.36%; N, 3.60%. UV-Vis (CH<sub>3</sub>CN)  $\lambda$ (nm) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 299 (64900), 351 (6300), 521 (8400).

Tris(4,4'-dimethyl-2,2'-bipyridine)iron(II) bromide, [Fe(dmb)<sub>3</sub>]Br<sub>2</sub>. This complex was prepared on a Schlenk line, under air-free conditions. [Fe(dmb)<sub>3</sub>]Br<sub>2</sub> was synthesized from

(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, 4,4'-dimethyl-2,2'-bipyridine, and NaBr. After allowing the reaction to stir for 2 hours, the solvent was removed by a rotary evaporator. The crude product was dissolved in acetonitrile and filtered. Diethyl ether was added to crash the product out of the filtrate. The solid product was collected by vacuum filtration. The last three steps were repeated. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta$  8.37 (s, 6H), 7.19 (m, 12H), 2.53 (s, 18H). TOF-MS [ESI, *m/z* (rel. int.)]: 212.07 (61) [C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>Fe]<sup>2+</sup>, 304.12 (100) [C<sub>36</sub>H<sub>36</sub>N<sub>6</sub>Fe]<sup>2+</sup>, 503.05 (41) {[C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>Fe]Br}<sup>+</sup>. Elemental Analysis for C<sub>36</sub>H<sub>36</sub>N<sub>6</sub>FeBr<sub>2</sub>·H<sub>2</sub>O, Calculated: C, 54.98%; H, 4.87 %; N, 10.69%. Found: C, 54.29%; H, 4.72%; N, 10.63%. UV-Vis (CH<sub>3</sub>CN)  $\lambda$ (nm) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 297 (64300), 356 (7300), 527 (8500).

*Tris*(5,5'-*dimethyl-2,2'-bipyridine*)*iron*(11) *bromide*, [*Fe*(5,5'-*dmb*)<sub>3</sub>]*Br*<sub>2</sub>. This complex was prepared on a Schlenk line, under air-free conditions. The reagents for this reaction were  $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ , 5,5'-dimethyl-2,2'-bipyridine, and NaBr. After allowing the reaction to stir for 2 hours, the solvent was removed by a rotary evaporator. The crude product was dissolved in acetonitrile and filtered. The product was recrystallized twice by diethyl ether vapor diffusion into a saturated acetonitrile solution of the complex. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta$  8.35 (d, 6H, J = 8 Hz), 7.88 (dd, 6H, J = 7.8, 1.3 Hz), 7.09 (s, 6H), 2.16 (s, 18H). TOF-MS [ESI, *m/z* (rel. int.)]: 212.07 (47) [C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>Fe]<sup>2+</sup>, 304.12 (100) [C<sub>36</sub>H<sub>36</sub>N<sub>6</sub>Fe]<sup>2+</sup>, 503.05 (27) {[C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>Fe]Br}<sup>+</sup>. Elemental Analysis for C<sub>36</sub>H<sub>36</sub>N<sub>6</sub>FeBr<sub>2</sub>·H<sub>2</sub>O, Calculated: C, 54.98%; H, 4.87%; N, 10.69%. Found: C, 54.81%; H, 5.11%; N, 10.58%. UV-Vis (CH<sub>3</sub>CN)  $\lambda$ (nm) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 306 (78700), 355 (6500), 510 (9400).

*Tris*(4,4'-di-tert-butyl-2,2'-bipyridine)iron(II) bromide, [*Fe*(dtbbpy)<sub>3</sub>]*Br*<sub>2</sub>. This complex was prepared on a Schlenk line, under air-free conditions.  $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ , 4,4'-di-*tert*-butyl-2,2'-bipyridine and NaBr were the starting materials for this reaction. After stirring for 2

hours, the solvent was removed from the reaction mixture by a rotary evaporator. The crude product was dissolved in acetonitrile and filtered. The filtrate was then recrystallized twice by diethyl ether vapor diffusion into a saturated acetonitrile solution of the complex. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz):  $\delta$  8.51 (d, 6H, J = 2.0 Hz), 7.39 (dd, 6H, J = 6.0, 2.0 Hz), 7.20 (d, 6H, J = 6.0 Hz), 1.41 (s, 54H). TOF-MS [ESI, m/z]: 430.26 [C<sub>54</sub>H<sub>72</sub>N<sub>6</sub>Fe]<sup>2+</sup>. Elemental Analysis for C<sub>54</sub>H<sub>72</sub>N<sub>6</sub>FeBr<sub>2</sub>, Calculated: C, 63.53%; H, 7.11%; N, 8.23%. Found: C, 63.35%; H, 6.84%; N, 8.34%. UV-Vis (CH<sub>3</sub>CN)  $\lambda$ (nm) ( $\epsilon$ (M<sup>-1</sup>cm<sup>-1</sup>)): 298 (67300), 357 (8500), 527 (10200).

# 3.2.3 Time-resolved transient absorption data

Femtosecond pump-probe measurements were collected on the Wile E laser system with approximately 130-fs resolution that has been described previously (see Chapter 2). Samples were excited on the low energy edge of the MLCT band – at 530 nm for  $[Fe(5,5'-dmb)_3]Br_2$  and 550 nm for  $[Fe(bpy)_3]^{2+}$ ,  $[Fe(dmb)_3]Br_2$ , and  $[Fe(dtbbpy)_3]Br_2$ . Probe wavelengths were selected from a white light continuum with 10-nm bandpass filters ranging between 500-530 nm, depending on the signal size and the amount of pump scatter at the Si photodiode. Polarizations for the pump and probe beams were set at magic angle (54.7°) relative to one another. A neutral density (ND) filter slide was used to give pump energies of 5 µJ at the sample position. A 0.3 ND filter was used to check for linearity between the signal response and the pump power.

Ground state electronic absorption spectra were measured on a Varian Cary 50 UV-visible spectrophotometer prior to and following time-resolved absorption measurements to ensure there was no degradation of the sample. Samples were prepared in air and had ground state absorbances between 0.38 and 0.42 (unless otherwise noted) at the excitation wavelength in 1-mm path length cells. All measurements were carried out at room temperature (ca. 20 °C). Each data set includes the signal average of at least twenty scans and was fit by Igor Pro software with a monoexponential

function, weighted to incorporate the standard deviation associated with each data point. Lifetimes reported herein are the average of at least four data sets. The error associated with each lifetime is derived from propagating the error associated with the four (or more) data sets.

#### 3.2.4 Computational methods

As noted in Chapter 2, calculations were carried out using the Gaussian 09 software package<sup>11</sup> on servers available through the High Performance Computing Center (HPCC) at Michigan State University. The singlet and quintet state geometries of each Fe(II) complex were optimized with UFF atomic radii under tight convergence criteria and an ultrafine integration grid at the spin-unrestricted B3LYP<sup>12-14</sup> level, using the SDD effective core potential and associated basis set<sup>15</sup> for the Fe atom, the 6-31G(d) basis set<sup>16,17</sup> for C and N atoms, and the 6-31G(d,p) basis set<sup>16,17</sup> for H atoms. No symmetry restrictions were imposed. The initial geometries of the molecules came from their crystal structures, downloaded from the Cambridge Structural Database<sup>18</sup> under the refcodes: ADEJOK ([Fe(dtbbpy)<sub>3</sub>]<sup>2+</sup>), ECAKUP ([Fe(5,5'-dmb)<sub>3</sub>]<sup>2+</sup>), MEMSON ([Fe(dmb)<sub>3</sub>]<sup>2+</sup>), and NUZKOI ([Fe(bpy)<sub>3</sub>]<sup>2+</sup>). Optimized structures were assessed by vibrational frequency analysis, the results of which were ultimately used to determine Gibbs free energies for all compounds at 293.15 K and standard pressure under vacuum and in solution. The Cartesian coordinates of all optimized structures discussed in this chapter will be included as a supplemental file associated with the electronic version of this document.

The purpose of these calculations is to estimate how the gas-to-solution phase Gibbs free energy of solvation ( $\Delta G_{solv}$ ) changes between the quintet and singlet states. The conductor-like polarizable continuum model (CPCM)<sup>19,20</sup> was used to compute solvation energy, with all solvents applied under the generic setting and distinguished by the following input parameters (keywords): stoichiometry, static dielectric constant (eps), optical dielectric constant (epsinf), solvent radius (rsolv), molar volume (molarvolume), and temperature (TAbs). All CPCM calculations also included the keywords cav, dis, and rep (for cavitation, dispersion, and repulsion) to incorporate non-electrostatic contributions. To compute the  $\Delta G_{solv}$  of an electronic state in a particular solvent, the difference was taken between the thermally-corrected Gibbs free energy in solvent versus under vacuum.<sup>21</sup> The differential solvation energy, or  $\Delta\Delta G_{solv}$ , was calculated as the difference between the  $\Delta G_{solv}$  values for the singlet and quintet states.

# 3.3 Results and discussion

# 3.3.1 Effect of solvent on the excited state dynamics of $[Fe(bpy)_3]^{2+}$

Research on Fe(II) polypyridyl complexes has typically aimed at pinpointing what controls the rapid relaxation process from the initially excited state to the lowest energy excited state in an effort either to optimize their use for photovoltaic applications<sup>22–24</sup> or to effectively utilize light-induced excited spin state trapping (LIESST) for molecular electronics.<sup>25,26</sup> In the case of  $[Fe(bpy)_3]^{2+}$ , photoexcitation with visible light initially populates the <sup>1</sup>MLCT state. Numerous studies, both experimental and theoretical, have been conducted in order to understand the deactivation process from the <sup>1</sup>MLCT state to the <sup>5</sup>T<sub>2</sub> state, the lowest energy excited state.<sup>27,28</sup> These studies have found that, after the initial excitation of the <sup>1</sup>MLCT state, the complex undergoes intersystem crossing (ISC) to populate the <sup>3</sup>MLCT state and then quickly evolves through a <sup>3</sup>T intermediate state to reach the <sup>5</sup>T<sub>2</sub> state, a LF state, before relaxing back to the <sup>1</sup>A<sub>1</sub> ground state.

Time-resolved experiments establish that this complex relaxes to the  ${}^{5}T_{2}$  state from the  ${}^{1}MLCT$  state within 130 fs and then relaxes on a timescale of 650 ps back to the ground state.<sup>29</sup> It should be noted that these lifetimes are with respect to water as the solvent. As stated in the introduction, it is not uncommon for the solvent choice to influence the dynamics of MLCT states,



**Figure 3-2.** Rates of ground state recovery for  $[Fe(bpy)_3]^{2+}$  in different solvents with excitation at 550 nm. The time constants are color-coded based on which counterion was associated with  $[Fe(bpy)_3]^{2+}$  in said solvent, which varied for solubility reasons: Br<sup>-</sup> (green) and BAr<sup>F</sup><sub>4</sub><sup>-</sup> (blue).

while LF states tend to be regarded as relatively unaffected. However, the data presented in Figure 3-2 reveal that the ground state recovery (GSR) lifetime for the LF relaxation process of  $[Fe(bpy)_3]^{2+}$  is indeed dependent on the solvent identity. This phenomenon does not seem to be restricted to  $[Fe(bpy)_3]^{2+}$  as it has also been observed in-house<sup>8</sup> in studying the relaxation rate of  $[Fe(tpy)_2]^{2+}$  (tpy = 2,2':6',2"-terpyridine) in water (3.05 ± 0.12 ns), acetonitrile (5.35 ± 0.32 ns), methanol (4.49 ± 0.21 ns), and dichloromethane (5.30 ± 0.31 ns) as well as commented on briefly by Tribollet et al. while studying  $[Fe(phen)_3]^{2+}$  (phen = 1,10-phenanthroline), where it was noted that the relaxation constant they recorded in acetonitrile (1.1 ± 0.1 ns)<sup>30</sup> differed from that published previously in aqueous solution (687 ± 30 ps).<sup>31</sup> Most recently, X-ray transient absorption (TA) spectroscopy was used to study  $[Fe(dmb)_3]^{2+}$  in water and acetonitrile, discovering that not only was there a difference in excited state lifetime (830 ± 10 ps and 1240 ± 12 ps, respectively), but a structural one as well in the  $\Delta R_{HS-LS}$  Fe-N bond elongations (0.181 ± 0.003 Å versus 0.199 ± 0.003 Å, respectively).<sup>32</sup>

	Dipole Moment (D)	Molar Volume <sup>c</sup> (cm <sup>3</sup> /mol)	Optical Dielectric Constant <sup>d</sup>	Polariz- ability <sup>e</sup> (Å <sup>3</sup> )	Static Dielectric Constant	Viscosity (cP)
Water	1.85	18.05	1.78	1.47	80.10	0.89
Dimethyl Sulfoxide	3.96	$70.97^{\mathrm{f}}$	2.19	7.98 <sup>g</sup>	47.24	1.99
Ethylene Glycol	2.36	55.74	2.05	5.73	41.40	16.06
1,3-Propanediol	2.55	72.21	2.07	7.54	35.10	41.11 <sup>h</sup>
1,4-Butanediol	2.58	88.60	2.09	9.37	32.86	71.14 <sup>h</sup>
1,5-Pentanediol	2.50	105.05	2.10	11.18	26.20	$86.79^{h}$
Propylene Carbonate	4.90	84.74	2.01	8.48	66.14	$2.47^{i}$
Methanol	1.70	40.49	1.77	3.26	33.00	0.54
Acetonitrile	3.93	52.25	1.81 <sup>j</sup>	4.39 <sup>g</sup>	36.64	0.37
Ethanol	1.69	58.37	1.85	5.12	25.30	1.07
Propionitrile	4.05	70.45	1.86	6.25	29.70	0.29
2-Propanol	1.58	76.95	1.90	7.03	20.18	2.04
Butyronitrile	3.82 <sup>k</sup>	87.08	1.92	8.07	24.83	0.55
1-Butanol	1.66	91.56	1.96	8.78	17.84	2.54
Tetrahydrofuran	1.75	81.63 <sup>f</sup>	$1.97^{\mathrm{f}}$	$7.93^{\mathrm{f}}$	7.56	0.46
Hexanenitrile	$3.48^{1}$	120.68	1.98	11.77	17.26 <sup>f</sup>	0.91
Diethyl Ether	1.10	103.84	1.83	8.92	4.27	0.22
Dichloromethane	1.60	64.02	2.03	6.48	9.00	0.41
<b>R<sup>2</sup> coefficient</b> <sup>m</sup>	0.068	0.198	0.043	0.091	0.698	0.096

**Table 3-1.** Properties associated with each solvent<sup>a,b</sup>

<sup>a</sup>From reference 33, unless otherwise indicated.

<sup>b</sup>All solvent properties but viscosity are based on a temperature of 20 °C, unless noted, with viscosity values established at 25 °C.

<sup>c</sup>Calculated from density (g/cm<sup>3</sup>) and molar mass (g/mol).

<sup>d</sup>Calculated from refractive index.

<sup>e</sup>Calculated from refractive index, density (g/cm<sup>3</sup>), and molar mass (g/mol).

<sup>f</sup>At 25 °C.

<sup>g</sup>Calculated from data encompassing two different temperatures.

<sup>h</sup>From reference 34.

<sup>i</sup>From reference 35.

<sup>j</sup>At 30 °C.

<sup>k</sup>Average dipole moment between *gauche* (3.91 D) and *anti* (3.73 D) conformers of butyronitrile. <sup>1</sup>From reference 36.

<sup>m</sup>From linear fit for ground state recovery time constant of [Fe(bpy)<sub>3</sub>]<sup>2+</sup> plotted against that solvent property.



**Figure 3-3.** Rates of GSR for  $[Fe(bpy)_3]^{2+}$  versus static dielectric constants.

In an effort to parse out possible trends, the solvents utilized in this study were selected to span a wide range of values for properties such as dielectric constant, viscosity, size, and dipole moment. This information is compiled by solvent in Table 3-1, along with the coefficient of determination ( $R^2$ ) associated with each property relative to the rate of GSR. From this, the  ${}^5T_2 \rightarrow {}^1A_1$  relaxation process tracks most strongly with static dielectric constant (shown in Figure 3-3). This suggests that the rates observed may reflect electrostatic interactions between the solute and solvent. Upon closer inspection, the data appear to group according to the type of solvent. For example, results from alcohol-based solvents show a linear response; the same can be said of results from diol-based and nitrile-based solvents. Via these groupings, the fits improve dramatically across all solvent properties such that no single property stands out as justification for the observed solvent dependence (see Figure 3-4). While this is an interesting discovery, strong correlations also exist when comparing solvent properties to one another once divided into their respective solvent families (Figure 3-5). Additionally, caution must be taken as the correlation may simply correspond to the systematic change associated with varying the number of methylene



**Figure 3-4.** Comparison of GSR lifetime for  $[Fe(bpy)_3]^{2+}$  versus (a) dipole moment, (b) molar volume, (c) optical dielectric constant, (d) polarizability, (e) static dielectric constant, and (f) viscosity for alcohols (red squares), diols (green triangles), and nitriles (blue circles). The results for water (black diamonds) are presented in the figures, but not included in any fits.



**Figure 3-5.** Comparison of the static dielectric constant versus (a) dipole moment, (b) molar volume, (c) optical dielectric constant, (d) polarizability, and (e) viscosity for alcohols (red squares), diols (green triangles), and nitriles (blue circles). The results for water (black diamonds) are presented in the figures, but not included in any fits.

groups in the alkyl chain of the solvent. Without a clear indication of what drives this dependence from solvent properties alone, it is important to understand the factors which contribute to the reaction rate.

# 3.3.2 Modeling changes to the rate of non-radiative decay

As a d<sup>6</sup> complex, the <sup>1</sup>A<sub>1</sub> and <sup>5</sup>T<sub>2</sub> states represent low-spin (LS) and high-spin (HS) states, respectively, where the difference between these two states is reflected in the electron configuration of the  $t_{2g}$  and  $e_g^*$  orbitals ( $t_{2g}^6$  versus  $t_{2g}^4 e_g^2$ ). Treating the HS-to-LS ISC as an internal electron transfer process allows us to relate the relaxation rate ( $k_{nr}$ , in s<sup>-1</sup>) to the standard Marcus expression,<sup>37</sup> such that:

$$k_{nr} = \frac{2\pi}{\hbar} |H_{ab}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(\Delta G^0 + \lambda)^2}{4\lambda k_B T}\right)$$
 Equation 3.1

where  $\hbar$  is the reduced Planck constant (in cm<sup>-1</sup>·s), H<sub>ab</sub> is the matrix element (in cm<sup>-1</sup>),  $\lambda$  is the reorganization energy (in cm<sup>-1</sup>), k<sub>B</sub> is the Boltzmann constant (in cm<sup>-1</sup>·K<sup>-1</sup>), T is the temperature (in K), and  $\Delta G^0$  is the free energy of the reaction (in cm<sup>-1</sup>). The rate is dependent on the degree of electronic coupling between the two states (incorporated in H<sub>ab</sub>), the energy difference between the <sup>1</sup>A<sub>1</sub> and <sup>5</sup>T<sub>2</sub> states (represented by  $\Delta G^0$ ), and the amount of energy needed to transform the reactant into the product configuration without transferring an electron (designated as  $\lambda$ ) – this last parameter is comprised of inner-sphere (vibrational) and outer-sphere (solvational) contributions. Figure 3-6 illustrates how these parameters map onto the potential energy diagram.

Since  $[Fe(bpy)_3]^{2+}$  is not emissive nor does it represent a true spin-crossover complex where changes in temperature or pressure alone are able to modulate which spin state (LS or HS) is accessed, we are left with three unknowns that are estimated rather than accurate. For instance, there are discrepancies in the literature regarding the zero-point energy difference between the



#### **Reaction Coordinate**

**Figure 3-6.** General depiction of the energy separations determining rates of relaxation from the  ${}^{5}T_{2}$  excited state to the  ${}^{1}A_{1}$  ground state in Fe(II) polypyridyl complexes with a LS ground state. H<sub>ab</sub> represents the matrix element,  $\lambda$  is the reorganization energy, and  $\Delta G^{0}$  is the free energy.

singlet and quintet states due to differences in the functional used for the calculations.<sup>27,38–41</sup> Based on a functional which does a better job of accounting for variations in exchange when the spin polarization and the metal-ligand bond length vary considerably,  $\Delta G^0$  is speculated to be around -6800 cm<sup>-1.41</sup> Given that the  ${}^5T_2 \rightarrow {}^1A_1$  transition is thought to be near the barrierless region (where  $-\Delta G^0 = \lambda$ ),<sup>42</sup> a value around 6800 cm<sup>-1</sup> is, therefore, predicted for the reorganization energy as well. As for H<sub>ab</sub>, electronic coupling between the  ${}^5T_2$  state and the  ${}^1A_1$  state is expected to be weak, considering there is a  $\Delta S = 2$  difference in spin multiplicities, and thus, there must be a second-order spin interaction through an intermediate  ${}^3T$  state. The work by Buhks et al. proposes that the matrix element is around 170 cm<sup>-1</sup> for Fe(II) complexes.<sup>43</sup> Based on these assumptions, how much would each parameter need to change to account for the two extreme rates observed in water and dichloromethane? Since more accurate values have yet to be determined experimentally, these values will be used as starting points in the discussion to follow. Equation 3.1 was rearranged to solve for either  $\Delta G^0$  or  $H_{ab}$  at the two limiting rates in Figure 3-2 as the other two unknowns were systematically varied. Unfortunately, it is not possible to simplify the equation to solve for  $\lambda$  directly, making it difficult to quantify as  $\Delta G^0$  and  $H_{ab}$  are varied without lengthy guess-and-check. Although  $\Delta G^0$  is expected to be around -6800 cm<sup>-1</sup> for [Fe(bpy)<sub>3</sub>]<sup>2+</sup>, calculations were carried out from -19,200 to -200 cm<sup>-1</sup> at increments of 10 cm<sup>-1</sup>. This range was chosen because the energy difference between the HS and LS states cannot be larger than the energy associated with the MLCT band (with a maximum around 520 nm), and a complex with a zero-point energy difference smaller than 200 cm<sup>-1</sup> (or k<sub>B</sub>T) should exhibit spin-crossover behavior. As for  $\lambda$ , it was varied from 10 to 16,100 cm<sup>-1</sup> at increments of 10 cm<sup>-1</sup>, where the maximum value was chosen because it is highly unlikely that the reorganization energy of this process would be larger than 2 V. And while  $H_{ab}$  is thought to be around 170 cm<sup>-1</sup>, it was varied between 0.1 and 200.0 cm<sup>-1</sup> at increments of 0.1 cm<sup>-1</sup>, with a maximum of 200 cm<sup>-1</sup> selected in order to maintain a weakly-coupled transition. In these calculations, the temperature was set to 20 °C to match the temperature of the ultrafast laser lab.

Some assumptions were made in analyzing the results of these calculations. When solving for  $\Delta G^0$ , it should be noted that two answers are possible since the summation of  $\Delta G^0$  and  $\lambda$  may be either positive or negative before being squared; only results based on the positive sum are reported here as that gives rise to values of  $|\Delta G^0|$  which are smaller than those of  $\lambda$ , and thus reflects the normal region according to Marcus theory. Additionally, the sign of  $\Delta G^0$  should be negative in order to signify a favorable relaxation process from the HS state to the LS state. And so, only values that fell between -19,200 and -200 cm<sup>-1</sup> were considered (constrained for the same reasons as above). Similarly, when solving for H<sub>ab</sub>, only values that were equal to or less than 200 cm<sup>-1</sup> were included. Contour plots of these results are shown in Figure 3-7 and Figure 3-8.



**Figure 3-7.** Theoretical findings from the non-radiative decay equation, calculating the (a) matrix element and the (b) change in free energy for  $[Fe(bpy)_3]^{2+}$  in water at 20 °C and  $\tau_{GSR} = 677.42$  ps.



**Figure 3-8.** Theoretical findings from the non-radiative decay equation, calculating the (a) matrix element and the (b) change in free energy for  $[Fe(bpy)_3]^{2+}$  in dichloromethane at 20 °C and  $\tau_{GSR} = 1281.75$  ps.



**Figure 3-9.** Theoretical findings from the non-radiative decay equation for  $H_{ab}$  of  ${}^{5}T_{2} \rightarrow {}^{1}A_{1}$  transition in  $[Fe(bpy)_{3}]^{2+}$  in water (purple,  $\tau_{GSR} = 677.42$  ps) and dichloromethane (green,  $\tau_{GSR} = 1281.75$  ps) at suggested values for the (a) change in free energy (-6800 cm<sup>-1</sup>) and the (b) reorganization energy (6800 cm<sup>-1</sup>).



 ${}^{5}T_{2} \rightarrow {}^{1}A_{1}$  transition in [Fe(bpy)<sub>3</sub>]<sup>2+</sup> in water (purple,  $\tau_{GSR} = 677.42$  ps) and dichloromethane (green,  $\tau_{GSR} = 1281.75$  ps) at suggested values for the (a) reorganization energy (6800 cm<sup>-1</sup>) and the (b) matrix element (170 cm<sup>-1</sup>).



**Figure 3-11.** The difference between the calculated (a)  $H_{ab}$  values and (b)  $\Delta G^0$  values for  $[Fe(bpy)_3]^{2+}$  in water ( $\tau_{GSR} = 677.42$  ps) and dichloromethane ( $\tau_{GSR} = 1281.75$  ps) at 20 °C.

Data for  $H_{ab}$  of  $[Fe(bpy)_3]^{2+}$  in both solvents at the recommended values for  $\lambda$  and  $\Delta G^0$  are presented in Figure 3-9. Likewise, the effect of varying  $\lambda$  and  $H_{ab}$  on  $\Delta G^0$  can be seen in Figure 3-10. While it is clear from these calculations that the estimated value for  $H_{ab}$  may span a wide range as  $\Delta G^0$  and  $\lambda$  are varied, the maximum difference between the results in water and dichloromethane is estimated to be around 55 cm<sup>-1</sup>, with nearly 50% of the data in Figure 3-11a represented by a difference of 5 cm<sup>-1</sup> or less. As for changes to  $\Delta G^0$  with changing solvent, the difference between the two  $\Delta G^0$  values is generally on the order of a few hundred cm<sup>-1</sup> (see Figure 3-11b), however, increasing by an order of magnitude when  $H_{ab}$  is less than 10 cm<sup>-1</sup> (an area which is likely for this relaxation). It does not seem to take much to modulate either the zeropoint energy difference or the amount of coupling between these states and, thus, dramatically alter the rate of relaxation. Considering the metal-localized nature of the electronic states being investigated here, what could cause one or more of these parameters to change with solvent?

#### 3.3.3 Precedent for ion pairing between Fe(II) polypyridyls and counterions

In 1989, Hendrickson and co-workers published variable-temperature TA data on a series of  $[Fe(tren(6-Me-py)_x(py)_{(3-x)})]^{2+}$  complexes (where x = 0-3 and tren(6-Me-py)\_3 is tris(6-methyl-2-pyridylmethyliminoethyl)amine.<sup>44</sup> This series, studied for their spin-crossover behavior, is interesting because as the value of x increases, the methyl groups stabilize the HS state, resulting in an inversion of the LS and HS states between the ground state and the lowest energy excited state. Over the course of their work, they discovered that the excited state lifetime of  $[Fe(tren(py)_3)]^{2+}$  was dependent on its concentration. Electrical conductivity measurements expanded on this by revealing ion pairing between the Fe(II) cation and the perchlorate anions. Based on these findings and the theoretical models<sup>43,45</sup> used to fit the relaxation data, they concluded that ion pairing affected the zero-point energy difference between the <sup>5</sup>T<sub>2</sub> and <sup>1</sup>A<sub>1</sub> states, where the zero-point energy difference increased with increasing solute concentration. I sought to see if the data in Figure 3-2 could be similarly explained.

Ion pairing refers to the electrostatic association of charged ions in solution without a formal chemical bond.<sup>46</sup> Its strength is dependent on the charge and size of the ions as well as the surrounding solvent. As such, the association (F, in N) between two charged ions can be described by Coulomb's law,<sup>47</sup> shown here:

$$F = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 \varepsilon_r d^2}$$
 Equation 3.2

where z represents the charge of the ion, *e* refers to the elementary electric charge (in C),  $\varepsilon_0$  is the vacuum permittivity (in F·m<sup>-1</sup>),  $\varepsilon_r$  is the relative permittivity of the solvent medium,<sup>48</sup> and d is the distance between the two ion centers (in m). As an outer limit, though arbitrary, Bjerrum suggested that two ions should no longer be considered ion paired once separated by a distance, q, where the work required to separate them is equal to  $2k_BT$ .<sup>49</sup> Now, this phenomenon is not limited to two

ions, but can also exist as triplets or larger aggregates as the electrolyte concentration increases. Additionally, several types of ion pairs exist, differentiated by their level of solvation: solvent-separated (solvation remains around each ion), solvent-shared (one level of solvent separation), and contact (no solvent between ions). Altogether, one can see that by simply changing the solvent environment, one can dramatically affect the level of attraction between ions when the dominant intermolecular forces are electrostatic in nature.

To understand whether ion pairing played an active role in the observed solvent dependence, the GSR rate of  $[Fe(bpy)_3]^{2+}$  was investigated at multiple concentrations in multiple solvents, spanning a large range of static dielectric constants. The assumption is that any change in rate across the different concentrations should correlate with ion pairing, where the likelihood of it occurring should increase both as the solute concentration increases and as the static dielectric constant decreases. If  $\Delta G^0$  is the only parameter being influenced, one would expect k<sub>nr</sub> to increase as the zero-point energy difference increases (based on Equation 3.1). However, revisiting the Arrhenius parameters associated with the variable-temperature TA data of  $[Fe(tren(py)_3)]^{2+}$  in acetone shows that both the activation energy  $(E_a)$  and the pre-exponential factor (A) are affected by changes in concentration.<sup>44</sup> Although the majority of the discussion had been on changes to the zero-point energy, changes in the pre-exponential factor make it clear that  $\Delta G^0$  is not the only parameter affected. Perhaps this makes sense since shifting one of the potential energy surfaces to increase the energy difference between the HS and LS states should also impact how the two surfaces couple to each other (thus, modulating  $H_{ab}$  and potentially  $\lambda$ ). Before turning to variable-temperature TA measurements to disentangle how parameters may be changing, the first step was to study whether concentration even impacts the GSR rate of  $[Fe(bpy)_3]^{2+}$  at room temperature.



**Figure 3-12.** Rates of GSR for  $[Fe(bpy)_3]Br_2$  in (a) water, (b) dimethyl sulfoxide, (c) methanol, (d) acetonitrile, and (e) 1-butanol at different concentrations after excitation at 550 nm.

The first experiment to examine the likelihood of ion pairing entailed studying the relaxation rate of  $[Fe(bpy)_3]Br_2$  in a handful of solvents, selected in order to cover a wide range of static dielectric constants, while varying the concentration of  $[Fe(bpy)_3]Br_2$  from approximately 0.00025 to 0.0025M. By ranging the static dielectric constant from 80.1 (water) to 17.84 (1-butanol), the force of attraction for ion pairing should be approximately 4.5 times stronger in 1-butanol than water; and yet, the results in Figure 3-12 reveal that the excited state lifetimes for  $[Fe(bpy)_3]Br_2$  are within error of one another for each concentration across all solvents. This suggests that either ion pairing is not playing a significant role in this concentration range, or significant ion pairing has already taken place. Since bromide is smaller than perchlorate, the anion used in the  $[Fe(tren(py)_3]^{2+}$  study, the latter option is feasible. Investigating the decay with other anions should help answer this question, where the smallest possible distance between  $[Fe(bpy)_3]^{2+}$  and the anion can then be altered.

The selected anions comprise a mixture of halides and polyatomic anions, spanning in size from chloride to the BAr<sup>F</sup><sub>4</sub><sup>-</sup> ion (Figure 3-13). For this study, acetonitrile was the solvent of choice as it had the lowest dielectric constant that all of the  $[Fe(bpy)_3]^{2+}$  complexes were soluble in. The same solute concentration range was maintained in these measurements as reported in the previous paragraph. Based on size, the halide ions should be most susceptible to ion pairing, especially at



**Figure 3-13.** Size comparison of each anion as well as  $[Fe(bpy)_3]^{2+}$ , for reference. Reproduced from crystal structures with refcodes: ABAJEV (Cl<sup>-</sup>), AAZDCO (Br<sup>-</sup>), PAFSIB (I<sup>-</sup>), AFODIJ (PF<sub>6</sub><sup>-</sup>), ABAHUH (BPh<sub>4</sub><sup>-</sup>), ABEBEQ (BAr<sup>F</sup><sub>4</sub><sup>-</sup>), and NUZKOI ([Fe(bpy)<sub>3</sub>]<sup>2+</sup>).

higher solute concentrations, whereas the BAr<sup>F</sup><sub>4</sub> ion should be relatively inert across the board. As can be seen in Table 3-2, however, exchanging the counterions does not appear to have made an impact on the GSR rate. Comparing the  $[Fe(bpy)_3]^{2+}$  complexes with halide anions in the same set of solvents as those shown in Figure 3-12 also exhibited consistent lifetimes across the series, as presented in Table 3-3.

**Table 3-2.** Relaxation times for  $[Fe(bpy)_3]^{2+}$  in acetonitrile for various anions at different concentrations after 550 nm excitation

	Ground State Recovery (ps)				
	Abs = 0.1	Abs = 0.4	Abs = 0.7	Abs = 1.0	
[Fe(bpy) <sub>3</sub> ]Cl <sub>2</sub>	$1015 \pm 40$	$1020 \pm 15$	$1005 \pm 45$	$1010 \pm 115$	
[Fe(bpy) <sub>3</sub> ]Br <sub>2</sub>	$1020 \pm 30$	$1015 \pm 15$	$1015\pm25$	$970 \pm 90$	
$[Fe(bpy)_3]I_2$	$1040 \pm 30$	$1015 \pm 15$	$1010 \pm 30$	$1045 \pm 110$	
$[Fe(bpy)_3](PF_6)_2$	$1025 \pm 25$	$1020 \pm 20$	$1005 \pm 40$	$1020 \pm 105$	
$[Fe(bpy)_3](BPh_4)_2$	$1030 \pm 40$	$1025 \pm 15$	$1005 \pm 30$	$1025 \pm 110$	
$[Fe(bpy)_3](BAr^F_4)_2$	$1045 \pm 45$	$1020 \pm 20$	$1030\pm30$	$1035\pm120$	

**Table 3-3.** Comparison of relaxation times for  $[Fe(bpy)_3]^{2+}$  as counterion is changed

_	Ground State Recovery (ps)			
_	[Fe(bpy) <sub>3</sub> ]Cl <sub>2</sub>	[Fe(bpy) <sub>3</sub> ]Br <sub>2</sub>	[Fe(bpy) <sub>3</sub> ]I <sub>2</sub>	
Water	$670 \pm 10$	$675 \pm 10$	$690 \pm 15$	
Dimethyl Sulfoxide	$800 \pm 5$	$805 \pm 10$	$800 \pm 15$	
Methanol	$975 \pm 10$	$985 \pm 20$	$995 \pm 20$	
Acetonitrile	$1020 \pm 15$	$1015 \pm 15$	$1015 \pm 15$	
1-Butanol	$1055 \pm 15$	$1060 \pm 20$	$1070 \pm 10$	

Between the results when changing the solvent and those when changing the counteranion, it is clear that if  $\Delta G^0$  is being modulated, it is not significant enough to show up in these data. It is possible that the effects of ion pairing are not observed here since  $[Fe(tren(py)_3]^{2+}$  should have a smaller zero-point energy difference than  $[Fe(bpy)_3]^{2+}$ ,<sup>50,51</sup> such that comparable adjustments to  $\Delta G^0$  may impact  $k_{nr}$  more strongly in the case of  $[Fe(tren(py)_3]^{2+}$ . Another possibility stems from the fact that there is another parameter which can alter both  $E_a$  and A from the Arrhenius equation and should be solvent-dependent: the reorganization energy.

#### 3.3.4 How solvation changes between LS and HS states

A study by Liu et al. was completed recently involving X-ray TA spectroscopic measurements on  $[Fe(dmb)_3]^{2+}$  in acetonitrile and water.<sup>32</sup> By using a high-resolution X-ray time-resolved spectroscopic technique, it was possible to study the spin, electronic, and nuclear degrees of freedom of this complex as the excited state evolved; this made it possible to detect structural changes due to solvent. As mentioned in Section 3.3.1, in studying the relaxation process from the  ${}^5T_2$  state to the  ${}^1A_1$  state, the data presented a noticeable difference between the two solvents that was outside of error in how much the Fe-N bond lengths changed between the HS and LS states, where  $\Delta R_{HS-LS}$  was 0.018 Å shorter in water. Since the Fe-N bond lengths were within error in the ground state, these Fe-N bond elongation changes stem from differences in the HS state, which the authors surmised were due to differences in solvation.

Solvation encompasses the interactions between the solute and solvent which stabilize the solvated species and are electrostatic in nature, comprising interactions such as hydrogen bonding and van der Waals forces. One way of estimating the Gibbs free energy of solvation ( $\Delta G_{solv}$ , in J·mol<sup>-1</sup>)<sup>52</sup> is with the Born equation:<sup>53</sup>

$$\Delta G_{solv} = -\frac{z^2 e^2 N_A}{8\pi\varepsilon_0 r} \left(1 - \frac{1}{\varepsilon_r}\right)$$
 Equation 3.3

where r is the radius of the solute (in m), and  $N_A$  refers to the Avogadro constant (in mol<sup>-1</sup>). In this expression, solvation represents the work done to transfer a spherical solute with uniform charge distribution from the gas phase to a solvent continuum. Equation 3.3 indicates that the LS state should be preferentially stabilized since it has a smaller radius, and solvation by solvents with higher static dielectric constants should give rise to larger  $\Delta G_{solv}$  values. However, while this equation works well when calculating the solvation energy of monatomic ions, transition metal complexes are not best represented as perfectly round entities with charges that are distributed evenly across the system. Instead, more complex models are required to effectively simulate the interactions of these molecules in solution. To assess the role of solvation in the GSR rate, density functional theory (DFT) was used, paired with a polarizable continuum model (PCM), to calculate  $\Delta G_{solv}$  of the singlet and quintet states of  $[Fe(bpy)_3]^{2+}$  in different solvents, followed by  $\Delta \Delta G_{solv}$ .

Although the solvation model based on density  $(SMD)^{54,55}$  represents the Gaussianendorsed option for computing solvation energy, no correlation between static dielectric constant and  $\Delta\Delta G_{solv}$  was observed (Table 3-4 and Figure 3-14). And so, in this study, the conductor-like polarizable continuum model (CPCM) was used,<sup>19,20</sup> with solvent properties added to the input file for each solvent individually. As suggested by Equation 3.3, the estimated solvation energies are more negative for the LS state than the HS state (Table 3-5); however, the trend based on the static dielectric constant follows the opposite of what is expected, exhibiting increasingly negative  $\Delta G_{solv}$ values with decreasing static dielectric constants. When  $\Delta\Delta G_{solv}$  is calculated, no significant correlation is immediately obvious between the estimated differential solvation energy and the rate **Table 3-4.** DFT Calculations for  $[Fe(bpy)_3]^{2+}$  with SMD<sup>a</sup> in various solvents at 20 °C

			In Hartrees		
	LS E <sub>0</sub> +G <sub>corr</sub> <sup>b</sup>	$LS \Delta G_{solv}$	HS E <sub>0</sub> +G <sub>corr</sub> <sup>b</sup>	HS AG <sub>solv</sub>	$\Delta\Delta G_{solv}$
Vacuum	-1609.37013	-	-1609.38197	-	-
Water	-1609.56560	-0.1954698	-1609.57259	-0.1906162	-0.0048537
Dimethyl Sulfoxide	-1609.58693	-0.2168002	-1609.59382	-0.2118440	-0.0049562
Ethylene Glycol	-1609.56853	-0.1984009	-1609.57427	-0.1922952	-0.0061057
Methanol	-1609.58493	-0.2147923	-1609.59037	-0.2083921	-0.0064002
Acetonitrile	-1609.59572	-0.2255867	-1609.60332	-0.2213455	-0.0042412
Ethanol	-1609.58511	-0.2149763	-1609.59195	-0.2099805	-0.0049959
Propionitrile	-1609.59652	-0.2263884	-1609.60378	-0.2218066	-0.0045818
2-Propanol	-1609.58322	-0.2130866	-1609.58819	-0.2062165	-0.0068702
Butyronitrile	-1609.59581	-0.2256783	-1609.60292	-0.2209429	-0.0047354
1-Butanol	-1609.58066	-0.2105282	-1609.58542	-0.2034492	-0.0070790
Tetrahydrofuran	-1609.57290	-0.2027650	-1609.58525	-0.2032761	0.0005111
Diethyl Ether	-1609.55464	-0.1845046	-1609.56334	-0.1813623	-0.0031423
Dichloromethane	-1609.58429	-0.2141604	-1609.59067	-0.2086932	-0.0054672

<sup>a</sup>Solvent environment was applied based on the solvent list and properties built into Gaussian 09. <sup>b</sup> $E_0+G_{corr}$  refers to the sum of electronic and thermal free energies.



**Figure 3-14.** Correlating the estimated change in Gibbs free energy of solvation of  $[Fe(bpy)_3]^{2+}$  from SMD calculations to the associated GSR rate for (a) all solvents in this study present in the solvent list and (b) all of the alcohol-based and nitrile-based solvents. The result for water is presented in (b), but is not included in the linear fit.

			In Hartrees		
	LS E <sub>0</sub> +G <sub>corr</sub> <sup>b</sup>	$LS\Delta G_{solv}$	HS E <sub>0</sub> +G <sub>corr</sub> <sup>b</sup>	HS AG <sub>solv</sub>	$\Delta\Delta G_{solv}$
Vacuum	-1609.37013	-	-1609.38197	-	-
Water	-1609.26289	0.1072421	-1609.25411	0.1278652	-0.0206231
Dimethyl Sulfoxide	-1609.41476	-0.0446283	-1609.41287	-0.0308920	-0.0137363
Ethylene Glycol	-1609.39519	-0.0250567	-1609.39280	-0.0108268	-0.0142298
1,3-Propanediol	-1609.41462	-0.0444901	-1609.41279	-0.0308172	-0.0136729
1,4-Butanediol	-1609.42815	-0.0580184	-1609.42696	-0.0449885	-0.0130298
1,5-Pentanediol	-1609.43691	-0.0667783	-1609.43625	-0.0542759	-0.0125024
Propylene Carbonate	-1609.42818	-0.0580446	-1609.52684	-0.0448625	-0.0131821
Methanol	-1609.36430	0.0058363	-1609.36036	0.0216145	-0.0157783
Acetonitrile	-1609.38901	-0.0188803	-1609.38653	-0.0045528	-0.0143276
Ethanol	-1609.39610	-0.0259674	-1609.39386	-0.0118836	-0.0140838
Propionitrile	-1609.41185	-0.0417146	-1609.40995	-0.0279817	-0.0137329
2-Propanol	-1609.41512	-0.0449839	-1609.41352	-0.0315477	-0.0134362
Butyronitrile	-1609.42517	-0.0550372	-1609.42395	-0.0419730	-0.0130642
1-Butanol	-1609.42536	-0.0552242	-1609.42431	-0.0423353	-0.0128889
Tetrahydrofuran	-1609.40347	-0.0333393	-1609.40218	-0.0202051	-0.0131342
Hexanenitrile	-1609.44073	-0.0705998	-1609.44049	-0.0585167	-0.0120832
Diethyl Ether	-1609.39917	-0.0290354	-1609.39877	-0.0167982	-0.0122372
Dichloromethane	-1609.38988	-0.0197435	-1609.38804	-0.0060699	-0.0136737

**Table 3-5.** DFT Calculations for [Fe(bpy)<sub>3</sub>]<sup>2+</sup> with CPCM<sup>a</sup> in various solvents at 20 °C

<sup>a</sup>Solvent environment was applied under generic setting, with properties written in directly.

 ${}^{b}E_{0}+G_{corr}$  refers to the sum of electronic and thermal free energies.



**Figure 3-15.** Correlating the estimated change in Gibbs free energy of solvation of  $[Fe(bpy)_3]^{2+}$  from CPCM calculations to the associated GSR rate for (a) all solvents in this study and (b) all of the straight-chain solvents (i.e. alcohols and nitriles). The result for water is presented in (b), but is not included in the linear fit.

of GSR, that is, until the data are separated into solvent families again (Figure 3-15). The similarity is especially striking in Figure 3-16, where the results for both the GSR rate and  $\Delta\Delta G_{solv}$  versus static dielectric constant in straight-chain solvents are superimposed. Since these models are based on a solvent continuum, there may be better correlation between similarly shaped solvents. These results show that the greater the differential solvation, the faster  $[Fe(bpy)_3]^{2+}$  will relax to the ground state. So again, why would solvent molecules be influenced by a transition that occurs on the metal center? To get at this, one needs to consider ligand field theory.

In an octahedral environment, the d orbitals on the metal center are split into three nonbonding  $t_{2g}$  orbitals and two antibonding  $e_g^*$  orbitals. Since the difference between a LS state and a HS state for a d<sup>6</sup> electron configuration is how the electrons fill these orbitals ( $t_{2g}^6$  versus  $t_{2g}^4 e_g^2$ ), the population of antibonding orbitals in the  ${}^5T_2$  state actually elongates the metal-ligand bond (designated as R). It is well-established that population of the  ${}^5T_2$  state results in a ~0.2 Å increase in the Fe-N bond length compared to the  ${}^1A_1$  state for [Fe(bpy)<sub>3</sub>]<sup>2+.39,56</sup> Thus, it should



**Figure 3-16.** The estimated change in  $\Delta G_{solv}$  between the HS and LS states for  $[Fe(bpy)_3]^{2+}$  in alcohol-based (red squares) and nitrile-based (blue circles) solutions are matched to their respective GSR lifetimes (purple triangles). Data plotted along the left and right axes have been standardized to each other. Arrows are included to direct the viewer to the appropriate y-axis based on colors matching the data points.

come as no surprise that this change in metal-ligand bond length contributes to a change in volume,  $\Delta V$ , of the complex between the two states. For similar Fe(II) complexes with a  $\Delta R_{HS-LS}$  value around 0.2 Å,  $\Delta V$  is generally reported as 25 Å<sup>3</sup> per complex.<sup>41,57–59</sup> This value stems from the difference in the unit cell volume of the HS and LS states divided by the number of formula units per unit cell. It is reasonable to believe that the response to a volume change between the <sup>5</sup>T<sub>2</sub> state and the <sup>1</sup>A<sub>1</sub> state would be solvent-specific, where that response would be dependent on solvation.

If the solvent dependence on the GSR rate originates from a solvent's response to  $\Delta V$  between the HS and LS states, then studying Fe(II) complexes with larger molecular volumes (but similar electronic structures) should result in larger negative slopes for  $\Delta\Delta G_{solv}$  versus static dielectric constant than that of  $[Fe(bpy)_3]^{2+}$  in, for example, the alcoholic series of solvents. Three complexes were included to test this:  $[Fe(dmb)_3]Br_2$ ,  $[Fe(5,5'-dmb)_3]Br_2$ , and  $[Fe(dtbbpy)_3]Br_2$ . Based on results from Co(III) analogs,<sup>60</sup> the LF strength appears to be similar across all ligands

	Transitions (cm <sup>-1</sup> )			Ligand Field Parameters (cm <sup>-1</sup> )		
	${}^{3}T_{1}$	${}^{3}T_{2}$	${}^{1}T_{1}$	$\Delta_{0}$	Racah <i>B</i>	Racah C
$[Co(bpy)_3](PF_6)_3$	13830	17340	21800	25780	440	3980
$[Co(dmb)_3](PF_6)_3$	14700	17840	21960	25590	390	3630
$[Co(5,5'-dmb)_3](PF_6)_3$	14420	17390	21820	25520	370	3700
$[Co(dtbbpy)_3](PF_6)_3$	13940	16890	21510	25300	370	3790

**Table 3-6.** Comparing ligand field strength of Co(III) polypyridyl complexes based on ligand field transition positions from electronic absorption spectra in acetonitrile<sup>a</sup>

<sup>a</sup>Data collected at room temperature and analyzed by Jonathan T. Yarranton.

(see Table 3-6). The molecular volumes of these Fe(II) complexes, calculated from their crystal structures by the Olex2 program,<sup>61</sup> rank from smallest to largest as:  $[Fe(bpy)_3]^{2+}$  (404.90 Å<sup>3</sup>)  $< [Fe(5,5'-dmb)_3]^{2+}$  (489.54 Å<sup>3</sup>)  $\sim [Fe(dmb)_3]^{2+}$  (489.61 Å<sup>3</sup>)  $< [Fe(dtbbpy)_3]^{2+}$  (748.06 Å<sup>3</sup>). Investigating both  $[Fe(dmb)_3]^{2+}$  and  $[Fe(5,5'-dmb)_3]^{2+}$  should help differentiate whether the solvent dependence stems from electronic effects or changes in volume, because the methyl groups in the 5,5'-positions are along nodes. Since the Fe-N bond lengths are not expected to differ much across these complexes,  $\Delta V$  should be largest for  $[Fe(dtbbpy)_3]^{2+}$ , which exhibits the largest molecular volume in the ground state. To test this, the alkyl-substituted Fe(II) complexes were synthesized.

The results from the TA measurements of these Fe(II) complexes are listed in Table 3-7. It is clear that, in addition to the impact of  $\Delta V$ , unforeseen effects are influencing the results of [Fe(dmb)<sub>3</sub>]Br<sub>2</sub>, giving rise to significantly prolonged lifetimes. This outcome is most likely a result of p orbitals on the methyl group overlapping with the  $\pi$ -system on the bipyridyl group, thus, **Table 3-7.** Comparison of relaxation times for [Fe(R-bpy)<sub>3</sub>]<sup>2+</sup> as substituent is changed

	Ground State Recovery (ps)					
	[Fe(bpy) <sub>3</sub> ]Br <sub>2</sub>	[Fe(dmb) <sub>3</sub> ]Br <sub>2</sub>	[Fe(5,5'-dmb) <sub>3</sub> ]Br <sub>2</sub>	[Fe(dtbbpy) <sub>3</sub> ]Br <sub>2</sub>		
Water	$675 \pm 10$	$860 \pm 10$	$635 \pm 10$	N/A <sup>a</sup>		
Methanol	$985 \pm 20$	$1210 \pm 10$	$1010 \pm 10$	$1035 \pm 10$		
Acetonitrile	$1015 \pm 15$	$1285 \pm 10$	$1040 \pm 10$	$1055 \pm 10$		
Ethanol	$1015 \pm 10$	$1210 \pm 10$	$1045 \pm 10$	$1125 \pm 10$		
2-Propanol	$1045 \pm 15$	$1225 \pm 10$	$1065 \pm 10$	$1235 \pm 10$		
1-Butanol	$1060 \pm 20$	$1285 \pm 10$	$1130 \pm 10$	$1300 \pm 10$		

<sup>a</sup>[Fe(dtbbpy)<sub>3</sub>]Br<sub>2</sub> is soluble, but not stable in water.



**Figure 3-17.** The GSR rate for  $[Fe(bpy)_3]Br_2$  (red circles),  $[Fe(dmb)_3]Br_2$  (yellow squares),  $[Fe(5,5'-dmb)_3]Br_2$  (green triangles) and  $[Fe(dtbbpy)_3]Br_2$  (blue diamonds) in alcohol-based solutions. The inset shows data which have been normalized to methanol.

altering the electron density on the nitrogen atom through conjugation.<sup>62</sup> Regardless, it is clear that the trend observed between  $[Fe(dmb)_3]Br_2$  and  $[Fe(5,5'-dmb)_3]Br_2$  are similar (see Figure 3-17), suggesting that electronic effects of the structure itself are not driving the solvent dependence. Altogether, the results show that incorporating a bulkier ligand does indeed appear to affect the solvent dependence of the GSR rate to a greater extent than the unsubstituted bpy, where the change in slope is more apparent between  $[Fe(dtbbpy)_3]Br_2$  and  $[Fe(bpy)_3]Br_2$ . Rather than relating to the change in volume, however, it is possible that these results are due to the ligand substitutions hindering the ability of solvent molecules to interact with the Fe(II) metal center.

To differentiate between these two hypotheses, the DFT-optimized structures of these Fe(II) complexes were analyzed by the Solid-G program,<sup>63</sup> described in Chapter 2, to get an idea of how protected the metal center is by the ligands around it. Figure 3-18 illustrates the solid angle parameter for the optimized (a) LS and (b) HS states of the  $[Fe(bpy)_3]^{2+}$  complex by projecting the coordination sphere coverage of each bpy ligand around the metal center. Each ligand is


**Figure 3-18.** Visualization of the extent of coordination sphere coverage of the (a) LS state and the (b) HS state of  $[Fe(bpy)_3]^{2+}$ .

**Table 3-8.** Average bond distances (Å), angles (°), and G values (%) of  $[Fe(bpy)_3]^{2+}$  in LS and HS states in alcohol-based solvents from computational results with CPCM

	Fe-N (Å)	N-Fe-N (°)	G Value (%)
LS state in Methanol	2.00	144.33	96.16
HS state in Methanol	2.20	130.43	85.34
LS state in Ethanol	2.00	144.10	95.95
HS state in Ethanol	2.20	130.29	85.29
LS state in 2-Propanol	2.01	143.92	95.96
HS state in 2-Propanol	2.20	130.11	85.17
LS state in 1-Butanol	2.01	143.83	95.91
HS state in 1-Butanol	2.21	130.02	85.14

**Table 3-9.** Average bond distances (Å), angles (°), and G values (%) in selected Fe(II) complexes from computational results under vacuum

	Fe-N (Å)	N-Fe-N (°)	G Value (%)
$\left[Fe(bpy)_3\right]^{2+}LS$	2.03	142.29	95.01
$[Fe(bpy)_3]^{2+}$ HS	2.23	128.57	84.16
$[Fe(dmb)_3]^{2+}$ LS	2.02	142.25	95.09
$\left[\mathrm{Fe}(\mathrm{dmb})_3\right]^{2+}\mathrm{HS}$	2.23	128.56	84.16
$[Fe(5,5'-dmb)_3]^{2+}$ LS	2.03	142.39	94.98
$[Fe(5,5'-dmb)_3]^{2+}$ HS	2.23	128.61	84.20
$[Fe(dtbbpy)_3]^{2+}$ LS	2.02	142.41	95.20
[Fe(dtbbpy) <sub>3</sub> ] <sup>2+</sup> HS	2.23	128.55	84.16

represented with a different color, and any overlap between each ligand is visible. As highlighted in Table 3-8, any changes to structure with changes in solvent are minimal. The steric parameters for the series of LS and HS states of related Fe(II) complexes under vacuum are presented in Table 3-9. Since an Fe(II) complex's molecular volume increases with the Fe-N bond lengthening, it should not be surprising that less of the metal center is shielded, exposing roughly 11% more of the metal center. What is interesting is that the G value does not appear to change much as the ligands around the metal center are exchanged with bulkier ligands. This is due, in part, to the substituents merely extending the ligand structure outward rather than blocking cavities to the metal center which are widened by the Fe-N bond elongation. As there is no significant change in the percentage of the metal center left unshielded across these complexes, any direct interactions between solvent molecules and the metal center, if there are any, are unlikely to differ much. And so, since a change in the slope is observed when fitting the GSR rate versus static dielectric constant, these results support the idea that the solvent dependence is driven by another factor.

Differential solvation energies for these Fe(II) complexes were then calculated from the computational results to see how they related to the observed solvent dependence, which is suggested to correlate with the associated change in volume between transitioning from the HS state to the LS state. The results of these calculations, where the solvent environment was still **Table 3-10.** DFT Calculations for  $[Fe(dmb)_3]^{2+}$  with CPCM<sup>a</sup> in various solvents at 20 °C

			In Hartrees		
	LS E <sub>0</sub> +G <sub>corr</sub> <sup>b</sup>	$LS \ \Delta G_{solv}$	HS E <sub>0</sub> +G <sub>corr</sub> <sup>b</sup>	HS AG <sub>solv</sub>	$\Delta\Delta G_{solv}$
Vacuum	-1845.17789	-	-1845.18962	-	-
Methanol	-1845.09063	0.0872584	-1845.08776	0.1018555	-0.0145971
Ethanol	-1845.13099	0.0469008	-1845.13293	0.0566820	-0.0097813
2-Propanol	-1845.15572	0.0221729	-1845.15916	0.0304588	-0.0082859
1-Butanol	-1845.17002	0.0078769	-1845.17375	0.1586907	-0.0079922

<sup>a</sup>Solvent environment was applied under generic setting, with properties written in directly. <sup>b</sup> $E_0+G_{corr}$  refers to the sum of electronic and thermal free energies.

			In Hartrees		
	LS E <sub>0</sub> +G <sub>corr</sub> <sup>b</sup>	$LS \ \Delta G_{solv}$	HS E <sub>0</sub> +G <sub>corr</sub> <sup>b</sup>	HS AG <sub>solv</sub>	$\Delta\Delta G_{solv}$
Vacuum	-1845.16317	-	-1845.17470	-	-
Methanol	-1845.08096	0.0822167	-1845.07879	0.0959086	-0.0136919
Ethanol	-1845.12244	0.0407359	-1845.12374	0.0509548	-0.0102189
2-Propanol	-1845.14763	0.0155465	-1845.14990	0.0247942	-0.0092477
1-Butanol	-1845.16131	0.0018668	-1845.16383	0.0108682	-0.0090014

**Table 3-11.** DFT Calculations for [Fe(5,5'-dmb)<sub>3</sub>]<sup>2+</sup> with CPCM<sup>a</sup> in various solvents at 20 °C

<sup>a</sup>Solvent environment was applied under generic setting, with properties written in directly. <sup>b</sup> $E_0+G_{corr}$  refers to the sum of electronic and thermal free energies.

**Table 3-12.** DFT Calculations for [Fe(dtbbpy)<sub>3</sub>]<sup>2+</sup> with CPCM<sup>a</sup> in various solvents at 20 °C

			In Hartrees		
	LS E <sub>0</sub> +G <sub>corr</sub> <sup>b</sup>	$LS \ \Delta G_{solv}$	HS E <sub>0</sub> +G <sub>corr</sub> <sup>b</sup>	HS AG <sub>solv</sub>	$\Delta\Delta G_{solv}$
Vacuum	-2552.36079	-	-2552.37123	-	-
Methanol	-2552.12755	0.2332390	-2552.12634	0.2448889	-0.0116499
Ethanol	-2552.19339	0.1673962	-2552.19253	0.1786976	-0.0113014
2-Propanol	-2552.23445	0.1263420	-2552.23299	0.1382321	-0.0118901
1-Butanol	-2552.25711	0.1036846	-2552.25508	0.1661434	-0.0124588

<sup>a</sup>Solvent environment was applied under generic setting, with properties written in directly. <sup>b</sup> $E_0+G_{corr}$  refers to the sum of electronic and thermal free energies.



**Figure 3-19.** The estimated change in  $\Delta G_{solv}$  between the HS and LS states for  $[Fe(bpy)_3]^{2+}$  (red circles),  $[Fe(dmb)_3]^{2+}$  (yellow squares), and  $[Fe(5,5'-dmb)_3]^{2+}$  (green triangles), and  $[Fe(dtbbpy)_3]^{2+}$  (blue diamonds) in alcohol-based solutions. The inset shows data which have been normalized to methanol.

imposed using the CPCM solvation model, can be seen in Tables 3-10 to 3-12. Excluding  $[Fe(dtbbpy)_3]^{2+,64}$  the results in Figure 3-19 reveal that the Fe(II) complexes with methyl-substituted ligands do exhibit a steeper dependence on  $\Delta\Delta G_{solv}$  versus static dielectric constant than  $[Fe(bpy)_3]^{2+}$ . If  $\Delta\Delta G_{solv}$  is driving the observed solvent dependence in the TA data, there should be a greater difference between the results for  $[Fe(dtbbpy)_3]^{2+}$  and  $[Fe(bpy)_3]^{2+}$ , and there is! It may be easier to detect a difference in the slopes between  $[Fe(dtbbpy)_3]Br_2$  and  $[Fe(bpy)_3]Br_2$  in the experimental results, because the percent increase in volume of the LS state is nearly 85% based on their crystal structures (compared to ~21% between either  $[Fe(dmb)_3]^{2+}$  or  $[Fe(5,5'-dmb)_3]^{2+}$  and  $[Fe(bpy)_3]^{2+}$ ), and thus,  $[Fe(dtbbpy)_3]Br_2$  must disrupt significantly more solvent-solvent and solvent-solute interactions as it relaxes back to the ground state.

How does this relate to non-radiative decay theory? Recall that the reorganization energy corresponds to both inner-sphere and outer-sphere components. Since the relaxation process from the HS state to the LS state represents a LF transition which takes place on the metal center, the outer-sphere contribution of  $\lambda$  was not expected to matter much. The correlation observed between the GSR rates and  $\Delta\Delta G_{solv}$  in Figure 3-16 suggests that this may not be true. The effect of solvation appears to track most strongly with these results, given that the change in volume associated with the HS-to-LS transition would require disrupting established solvent-solvent and solvent-solute interactions. Considering that Marcus derived the equation for outer-sphere reorganization energy ( $\lambda_0$ ) from the Born expression,<sup>37</sup>  $\Delta\Delta G_{solv}$  and  $\lambda_0$  are definitely related to one another – however, Marcus' equation cannot be used to solve for  $\lambda_0$  directly in this situation since this HS-to-LS transition does not actually involve transferring an electron from one complex to another.

While some of the computational work shown here correlates well with experimental results, the data are based on implicit solvation models, where solvent is incorporated as a

continuum and thus ignores key solute-solvent and solvent-solvent interactions, such as hydrogen bonding. In order to account for these specific interactions, explicit solvation models should be used – models which are too computationally demanding for my present skill set. Without molecular dynamics simulations which accurately reproduce experimental data, it is not clear exactly how solvent molecules are interacting with these Fe(II) complexes in the HS and LS states. However, the experimental and computational results presented here definitely suggest that solvation, and by extension  $\lambda_0$ , plays a large role in the observed solvent dependence. This idea is supported by the work of Liu et al., which shows that the Fe-N bond lengths of  $[Fe(dmb)_3]^{2+}$  are actually changing between two solvents;<sup>32</sup> however, drawing comparisons between acetonitrile and water may not be appropriate, as will be discussed in the next section.

# 3.3.5 A closer look at $[Fe(bpy)_3]^{2+}$ in aqueous solution

Recall that in earlier figures of this chapter, results collected in water were ignored in order to fit the data more accurately. This deviation may correlate with findings from recent computational and X-ray spectroscopic studies. In 2010, Lawson Daku and Hauser published an *ab initio* molecular dynamics study of  $[Fe(bpy)_3]^{2+}$  in aqueous solution whose purpose was to explore the influence of solvent on the early evolution of the excited complex.<sup>65</sup> Results from radial distribution functions, g(r), associated with the oxygen and hydrogen atoms of water, as determined by their distance from the metal center, suggest that water molecules are intercalated between the bpy ligands. Interestingly, looking at how the Fe-O (or Fe-H) running coordination number changes between the LS and HS states indicates that a few water molecules are released in going from the <sup>1</sup>A<sub>1</sub> ground state to the <sup>5</sup>T<sub>2</sub> excited state. Computational work by Das et al. came to the same conclusion, although they disagree on why the number changes, suggesting that it is induced by electronic effects in the CT state as opposed to structural ones upon forming the HS



**Figure 3-20.** TA results for GSR rate of  $[Fe(bpy)_3]Br_2$  in binary solvent mixtures of water (H<sub>2</sub>O) and acetonitrile (MeCN), pumped at 550 nm. In (b), the result collected in 100% water, plotted as 0% acetonitrile by mass, is not included in the fit.

state.<sup>66</sup> Results based on X-ray emission and X-ray diffuse scattering spectroscopies have since supported the idea of water molecules being expelled, as data could only be fit when incorporating an increase in the solvent density of the bulk solvent.<sup>67–69</sup> Although a new study by Lawson Daku with improved resolution now suggests that more solvent molecules can be found in the HS state than the LS state,<sup>70</sup> all of the computational results discussed here show water present within the inner shell of  $[Fe(bpy)_3]^{2+}$ .

With water molecules interspersed between the bpy ligands of the  $[Fe(bpy)_3]^{2+}$  complex, I wondered if this situation does actually allow for interactions directly between solvent molecules and the metal center, which, in turn, may influence excited state dynamics. And since water is a small molecule that may exist as an impurity in other solvents, tests were done to see if the presence of water itself was behind the variance in decay rates by systematically changing the ratio, by mass, between water and acetonitrile and measuring the rate of GSR for  $[Fe(bpy)_3]^{2+}$ . As shown in Figure 3-20, the GSR rate did not change dramatically as small amounts of water are added, but,



**Figure 3-21.** Ground state electronic absorption spectra for  $[Fe(bpy)_3]Br_2$  in a series of alcohols: water (red), methanol (yellow), ethanol (green), and 2-propanol (blue). The data are normalized at 505 nm to highlight changes to the MLCT band structure between the solvents.

rather, fit to a line as the percentage of acetonitrile changed. The trend also held when compared to previously reported dielectric constants for water/acetonitrile mixtures.<sup>71</sup> That said, Figure 3-20 also makes apparent that the GSR rate for  $[Fe(bpy)_3]^{2+}$  in pure water does not fit the trend. Additionally, when comparing the ground state absorbance spectra for  $[Fe(bpy)_3]^{2+}$  in different solvents to one another, it is clear that the solute response in water differs slightly from other solvents (see Figure 3-21), with the MLCT peak displaying slightly more vibronic structure. The observation of extra structure in the electronic absorption spectrum in a solvent with such a high static dielectric constant and straying from the line of best fit suggest that water behaves differently and needs to be treated as such.

# 3.4 Conclusions

A solvent dependence has been observed regarding the dynamics of LF transitions in  $[Fe(bpy)_3]^{2+}$  and related derivatives. Continuing to expand the series of solvents could refine our understanding of which solvent properties correlate most strongly with the observed GSR rate

dependence, especially by including more linear chain alcohol- and nitrile-based solvents. One suggestion on how to explain the phenomenon was as a result of ion pairing; however, there was no discernable change in the GSR rate over a range of concentrations regardless of the solvent or anion. At present, the effect of solvation appears to track most strongly with our results, given that the volume change associated with the HS-to-LS transition would require disrupting established solvent-solvent and solvent-solute interactions – interactions that would obviously change with solvent. Using an explicit solvation model to incorporate these specific interactions should more accurately assess how  $\Delta G_{solv}$  varies between the HS and LS states.

Additional measurements utilizing variable-temperature time-resolved spectroscopy, an experiment that has recently been added to our repertoire,<sup>72</sup> will help to identify trends, if not qualitative values, as to how the parameters of non-radiative decay change with solvent. Preliminary results of variable-temperature TA measurements on [Fe(dtbbpy)<sub>3</sub>]<sup>2+</sup> in methanol and 1-butanol, conditions which offer the largest difference in GSR rates, can be found in Appendix 3.A. Unfortunately, the parameters determined from Arrhenius and Eyring plots are within error of one another, prompting the need for further study. Other complementary experiments to employ are time-resolved X-ray spectroscopic measurements, which will lend valuable information as to the physical changes in structure associated with changes in solvent. Even if the main cause of the observed solvent dependence is not due to changes to the outer-sphere reorganization energy, the results from all of these experiments will be vital when it comes to running and interpreting meaningful DFT calculations. And so, while more work needs to be done to definitively answer why solvent affects the LF excited states of these complexes, the fact that it is happening at all is interesting and should be taken into consideration when discussing LF transitions in the future.

APPENDIX

# Appendix 3.A



# **Supplemental Information**

Figure 3A-1. Electronic absorption spectrum of [Fe(bpy)<sub>3</sub>]Cl<sub>2</sub> in acetonitrile.



Figure 3A-2. Electronic absorption spectrum of [Fe(bpy)<sub>3</sub>]Br<sub>2</sub> in acetonitrile.



**Figure 3A-3.** Electronic absorption spectrum of [Fe(bpy)<sub>3</sub>]I<sub>2</sub> in acetonitrile.



Figure 3A-4. Electronic absorption spectrum of [Fe(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in acetonitrile.



Figure 3A-5. Electronic absorption spectrum of [Fe(bpy)<sub>3</sub>](BPh<sub>4</sub>)<sub>2</sub> in acetonitrile.



**Figure 3A-6.** Electronic absorption spectrum of  $[Fe(bpy)_3](BAr^{F_4})_2$  in acetonitrile.



Figure 3A-7. Electronic absorption spectrum of [Fe(dmb)<sub>3</sub>]Br<sub>2</sub> in acetonitrile.



Figure 3A-8. Electronic absorption spectrum of [Fe(5,5'-dmb)<sub>3</sub>]Br<sub>2</sub> in acetonitrile.



Figure 3A-9. Electronic absorption spectrum of [Fe(dtbbpy)<sub>3</sub>]Br<sub>2</sub> in acetonitrile.



**Figure 3A-10.** GSR dynamics for  $[Fe(dtbbpy)_3]Br_2$  as a function of temperature after excitation at 550 nm in (a) methanol and (b) 1-butanol. Data collected by Monica C. Carey and analyzed by Jennifer N. Miller.



**Figure 3A-11.** (a) Arrhenius and (b) Eyring plots of GSR dynamics for  $[Fe(dtbbpy)_3]Br_2$  in methanol (red squares) and 1-butanol (blue circles) following excitation at 550 nm. Data collected by Monica C. Carey and analyzed by Jennifer N. Miller.

<b>Table JA-1.</b> Litenines for [Fe(0)y]3[D12 iii water/accioniume solvent mixture	Table 3/	A-1.	Lifetimes	for	[Fe(bpy) <sub>3</sub>	$Br_2$	in	water/ace	tonit	rile	solvent	t mixture
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Percent MeCN by Mass	Dielectric Constant <sup>a</sup>	Ground State Recovery (ps)
0	80.14	$675 \pm 10$
25	69.71	$855 \pm 15$
50	56.92	$920 \pm 10$
75	46.86	$965 \pm 15$
100	36.62	$1015 \pm 15$

<sup>a</sup>Dielectric constants (at 20 °C) are reported in Reference 71, with the 25% and 75% acetonitrile by mass values calculated by solving Equation 6 (within reference) with the parameters listed in Gagliardi et al.'s Table 2.

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# 4 Tuning injection and device performance of solar cells sensitized by *cis*-bis(cyano)bis(4,4'-dicarboxylic acid-2,2'-bipyridine)iron(II) via electrolyte additive control

#### 4.1 Introduction

Dye-sensitized solar cells (DSSCs) are designed to harness solar energy and convert it into electrical energy. As described in Chapter 1, this type of cell employs a chromophore to absorb sunlight and generate the electrons which are transported to and from the electrodes of the solar cell by semiconductor particles and a redox shuttle in the electrolyte, respectively. Although the idea to sensitize n-type semiconductor substrates with dye molecules dates from the 1960s,<sup>1,2</sup> it took until the early 1990s for work by O'Regan and Grätzel to show them as a tour de force for solar energy conversion in comparison to conventional silicon-based cells.<sup>3</sup> This report transformed the field of DSSCs by adsorbing a Ru(II)-based dye to a porous film of nanocrystalline titanium dioxide (TiO<sub>2</sub>) particles. The simple shift to use semiconductor nanoparticles rather than the single crystal surfaces before it substantially increased the surface area available for binding dye molecules and, thus, dramatically increased the amount of light absorbed.

Over the past three decades, significant effort has gone into the synthesis and survey of materials for use in DSSCs; however, the most efficient and well-studied devices tend to incorporate Ru(II) polypyridyl complexes, such as *cis*-bis(thiocyanato)bis(4,4'-dicarboxylic acid-2,2'-bipyridine)ruthenium(II) (known as the N3 dye). Unfortunately, ruthenium is an exceptionally rare and expensive metal,<sup>4</sup> and thus does not represent a sustainable option for use on a larger scale. This has spurred research directions concentrated on using more earth-abundant transition metals<sup>5–7</sup> or metal-free organic dyes<sup>8,9</sup> when designing new sensitizers. In pursuing new alternatives, attention within the McCusker group has been on studying first-row transition metal

complexes (e.g. Fe(II) and Cu(I) sensitizers), with iron-based complexes, specifically, being a major focus of my research.

# 4.1.1 Iron(II)-based sensitizers

Iron(II) complexes are desirable as potential sensitizers to replace ruthenium because they are isoelectronic with Ru(II) systems, as both metals are found in Group 8 of the periodic table. The first example of a Grätzel-type cell incorporating an iron-based sensitizer was reported in 1998 by Ferrere and Gregg,<sup>10</sup> which provided a proof of concept that iron can indeed be used to produce a photocurrent in a DSSC. Despite the structural similarity of that iron(II) sensitizer, *cis*-bis(cyano)bis(4,4'-dicarboxylic acid-2,2'-bipyridine)iron(II) (hereafter referred to as F2CA), to the so-called N3 dye (see Figure 4-1), the overall efficiency of the cell was measured to be roughly two orders of magnitude less than the comparable ruthenium-based device ( $\eta$  of 0.1% versus 10.2%, respectively).<sup>10,11</sup> Based on parameters from the J-V curve (Figure 4-2), this diminished efficiency most likely stems from a low level of current passing through the cell.



Figure 4-1. Molecular structures of complexes in this chapter: F2CA and N3.



**Figure 4-2.** Results of first iron(II) dye-sensitized solar cell. (a) J-V curve of F2CA on TiO<sub>2</sub> under illumination (top curve) versus in the dark (bottom curve). The electrolyte contained 0.5M lithium iodide, 0.05M iodine, and 0.2M 4-*tert*-butylpyridine in a mixture of acetonitrile (90% by volume) and 3-methyl-2-oxazolidinone. Device parameters:  $J_{SC} = 0.29 \text{ mA/cm}^2$ ,  $V_{OC} = 360 \text{ mV}$ , ff = 0.75,  $P_{in} = 75 \text{ mW/cm}^2$ ,  $\eta = 0.1\%$ . (b) Comparison of the absorption spectrum (dotted line) and absorbed photon-to-current conversion efficiency spectrum (solid line) of F2CA on TiO<sub>2</sub>. The absorption spectrum was collected with 0.5M lithium iodide in acetonitrile, while the APCE data reflects the same conditions as reported for the J-V curve. Reprinted with permission from Reference 10. Copyright (1998) American Chemical Society.

Although Ferrere and Gregg did not optimize the conditions of the Fe(II)-based DSSC, rather basing the electrolyte components on those favored for Ru(II) sensitizers, the real culprit behind the dismal photocurrent is ultrafast deactivation from the injecting charge transfer (CT) states to lower-lying ligand field (LF) transitions, located on the metal center. For this kind of application, however, a metal-to-ligand charge transfer (MLCT) state as the lowest energy excited state is desirable, because the electronic coupling strength between the dye excited states and the semiconductor substrate impacts the rate of injection, thus affecting the injection yield. The difference between first-row and second-row transition metals lies in the ligand field splittings, which increase about 25-30% with each successive increase in principle quantum number.



**Figure 4-3.** Depiction of energetics and excited state evolution for F2CA and N3 sensitizers relative to anatase TiO<sub>2</sub>. MLCT stands for metal-to-ligand charge transfer, LF is ligand field, and GS represents ground state.

Since the energetics of CT states are more dependent on the redox potential of the ligands than the ligand field strength, LF states tend to lie lower in energy than the lowest CT state for first-row transition metals while the lowest energy state is CT in nature for second- and third-row systems; the impact of this on the performance of DSSCs can be seen in Figure 4-3. Now, having a LF state as the lowest energy excited state would not be a problem if the MLCT state lifetime is sufficiently long and the injection rate is sufficiently fast. Unfortunately, that is not the case for Fe(II) polypyridyl complexes, where rapid conversion from the MLCT manifold to a ligand field (LF) state occurs in the first few hundred femtoseconds (fs) after excitation.<sup>12,13</sup> Since the rate of injection occurs on the same timescale as MLCT state deactivation for these Fe(II) complexes, the lower-lying LF states essentially prevent high injection yields from a proximity standpoint as well as energetically relative to the conduction band of TiO<sub>2</sub>.

Another interesting finding was noted in the 1998 seminal Fe(II) DSSC paper: an overlay of the absorption spectrum of F2CA on  $TiO_2$  with a spectrum of the cell's absorbed photon-to-

current conversion efficiency (APCE, see Figure 4-2b) illustrates that there is increased injection efficiency from the higher energy MLCT absorption band (10-11%) relative to the lower one (~2%). This discrepancy represents a band selectivity for injection. Since the electronic absorption spectrum and the incident photon-to-current conversion efficiency (IPCE) spectrum tend to match well for ruthenium-based sensitizers (suggesting that the photocurrent flowing through the cell is associated with the absorptivity of the dye at each wavelength), this is an unusual discovery. In Figure 4-2b, however, the absorption spectrum is compared to the APCE spectrum rather than the IPCE spectrum. The APCE spectrum, as stated in its title, is based on the quantum efficiency of the *absorbed* photons, so the same theory may not apply, but it is still an interesting result that initiated further discussion. One consideration was that this discrepancy may be a result of binding through a cyano group as opposed to carboxylic acid.<sup>14,15</sup> Another, more likely solution, to be described next, comes from computational work that has been conducted to resolve this question.

#### 4.1.2 Rationalizing band selectivity for injection in F2CA-TiO<sub>2</sub> devices

Work by the Jakubikova group has contributed to understanding the origin behind the band-selective behavior observed in F2CA-TiO<sub>2</sub> devices via quantum dynamics simulations.<sup>16,17</sup> Following the optimization of the ground state of F2CA, the absorption spectrum was simulated utilizing time-dependent density functional theory (TDDFT) methodology, where two absorption bands were observed in the visible region. The majority of the transitions within these bands were attributed to MLCT-based transitions, although a few exhibited metal-centered character. The orbitals associated with these transitions were matched to those that arise when F2CA is adsorbed to TiO<sub>2</sub> for consideration as donor states for injection. Interfacial electron transfer (IET) time constants for F2CA-TiO<sub>2</sub> were then calculated using quantum dynamics simulations and are based on the fraction of the total electron density still on the dye at different time points



**Figure 4-4.** IET times for the main LUMO states of F2CA adsorbed to the  $TiO_2$  surface. When anchored via carboxylic acid (CA), the parallel and perpendicular distinctions refer to the orientation of the unbound 4,4'-dicarboxylic acid-2,2'-bipyridine ligand to the  $TiO_2$  surface. The red line at 100 fs represents the typical intersystem crossing rate to low-lying LF states in Fe(II) polypyridyl complexes. Band 1 refers to the lower energy absorption band, while Band 2 is the higher energy band observed in the visible region of the absorption spectrum for F2CA. Reprinted with permission from Reference 17. Copyright (2013) American Chemical Society.

following excitation. These results can be found in Figure 4-4 and are divided based on the binding mode: cyano versus carboxylic acid, where the carboxylic acid can exhibit monodentate or bidentate binding, and the unbound 4,4'-dicarboxylic acid-2,2'-bipyridine ligand can be oriented either parallel or perpendicular to the TiO<sub>2</sub> surface. Since the horizontal red line symbolizes the typical MLCT state deactivation lifetime of Fe(II) polypyridyl complexes ( $\tau = 100$  fs), injection should occur from donor states with equal or faster lifetimes, represented by bars which lie at or below it.

Overall, there are states which exhibit injection rates that are competitive with relaxation to LF states, and they all happen to reside in the higher energy MLCT absorption band. This band selectivity can now be rationalized when one takes into account how the energy levels of the lowest unoccupied molecular orbitals (LUMOs) for F2CA map onto the density of states for the conduction band of TiO<sub>2</sub>. As the LUMO levels associated with the lower energy absorption band are positioned at the conduction band edge of TiO<sub>2</sub>, there is a diminished driving force for injection and poor coupling between dye donor states and states in the conduction band. These findings suggest that one way to improve the efficiency of injection from the lower energy absorption band would be to raise the dye energy levels (although lowering the conduction band edge would have the same effect).

#### 4.1.3 Optimizing the efficiency of Fe(II)-based DSSCs

If the issue preventing Fe(II)-based sensitizers from being practical replacements for their Ru(II) counterparts in DSSCs is the MLCT state lifetime, the two options to improve the injection yield are to either prolong the MLCT state lifetime or increase the electron injection rate. For the former, there has been success recently in synthesizing new Fe(II) complexes based on *N*-heterocyclic carbene ligands which, as a result of increased ligand field strength compared to traditional polypyridyl complexes, reach MLCT state lifetime such that the injection yield to a TiO<sub>2</sub> substrate reaches an incredible 92%,<sup>21</sup> this has not resulted in improvements to the overall cell efficiency – recombination of the injected electron with the oxidized dye appears to be much faster than dye regeneration.<sup>21,22</sup> This suggests that further modification to the dye structure may be necessary to promote efficient dye regeneration with the redox mediator, or the redox couple itself could be changed to achieve an optimal driving force associated with the dye regeneration process.

Given how easily changing one component of the cell to improve one particular process may inadvertently also negatively impact another, it is important to balance the opposing rates effectively. A more extensive discussion of how different substitutions of the major components within these solar cells (e.g. new dye, new semiconductor, new redox couple) impact the function and efficiency of the DSSC can be found in Chapter 1. Rather than changing the core solar cell components from those used in the original study by Ferrere and Gregg,<sup>10</sup> changes to the injection dynamics can actually be achieved by modifying the additives present in the electrolyte solution. In addition to the redox mediator and the solvent it is dissolved in, the electrolyte may contain cations and other additives that actively influence the electron transfer properties at the photoanode.

Fine-tuning the additives and their concentrations to optimize the performance of a DSSC is not new.<sup>23,24</sup> Cations are able to intercalate between the nanoparticles in the TiO<sub>2</sub> film, and like protons, this shifts the conduction band edge to more positive potentials.<sup>25</sup> Lithium-based salts are typically added in order to increase the photocurrent of a system, since a lower conduction band edge should increase the rate of injection;<sup>26</sup> however, this shift may also speed up recombination, a process which is said to occur in the Marcus inverted region. While lithium is one of the most common positively-charged additives, these affects are not limited to Li<sup>+</sup> ions; however, the extent of shifting the conduction band potential does seem to track with the charge-to-radius ratio (or charge density).<sup>27</sup> Other additives can be included in the event that cell performance is improved with a conduction band edge that occurs at a more negative potential.<sup>28,29</sup> Such an effect may be desired in order to increase the photovoltage of the device. In these cases, complexes which tend to passivate the surface are used, such as 4-*tert*-butylpridine (TBP). The surface passivation also has the added benefit of blocking sites for back electron transfer to the redox shuttle.

In general, optimal cell performance occurs when the rate of injection *just* outpaces the relaxation dynamics associated with the excited dye, as the energy of the conduction band edge of the semiconductor in this situation will also exhibit the slowest recombination kinetics. This concept of balancing the opposing processes rather than making injection as fast as possible (since

any increase in injection yield will be lost through faster recombination) is referred to as kinetic redundancy.<sup>30</sup> This idea still applies to the processes in F2CA-TiO<sub>2</sub> assemblies, but considering the IET process itself is the rate-limiting step in the F2CA-TiO<sub>2</sub> cell, it is possible that any improvement in the injection yield (as a result of a faster injection rate) may offset additional losses due to recombination. Preliminary studies involving different electrolytes have been done by Ferrere, focusing on how the IPCE spectrum changed with and without TBP in a solution of lithium iodide (LiI) and iodine (I<sub>2</sub>) dissolved in methoxypropionitrile.<sup>31</sup> The results did show increased injection from the lower energy MLCT band (henceforth referred to as MLCT<sub>1</sub>) when TBP was omitted from the electrolyte. Ferrere attributed the improvement to changes in the driving force for the injection process that had little impact on the higher energy MLCT band (MLCT<sub>2</sub>). To better understand whether this change is due to changes in driving force, orbital overlap between the excited dye donor and the density of states for the conduction band of TiO<sub>2</sub>, or both (and to continue to optimize Fe(II)-sensitized DSSCs), work has been done here to measure the energetics, dynamics, and device metrics of F2CA-TiO<sub>2</sub> solar cells under a variety of electrolyte conditions.

#### 4.2 Experimental details

#### 4.2.1 Synthesis and characterization

Synthesis of F2CA and preparation of the DSSCs studied in this chapter, the details of which will be available in a future paper,<sup>32</sup> were completed by Dr. Christopher Tichnell, a fellow member of the McCusker group. The general idea behind the synthesis, fabrication, and characterization techniques are discussed in Chapter 2 of Dr. Lisa Harlow's dissertation,<sup>33</sup> modified here such that all of the solar cells are 'sealed' with binder clips and a silicone spacer (McMaster-Carr, 0.1 inch) rather than Surlyn. This is due to the fact that the heating process used to melt the Surlyn has the unintended effect of oxidizing the iron(II) molecules. One downside to

using binder clips is that they do not prevent leaking, which can make studies time-sensitive. Although F2CA is the dye of interest, N3 has also been included in the discussion in order to study the differences in cell performance when a long-lived MLCT state is available, as well as to provide a frame of reference to other bodies of work.

The oxidation potential of F2CA bound to  $TiO_2$  in different electrolyte solutions was measured by electrochemistry with a homemade electrochemical cell. The MLCT band energies were calculated from the Fe(II/III) couple and the absorption spectra in the different electrolyte mixtures. The conduction band edge of  $TiO_2$  in the different electrolyte mixtures was determined by the photocurrent onset from photoelectrochemical measurements. Cell performance was tested with current-voltage (J-V) curves and IPCE measurements. All of this was done by Dr. Tichnell.

#### 4.2.2 Fabrication of solar cells

Fully operational dye-sensitized solar cells were prepared with fluorine-doped tin oxide (FTO) glass substrates. Both a  $TiO_2$  blocking layer and the active layer were applied to one of the conductive substrates, the photoanode, by doctor blading, which was followed by sintering. The sintered  $TiO_2$  films were then left to soak for about a day in a 0.5M ethanolic solution of the dye of choice (F2CA or N3) for the dye-loading process. The counter electrode was prepared from a second FTO substrate covered with a platinum source. The full solar cell was assembled by sandwiching a silicone spacer and the desired electrolyte between the two substrates. As mentioned above, each cell was held together by binder clips. The cells were set aside and left in the dark, overnight before any measurements were done in order to allow for complete interaction between the substrate and the additives in the electrolyte.

Half-cells were used to study the injection process via time-resolved ultrafast spectroscopic measurements as well as to measure the Fe(II/III) couple in different electrolytes with dye-

adsorbed TiO<sub>2</sub> on a glass slide for the former and FTO for the latter. These resemble the solar cells described previously, but the redox mediator ( $I_2$  and  $\Gamma$ ) is omitted from the electrolyte used here in order to simplify the dynamics observed on the ultrafast timescale, since the focus is not on the dye regeneration processes (at least not at present). The electrolyte additives known to impact the conduction band edge are included, however, as the point of this study is to understand their influence on injection and parse out whether cell efficiencies are increased as a result of driving force or electronic coupling between the TiO<sub>2</sub> acceptor and dye donor states. Freshly prepared half-cells were still allowed to sit overnight before running any measurements on them.

## 4.2.3 Electrolyte conditions

Table 4-1 describes the electrolytes studied throughout this work, distinguishing between the solutions in a fully operational solar cell and those utilized in the half-cells as redox-active and redox-inert, respectively. Intercalation by the cations  $Li^+$  and tetrabutylammonium (TBA<sup>+</sup>) is expected to shift the TiO<sub>2</sub> conduction band edge to more positive potentials and speed up the injection rate, with  $Li^+$  having a greater effect than TBA<sup>+</sup>. Passivation by TBP and 2,6-di-*tert*butylpyridine (DTBP) is expected to push the conduction band edge of TiO<sub>2</sub> up in energy,

Redo	x-Active	Redo	x-Inert
ID	Composition	ID	Composition
Li	$\begin{array}{c} 0.5M \ \text{LiI} \\ \text{and} \ 0.05M \ \text{I}_2 \end{array}$	Li'	0.5M LiClO <sub>4</sub>
Li + DTBP	0.5M LiI, 0.05M $I_2$ , and 0.3M DTBP	Li + DTBP'	0.5M LiClO <sub>4</sub> and 0.3M DTBP
Li + TBP	0.5LiI, 0.5M I <sub>2</sub> , and 0.3M TBP	Li + TBP'	0.5M LiClO <sub>4</sub> and 0.3M TBP
TBA	$\begin{array}{c} 0.5M \text{ TBAI} \\ \text{and} \ 0.05M \ I_2 \end{array}$	TBA'	0.5M TBAClO <sub>4</sub>
TBA + TBP	0.5M TBAI, 0.05M $I_2$ , and 0.3M TBP	TBA + TBP'	0.5M TBAClO <sub>4</sub> and 0.3M TBP

Table 4-1. Electrolyte mixtures used in this work, with all dissolved in acetonitrile

which has the effect of increasing  $V_{OC}$  but slowing down the injection rate. TBP, as a smaller molecule, should do a better job of passivating the surface than DTBP.

#### 4.2.4 Time-resolved transient absorption data

Since the timescales associated with the injection and excited state dynamics of traditional dyes range from sub-100 fs to the ps timescale, both of the ultrafast laser systems within the McCusker group (discussed in Chapter 2) were used to study F2CA in solution (in methanol and 0.1M NaOH) and on TiO<sub>2</sub> surfaces with different electrolytes (the redox-inert mixtures listed in Table 4-1). To check whether results depended on which MLCT band was excited, half-cells were typically pumped at 600 nm and 415 nm, while solution-based samples were excited at 610 nm and 433 nm in methanol, and 560 nm and 415 nm in basic water (0.1M NaOH). Some wavelengths used to excite the MLCT<sub>2</sub> band of F2CA were limited by how readily the laser systems could generate wavelengths in the fourth-harmonic region. The difference between the polarizations of the pump and probe beams was set at magic angle (54.7°). At the sample position, pump energies were 5  $\mu$ J when exciting the MLCT<sub>1</sub> band and between 1-2  $\mu$ J for the MLCT<sub>2</sub> band. To prevent data collection with multiphoton absorption, a 0.3 ND filter was used to make sure there was a linear dependence between the pump power and the signal response for each sample.

All samples were prepared in air. Solution-based samples of F2CA had ground state absorbances between 0.3 and 0.4 at the excitation wavelength in 1-mm path length cuvettes. The ground state absorbances for the F2CA-TiO<sub>2</sub> cells were more varied, ranging from 0.56 to 1.35 at the excitation wavelength. Transient absorption (TA) spectroscopic measurements were carried out at room temperature (ca. 20 °C). Although I had hoped that having solvent present would help dissipate heat effectively, ablation of dye molecules from the TiO<sub>2</sub> surface was still an issue, even with heavily defocused laser beams. And so, during TA measurements, the half-cells were

translated by 0.25 mm between each scan (via a Thorlabs PT1-Z8 translation stage with a KDC101 K-cube motor controller), regardless of which laser system was used. Since dye adsorption can vary over the film, an acceptable area of the half-cell was chosen when the I<sub>0</sub> did not change as the cell was translated. Unfortunately, the current operating system on the Road Runner computer is too outdated for the LabVIEW software that accompanied the 1" translation stage, and so the desired adjustments were initiated by hand between each scan (whereas it was incorporated into the LabVIEW data collection program on the Wile E laser system). It may be desirable to program the translation stage to constantly move (similar to the calcium fluoride mover) in future studies.

When probing in the visible region, proper alignment of the pump and probe beams was assessed with a standard in solution before switching out the cuvette sample holder for a binder clip to hold a half-cell sample. Proper overlap of the beams was maintained when studying half-cells by orienting each cell to match the angle of the back reflections observed with the standard solution. When probing in the near-IR region, depending on the excitation wavelength, alignment was checked with either  $[Ru(dpb)_3]^{2+}$  (where dpb is 4,4'-di-phenyl-2,2'-bipyridine), a molecule with a long excited state lifetime compared to the stage delay line, or with a silicon wafer (based on precedent reported by the Lian group).<sup>34</sup>

#### 4.3 **Results and discussion**

#### 4.3.1 Investigating the effect of electrolyte on solar cell performance

## 4.3.1.1 Anion dependence on electronic absorption spectra of F2CA-TiO<sub>2</sub> films

Since many of the measurements to determine the energetics of the F2CA-TiO<sub>2</sub> system were carried out under redox-inert conditions, it was important that aspects of the half-cell were as close as possible to the fully operational solar cell. Before settling on lithium perchlorate (LiClO<sub>4</sub>) as the Li<sup>+</sup> source in redox-inert studies, other options were considered. LiI was purposely

excluded in order to prevent the dye regeneration process from taking place, as that would obscure results. Although the availability of LiCl in the lab made it an ideal first choice, it is not soluble in acetonitrile (the solvent used in the fully operational solar cells described previously), thus preventing it from being a reliable comparison to normal cell conditions. Other Li<sup>+</sup> sources considered, in addition to LiClO<sub>4</sub>, included lithium tetrafluoroborate (LiBF<sub>4</sub>) and lithium tetraphenylborate (LiBPh<sub>4</sub>), where all were dissolved in acetonitrile.



**Figure 4-5.** Electronic absorption spectra of F2CA-TiO<sub>2</sub> half-cells with different  $\text{Li}^+$  sources: 0.5M LiBF<sub>4</sub> in acetonitrile (red), pure acetonitrile (yellow), 0.5M LiBPh<sub>4</sub> in acetonitrile (green), 0.5M LiCl in methanol (blue), 0.5M LiClO<sub>4</sub> in acetonitrile (purple), and 0.5M LiI in acetonitrile (black). The absorption spectra are normalized to the maximum of the MLCT<sub>1</sub> band.

Despite having the same concentration and existing in the same solvent environment, Figure 4-5 shows that the electronic absorption spectra of the F2CA-TiO<sub>2</sub> half-cells with these different electrolytes are drastically different. It is unclear what role the anion is playing in these absorption spectra, but it is possible that they influence the solvatochromic nature of the cyano ligands on the dye or perhaps are shifting the protonation level of the acidic groups of more labile protons. Although significant shifts in the conduction band edge of TiO<sub>2</sub> may not be occurring with these different solutions, salts with the ClO<sub>4</sub><sup>-</sup> anion in acetonitrile were chosen for the redox-inert electrolytes as they most closely matched the absorption spectra of the fully operational solar cells.

### 4.3.1.2 Device characterization

Data from the spectroscopic, electrochemical, and photoelectrochemical measurements of the F2CA-TiO<sub>2</sub> systems are presented in Figure 4-6. The biggest takeaway from these results is the trend regarding the energetics of the TiO<sub>2</sub> conduction band in the various electrolytes, which spans Li < Li + DTBP < Li + TBP < TBA < TBA + TBP from most positive (stabilized) to least positive (destabilized) potentials. This ordering matches what was expected, where  $Li^+$  can intercalate into TiO<sub>2</sub> to a greater extent than TBA<sup>+</sup>, and thus shift the conduction band to more positive potentials, and the pyridyl sources drive the conduction band edge to more negative potentials, with TBP having a greater effect than DTBP. In terms of the Fe(II/III) redox potentials and MLCT band positions, no trend is readily observed as a result of the electrolyte mixture.



**Figure 4-6.** Electrochemical potential energies of F2CA (labeled GS) relative to the conduction band of  $TiO_2$ , as influenced by the additives present in the electrolyte. The energy levels for the MLCT bands were calculated from the band maxima in the absorption spectra. Dr. Christopher Tichnell conducted the optical, electrochemical, and conduction band experiments that measured these values.



**Figure 4-7.** IPCE plots of F2CA bound to  $TiO_2$  under the following electrolyte conditions: Li (pink), Li + DTBP (yellow), Li + TBP (green), TBA (blue), and TBA + TBP (black). The inset portrays the IPCE curves normalized to the MLCT<sub>2</sub> band. Data collected by Dr. Christopher Tichnell.

The photovoltaic performance of fully operational F2CA- and N3-sensitized solar cells were examined with IPCE and J-V curve measurements. The impact of the different electrolyte conditions on the wavelength-specific quantum efficiency of F2CA-sensitized cells is shown in Figure 4-7. The IPCE percentages for both MLCT bands increase in the following manner: TBA < TBA + TBP < Li + TBP < Li + DTBP < Li. From these IPCE spectra, it is clear that the performance of Fe(II)-based cells improves with the addition of Li<sup>+</sup> and the exclusion of pyridyl sources, where the greatest efficiency, afforded by the Li electrolyte, reveals maxima around 16% for the MLCT<sub>2</sub> band and around 2.5% for MLCT<sub>1</sub>. These findings echo those seen by Ferrere.<sup>31</sup>

Table 4-2. Parameters from device characterization of F2CA-TiO<sub>2</sub> devices<sup>a</sup>

	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>OC</sub> (mV)	ff	η(%)
Li	$1.46 \pm 0.20$	$-378 \pm 34$	$0.63\pm0.03$	$0.35\pm0.04$
Li + DTBP	$0.65 \pm 0.12$	$-424 \pm 16$	$0.60\pm0.04$	$0.17\pm0.03$
Li + TBP	$0.25\pm0.04$	$-438 \pm 13$	$0.67\pm0.03$	$0.08\pm0.01$
TBA	$0.14\pm0.04$	$-386 \pm 20$	$0.57\pm0.02$	$0.03\pm0.01$
TBA + TBP	$0.10\pm0.02$	$-426 \pm 23$	$0.59\pm0.03$	$0.02\pm0.01$

<sup>a</sup>Data collected by Dr. Christopher Tichnell.
	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>OC</sub> (mV)	ff	η(%)
Li	$8.42 \pm 1.56$	$-416 \pm 34$	$0.63\pm0.04$	$2.23 \pm 0.41$
Li + DTBP	$5.19 \pm 1.89$	$-595 \pm 41$	$0.59 \pm 0.11$	$2.11 \pm 0.65$
Li + TBP	$3.69 \pm 1.12$	$-699 \pm 32$	$0.75\pm0.03$	$1.94\pm0.48$
TBA	$4.34\pm0.62$	$-704 \pm 16$	$0.70\pm0.06$	$2.19 \pm 0.39$
TBA + TBP	$4.88\pm0.33$	$-700 \pm 13$	$0.71\pm0.04$	$2.46\pm0.26$
20 11 11		11		

Table 4-3. Parameters from device characterization of N3-TiO<sub>2</sub> devices<sup>a</sup>

<sup>a</sup>Data collected by Dr. Christopher Tichnell.

Results from J-V curves of F2CA- and N3-sensitized TiO<sub>2</sub> assemblies are represented in Tables 4-2 and 4-3, respectively. It should be noted that the cell efficiencies for N3-based solar cells are generally lower than values reported by others in the literature; this is expected to be a result of differences in material quality and personal cell fabrication techniques, and should not impact interpretation of these results. For both dyes, it is apparent that the addition of Li<sup>+</sup> leads to the production of a higher photocurrent relative to the cells containing TBA<sup>+</sup>. Additionally, the trend follows that adding the pyridyl additives improves the open-circuit voltage (with TBP > DTBP) at the expense of the short-circuit current. This kind of improvement in one area at the expense of the other essentially voids any overall increase in cell performance for the N3-based solar cells. When looking at the F2CA-based cells, however, this is not the case. The cell efficiency increases in order from lowest to highest as TBA + TBP < TBA < Li + TBP < Li + DTBP < Li.

When the results from these tables are depicted as percent changes (in Figure 4-8), it puts in perspective just how much the Fe(II)-based devices improve when the pyridyl sources are removed and  $\text{Li}^+$  is included. Relative to the traditional electrolyte combination (Li + TBP), a 484% increase in the short-circuit current density overcomes a 14% decrease in the open-circuit voltage and 6% decrease in the fill factor to give a 360% increase in the cell efficiency for F2CA-TiO<sub>2</sub> solar cells which utilize the Li electrolyte. The trend observed in the conduction band edge shift for these electrolytes, visible in Figure 4-6, matches well with the increase in cell



**Figure 4-8.** Percent change in (a) short-circuit current density, (b) open-circuit voltage, (c) fill factor, and (d) cell efficiency for N3-TiO<sub>2</sub> solar cells (red circles) and F2CA-TiO<sub>2</sub> devices (green triangles) in different electrolyte compositions relative to the values obtained for Li + TBP.

efficiency for these F2CA-TiO<sub>2</sub> devices and the percent change in the photocurrent measured for these solar cells (from Figure 4-8). This suggests that the increase in cell efficiency is tied to the increase in photocurrent. Following this up with time-resolved measurements to investigate the injection process directly will help to assess how the dynamics and injection yield change with changes to the conduction band edge of  $TiO_2$  across the various electrolytes.

#### 4.3.2 Excited state dynamics of F2CA in solution

The F2CA-TiO<sub>2</sub> assembly has only been analyzed by time-resolved methods once previously, where a 100-fs time constant was measured for the interfacial electron transfer rate of that device.<sup>35</sup> But before analyzing how the interfacial electron transfer between F2CA and TiO<sub>2</sub> changes with the different electrolyte additives, it was important to be familiar with the excited state dynamics associated with the sensitizer itself. And so, studies to measure the lifetime of the MLCT-to-LF transition and the ground state recovery rate were undertaken.



**Figure 4-9.** Single wavelength kinetic traces of F2CA: (a) ground state recovery in methanol (blue trace) and basic water (0.1M NaOH, green trace) and (b) MLCT state deactivation in methanol (blue trace, with the solvent response in yellow). Samples were excited at 610 nm in methanol, and 560 nm in basic water.

The excited state decay of F2CA back to the ground state was measured in both methanol and a 0.1M NaOH solution. There does appear to be a solvent dependence on the ground state recovery of F2CA between these two solvents (Figure 4-9a). Although this solvent dependence seems to follow the findings from Chapter 3, it may also reflect the level of protonation of the anchoring group, as the number of acidic protons is known to impact the excited state dynamics of the dye.<sup>36</sup> The insolubility of this dye in other solvents prevented studying this further in a more extensive range of solvents. No excitation dependence was observed on the ground state recovery dynamics of this complex in either solution, suggesting that, even if the two bands in the absorption spectrum represent different types of transitions, both reach the same lowest energy excited state.

To measure the lifetime of the MLCT manifold, a spectroscopic handle was sought – in this case, a change in sign in the TA data, as this is indicative of a transition from one excited state to another, as opposed to relaxation within a particular excited state.<sup>37</sup> The results of such a transition can be seen in Figure 4-9b, where a positive signal decays to a negative one. Measuring a lifetime of 530 fs for the MLCT-to-LF deactivation process is considerably longer than the time constant that was assumed for the computational studies conducted by our collaborators in the Jakubikova group at North Carolina State University. As has been stated before, there is a desire for the MLCT state lifetime to persist as long as possible, because this prolongs the amount of time the excited electron has to inject into the conduction band of the semiconductor. Interestingly, experimental determination of this transition's lifetime would allow for refinement of those same computational studies, as their conclusions are based on donor states that exhibit IET lifetimes that are faster than 100 fs (see Figure 4-4).

However, results shown here are in solution rather than adsorbed to a semiconductor substrate. Considering how the choice of solvent is known to impact the lifetimes associated with a MLCT transition,<sup>38</sup> the time constant measured here may not accurately reflect the amount of time the MLCT state deactivation takes in a fully operational solar cell. Next steps to improve our understanding of the relaxation dynamics inherent to the dye would be to study it when bound to an inert semiconductor, such as alumina or zirconia, where injection is not possible. Under these conditions, the same electrolyte can be employed, and the only dynamics observed should be due to excited state relaxation. This is discussed in greater detail in Chapter 6.

#### 4.3.3 Investigating the interfacial electron transfer of F2CA-TiO<sub>2</sub> assemblies

Considering how much the conduction band edge shifts with changes in the electrolyte solution, the previously measured upper limit of 100 fs for the IET lifetime of the F2CA-TiO<sub>2</sub> assembly,<sup>35</sup> measured by Asbury and co-workers without any surrounding solvent, may not reflect what takes place under operational conditions. This work has sought to provide a better understanding of how the injection dynamics relate to the energetics of these systems, as well as to relate these results back to the device metrics described earlier. All of the F2CA-TiO<sub>2</sub> assemblies studied in this section were half-cells, meaning that there was no redox couple present in the solution. To maintain consistent pump-probe overlap in each sample, all of these half-cells were excited at the same pump wavelengths ( $\lambda_{ex} = 600$  nm for the MLCT<sub>1</sub> band and  $\lambda_{ex} = 415$  nm for MLCT<sub>2</sub>), chosen as energetic halfway points associated with the MLCT band maxima of each sample (see Figure 4-10). Under these experimental conditions, no signal due to excitation of bare TiO<sub>2</sub> was observed under any of the electrolyte conditions.



**Figure 4-10.** Electronic absorption spectra of F2CA bound to  $TiO_2$  with Li' (pink), bound to  $TiO_2$  with Li + DTBP' (yellow), bound to  $TiO_2$  with Li + TBP' (green), bound to  $TiO_2$  with TBA' (blue), bound to  $TiO_2$  with TBA + TBP' (black), dissolved in methanol (gray), and dissolved in 0.1M NaOH (purple). The absorption spectra are normalized to the maximum of the MLCT<sub>1</sub> band.

4.3.3.1 Studying band selectivity of F2CA-TiO<sub>2</sub> assemblies in various electrolytes

While probing the ground state bleach region of F2CA in these half-cells, it became apparent that the transient signal persisted beyond the expected timescale of ground state recovery. This suggested that the signal that remained was a result of the oxidized dye following injection to the TiO<sub>2</sub>. And so, this offset was used as a way to qualitatively compare between samples and excitation wavelengths. Since the MLCT excited state of F2CA undergoes ultrafast deactivation to a lower-lying LF state, any offset illustrates that hot injection must be occurring. A similar assessment is not possible with Ru(II)-based cells due to the long-lived excited state lifetime of those dyes, after which other processes such as dye recombination, which is expected to occur on the  $\mu$ s to ms timescale,<sup>39,40</sup> may start to complicate the analysis.

The data in Figure 4-11, based on the average of four data sets of four separate half-cells, display the remaining offset measured for each electrolyte and are differentiated by which MLCT band was excited. As can be seen, there is a band selectivity present for all electrolyte conditions, where the magnitude of the offset is larger following excitation of the MLCT<sub>2</sub> transition compared to that of MLCT<sub>1</sub>. This is consistent with the band-selective results from the IPCE spectra discussed previously, although not necessarily expected since those measurements take place under steady-state conditions and encompass the efficiencies of a number of solar cell processes (see Chapter 1). Given the fact that hot injection is occurring due to the excited state dynamics associated with the F2CA dye, differences in the signal offset based on which MLCT band is excited may indicate how the rate of IET changes as a result of changes to the driving force (e.g. pumping the MLCT<sub>2</sub> band has a larger driving force for the electron transfer process). Nonetheless, it is important that when making comparisons between the different samples and the different excitation wavelengths that all of the TA data are normalized to the same time delay.



**Figure 4-11.** TA data representing the qualitative injection yield following excitation into the MLCT<sub>1</sub> band ( $\lambda_{ex} = 600$  nm, red triangles) versus MLCT<sub>2</sub> ( $\lambda_{ex} = 415$  nm, blue squares) as the additives in the electrolyte are changed: (a) Li', (b) Li + DTBP', (c) Li + TBP', (d) TBA', and (e) TBA + TBP'. All data are normalized at t = 6 ps.

If the driving force for injection is represented by the difference in energy between the MLCT band energy level and the TiO<sub>2</sub> conduction band edge, the injection yield is expected to increase in the following order, regardless of which MLCT band is excited: TBA + TBP < TBA < Li + TBP ~ Li + DTBP < Li. However, the results (grouped by excitation wavelength in Figure 4-12) show increases to the signal offset in the following manner: Li + TBP' < Li + DTBP' < TBA + TBP' < Li + DTBP' < Li after excitation into the MLCT<sub>1</sub> band, and Li + TBP' < TBA + TBP' < Li + DTBP' < Li + DTBP' < Li after excitation into MLCT<sub>2</sub>. It is unclear why these orders do not match what was expected; however, it is interesting that the trends do hold when separated by cation type (Li<sup>+</sup>- versus TBA<sup>+</sup>-containing electrolytes).



**Figure 4-12.** TA data representing the effect of electrolyte on the qualitative injection yield (as related to the y-offset) of F2CA-TiO<sub>2</sub> half-cells after excitation into (a) MLCT<sub>1</sub> band ( $\lambda_{ex} = 600$  nm) and (b) MLCT<sub>2</sub> band ( $\lambda_{ex} = 415$  nm). The electrolyte combinations include Li' (in pink), Li + DTBP' (in yellow), Li + TBP' (in green), TBA' (in blue), and TBA + TBP' (in black). The error associated with each data point has been omitted for clarity. Data are normalized at 6 ps.

It is possible that the normalized TA offsets are inaccurate due to the decision to select a single excitation wavelength for each MLCT band with which to study all of the electrolyte combinations, and thus, some samples have either more or less energy than necessary relative to

the MLCT band maximum. However, initial studies do not show discernable changes in the normalized offsets following 10-15 nm shifts in the excitation wavelength within the same MLCT band. As for inconsistencies with the IPCE measurements, the TA results represent injection yield rather than the efficiency of the entire circuit at that particular wavelength; therefore, there may be losses in a fully operational cell that are not accounted for by these time-resolved measurements. Further studies are needed to assess these concerns.

#### 4.3.3.2 Probing interfacial electron transfer in the near-IR region

One of the major goals of this project is to quantify the IET rate. To get a direct measurement, or at least one that is not obscured by multiple signal sources, probing in the near-to mid-IR region is necessary. Signals in the visible region are more likely to be due to the loss of the excited state or the formation of the oxidized dye, instead of the transfer of electrons to the conduction band of the semiconductor. Additionally, it is more challenging to separate overlapping signal sources in this region – thus, underscoring one of the reasons why it is so important to distinguish signal sources by examining solar cell components individually when possible. Probing at redder wavelengths has been shown to improve the likelihood of measuring excited electrons being transferred to the conduction band of the semiconductor directly.<sup>34</sup>

Attempts to scan the signal of F2CA-TiO<sub>2</sub> assemblies with the Li' electrolyte at probe wavelengths between 1200 and 1700 nm are shown in Figure 4-13 and Figure 4-14, figures which differ based on which MLCT band was excited. Based on the solvent response from bare TiO<sub>2</sub> cells, it is clear that the pulse duration is longer than ideal in order to actually quantify the injection rate that occurs on the 100-fs timescale. Thus, pulse compression will be necessary in the future. Additionally, a positive signal is expected to represent this type of process, and yet both positive and negative features are observed. It is clear that a better understanding of the excited state



**Figure 4-13.** TA data of bare  $TiO_2$  (yellow trace) and  $F2CA-TiO_2$  (blue squares) with the Li' electrolyte after excitation at 430 nm and probing at (a) 1200 nm, (b) 1300 nm, (c) 1400 nm, (d) 1500 nm, (e) 1600 nm, (f) 1700 nm.



**Figure 4-14.** TA data of bare  $TiO_2$  (yellow trace) and  $F2CA-TiO_2$  (red circles) with the Li' electrolyte after excitation at 600 nm and probing at (a) 1200 nm, (b) 1300 nm, (c) 1400 nm, (d) 1500 nm, (e) 1600 nm, (f) 1700 nm.

dynamics occurring in these wavelength regions are necessary. This speaks to the need to study F2CA when bound to an inert semiconductor surface that would prohibit the injection process, thus leaving only responses that are due to the relaxation process. The fact that any signal is observed at all at these different probe wavelengths is exciting, especially after pumping into the MLCT<sub>1</sub> band. Considering that the other electrolyte conditions are expected to have decreased injection from the MLCT<sub>1</sub> band, it is possible that even redder probe wavelengths may be needed in order to detect signal due to injection. More discussion on these concerns can be found in Chapter 6.

# 4.4 Conclusions

An investigation regarding different electrolyte additives was carried out to study their impact on the injection yield and device parameters characterizing the efficiency of Fe(II)-based DSSCs. Results show that the cell performance of F2CA-TiO<sub>2</sub> assemblies improves when Li<sup>+</sup> is added and pyridyl-based additives are excluded – these adjustments alone led to a 250% increase in cell efficiency from the previously published results with the same dye-semiconductor system. The aim is to understand what it is about shifting the conduction band to more positive potentials with the Li<sup>+</sup> cation that improves the efficiency of Fe(II)-sensitized solar cells. Since computational work by the Jakubikova group suggests that the band selectivity of the IPCE spectrum for F2CA on TiO<sub>2</sub> potentially arises from a diminished driving force for injection and poor coupling between dye donor states and the density of states in the conduction band, being able to quantify the injection dynamics and any changes to them as the electrolyte is changed should help to distinguish which of those two possibilities plays a larger role in the changes to cell efficiency.

For the time-resolved measurements of these systems, it will be necessary to study the excited state dynamics of F2CA when adsorbed to a substrate that prevents injection. This will

allow the conditions for the half-cells to be mimicked without obscuring the TA signal with injection. This will be especially useful when trying to identify the signals present in the near-IR, a probe region that should also allow for the direct measurement of interfacial electron transfer between the excited dye and the semiconductor substrate. Additionally, to accurately measure the rate of injection in the near-IR region, shorter pulses will be needed which can be accomplished with the prism compressors on the laser table (in theory, anyway).

As for the TA measurements which probed in the visible region, band-selective behavior was observed with regard to the injection yield produced between the two MLCT bands in the absorption spectrum of F2CA. The trend regarding the magnitudes as the electrolyte was changed, however, did not appear to follow the order expected based on either the driving force or the results from IPCE measurements. This may be due to inherent differences in what processes are being studied, where TA data reflects injection dynamics and IPCE spectra are also based on the efficiencies of charge collection and dye regeneration. An experiment that may help to identify the rate of loss pathways entails using the nanosecond laser system to measure the rate of recombination for these half-cells as the electrolyte is changed. While these experiments will help to better understand how modulating the conduction band edge impacts the processes involved in Fe(II)-based solar cells, an alternative route to increase the rate of interfacial electron transfer involves modifying the anchoring group, a topic that will be discussed in Chapter 5.

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# 5 Probing interfacial electron transfer dynamics of Fe(II) polypyridyl-sensitized solar cells as a function of linker

# 5.1 Introduction

Dye-sensitized solar cells (DSSCs) capture solar energy and turn it into electricity using dye molecules bound to semiconductor nanoparticles. Most champion cells tend to feature Ru(II)-based dyes. Since ruthenium is rare, iron is seen as a convenient alternative that is more environmentally-friendly. Unfortunately, Fe(II) polypyridyl complexes are known to have lowest energy excited states that are ligand field (LF) in nature rather than metal-to-ligand charge transfer (MLCT) states, which are capable of injection.<sup>1–3</sup> Since this MLCT state deactivation process occurs on the sub-picosecond timescale, and thus is competitive with the injection pathway, some research has focused on increasing the rate of interfacial electron transfer (IET) to improve the cell efficiencies of Fe(II)-based solar cells. While the previous chapter of this dissertation discussed modifying the electrolyte composition to optimize cell performance, other options focus on the binding modes involved in the attachment to the semiconductor surface.

# 5.1.1 Dependence of anchoring group on interfacial electron transfer rate

The dye itself may be one of the more important components of a solar cell for how well it absorbs sunlight and how its excited states map onto the semiconductor substrate for injection, but the quality of the connection between the two is imperative for effective interfacial electron transfer. This is achieved with what it known as an anchoring group (also referred to as the linker) that covalently attaches the dye to the semiconductor surface. The choice of the anchoring group is important not only for withstanding the conditions under which the device is run (e.g. its susceptibility to hydrolysis), but the binding modes, and thus electronic coupling, also control the rate of injection in DSSCs.<sup>4–6</sup> Chromophores are most commonly attached to wide band gap semiconductors with the carboxylic acid group, but phosphonate is also widespread. Recent work

by the Jakubikova group set out to identify how different attachments impacted the IET between cis-bis(cyano)bis(4,4'-dicarboxylic acid-2,2'-bipyridine)iron(II) (expressed as F2CA from here on) and titanium dioxide (TiO<sub>2</sub>).<sup>7</sup>

The F2CA-TiO<sub>2</sub> system was the first published example of an Fe(II)-based sensitizer.<sup>8</sup> Unfortunately, this solar cell exhibited a 100-fold decrease in efficiency to a comparable Ru(II)-sensitized device,<sup>8,9</sup> attributed to poor photocurrent as a result of ultrafast relaxation from the injecting MLCT manifold. Seeking improved injection yields, the computational study by Bowman et al. examined the following linkers on the [Fe(bpy-L)<sub>2</sub>(CN)<sub>2</sub>] platform (where bpy = 2,2'-bipyridine and L = linker group): carboxylic acid, phosphonic acid, hydroxamate, catechol, and acetylacetonate (see Figure 5-1 for their structures).



**Figure 5-1.** (Left) Functional groups studied as anchoring groups for  $[Fe(bpy-L)_2(CN)_2]$  attached to a TiO<sub>2</sub> surface. (Right) Theoretical internal quantum efficiencies (TIQE) for dye-TiO<sub>2</sub> systems overlaid with their simulated electronic absorption spectra. Reprinted with permission from Reference 7.

One of the discoveries that came from the report of the first Fe(II)-based sensitizer involved the concept of 'band selectivity'.<sup>8</sup> This refers to the finding that, of the two MLCT bands present in the absorption spectrum of F2CA, the absorbed photon-to-current conversion efficency (APCE) spectrum showed that injection preferentially occurred from the higher energy band. In a separate

study, Bowman and co-workers concluded that this discrepancy arose as a result of energetic mismatch between the dye excited state and the density of states of the conduction band of  $TiO_2$ .<sup>10</sup> Essentially, the driving force and the electronic coupling, two things that are essential for fast IET, were too small for the lower energy MLCT band (MLCT<sub>1</sub>) compared to the higher energy MLCT band (MLCT<sub>2</sub>). And so, while undesirable, it is not wholly unexpected that there could still be band-selective behavior present across all of these anchoring groups (see data in Figure 5-1).

The graph in Figure 5-1 shows the theoretical internal quantum efficiency (TIQE) of each of these complexes, which represents the ratio of the electrons injected to the number of photons absorbed by the chromophore. To determine these efficiencies, only donor states that inject on a timescale faster than 100 fs were considered (as that signifies the expected lifetime of the MLCT manifold). Based on the quantum dynamics simulations, the hydroxamate linker is suggested to afford the most efficient IET in Fe(II)-sensitized DSSCs across the absorption spectrum, with the more traditional carboxylic acid ranking second. The remaining three linkers ranked worse due to weak coupling between the donor and acceptor states. In addition to improved IET rates, there is also evidence to suggest that a hydroxamate linker has increased stability in aqueous environments compared to the carboxylic acid linker, which is affected by hydrolysis. Based on these computational results, work has been done here to see how experimental results compare, with the aim of preparing more efficient Fe(II)-based DSSCs simply by changing the anchoring group.

#### 5.1.2 Impact of cyano groups on injection

It has also been postulated that the band-selective behavior observed in the APCE spectrum of the F2CA-TiO<sub>2</sub> device may arise from F2CA binding to TiO<sub>2</sub> through two different attachment modes – one through the carboyxlate linker and one through the cyano group. The difference in efficiency could then be explained as a result of different levels of electronic coupling between the

dye excited state and the semiconductor substrate. In fact, examples do exist which show that injection from hexacyano iron(II) to  $TiO_2$  is possible through metal-to-particle charge transfer.<sup>11,12</sup> To discern whether this band selectivity originates as a result of the attachment mode as opposed to the electronic coupling and driving force argument, complexes were synthesized which vary the number of polypyridyl ligands to the number of cyano groups, based on the following form:  $[Fe(bpy-L)_n(CN)_{6-2n}]^{(2n-4)}$ , where L is either carboxylic acid or hydroxamic acid and n = 2 or 3. The objective is to determine if and how the number of cyano groups on the Fe(II) sensitizer matters.

#### 5.2 Experimental details

The experimental details for this chapter follow the same procedures listed in Chapter 4, and so, the reader is directed to that chapter for a more extensive discussion regarding the fabrication and study of solar cells. As before, the synthesis and characterization of the DSSCs discussed here were carried out by Dr. Christopher Tichnell of the McCusker group.



**Figure 5-2.** Dyes studied throughout this chapter. F3COMe, F3HOMe, F2COMe, and F2HOMe were only studied in solution. F3HA and F2HA were only studied as a part of a dye-TiO<sub>2</sub> solar cell.

While the previous chapter focused on changes to the electrolyte composition, this work is based on studying how changes in the structure of the dye impact the injection dynamics and device metrics of Fe(II)-based solar cells. A number of different complexes were examined for this purpose, displayed in Figure 5-2. The naming scheme is based on F#X, where F refers to Ferrere (similar to how the 'N' in the N3 and N719 dyes stands for Nazeeruddin), # represents the number of bpy-L ligands in the dye, and X refers to the type of anchoring group. From that figure, F3COMe is tris(4,4'-dimethoxycarbonyl-2,2'-bipyridine)iron(II), F3CA is tris(4,4'-dicarboxylic acid-2,2'-bipyridine)iron(II), F3HAM is tris(4,4'-di-*N*-methyl-hydroxamic acid-2,2'-bipyridine)iron(II), F3HA is tris(4,4'-di-hydroxamic acid-2,2'-bipyridine)iron(II), and F2COMe is *cis*-bis(cyano)bis(4,4'-di-*N*-methyl-hydroxamic acid-2,2'-bipyridine)iron(II), F2HAM is *cis*-bis(cyano)bis(4,4'-di-*N*-methyl-hydroxamic acid-2,2'-bipyridine)iron(II), and F2HOMe is *cis*-bis(cyano)bis(4,4'-di-*N*-methyl-hydroxamic acid-2,2'-bipyridine)iron(II), and F2HOMe is *cis*-bis(cyano)bis(4,4'-di-*N*-methyl-hydroxamic acid-2,2'-bipyridine)iron(II), F2HAM is *cis*-bis(cyano)bis(4,4'-di-*N*-methyl-hydroxamic acid-2,2'-bipyridine)iron(II), F2HAM is *cis*-bis(cyano)bis(4,4'-di-*N*-methyl-hydroxamic acid-2,2'-bipyridine)iron(II), F2HAM is *cis*-bis(cyano)bis(4,4'-di-*N*-methyl-hydroxamic acid-2,2'-bipyridine)iron(II), F2HAM is *cis*-bis(cyano)bis(4,4'-di-*N*-methyl-hydroxamic acid-2,2'-bipyridine)iron(II), and F2HOMe is *cis*-bis(cyano)bis(4,4'-di-*N*-methyl-hydroxamic acid-2,2'-bipyridine)iron(II), F2HAM is *cis*-bis(cyano)bis(4,4'-di-*N*-methyl-hydroxamic acid-2,2'-bipyridine)iron(II), and F2HOMe is *cis*-bis(cyano)bis(4,4'-di-*N*-methoxy-carboxamide-2,2'-bipyridine)iron(II).

#### 5.3 **Results and discussion**

### 5.3.1 Investigating effect of anchoring group on device performance

The photovoltaic performance of fully operational Fe(II)-sensitized solar cells was tested by current-voltage (J-V) measurements. As can be seen from Table 5-1, the solar cells which incorporate an F2X-based sensitizer have improved device metrics across the board compared to the F3X-based devices. Although the electrolyte of DSSCs studied in a previous report differed slightly from those examined here (in that the cells omitted the 4-*tert*-butylpyridine additive, and the solvent was methoxypropionitrile), this disparity is similar to the results observed by Ferrere in the APCE spectra of F2CA- and F3CA-sensitized devices, where the MLCT<sub>2</sub> band exhibited an efficiency of roughly 33% for F2CA and 5% for F3CA, and the MLCT<sub>1</sub> band had an efficiency of

	$J_{SC}$ ( $\mu$ A/cm <sup>2</sup> )	V <sub>OC</sub> (mV)	ff	η(%)
F2CA	$250 \pm 40$	$-438 \pm 13$	$0.67\pm0.03$	$0.08\pm0.01$
F2HA	$318 \pm 19$	$-407 \pm 46$	$0.60\pm0.04$	$0.08\pm0.02$
F2HAM	$69 \pm 12$	$-339 \pm 36$	$0.51 \pm 0.05$	$0.01 \pm 0.004$
F3CA	$1.06 \pm 0.41$	$-22 \pm 1$	$0.26 \pm 0.01$	$6.8E-6 \pm 4.6E-6$
F3HA	$53.97 \pm 9.58$	$-248 \pm 1$	$0.51 \pm 0.01$	$6.9E-3 \pm 1.2E-3$
F3HAM	$6.70 \pm 0.37$	$-126 \pm 1$	$0.36 \pm 0.04$	$3.1E-4 \pm 5.1E-5$

Table 5-1. Parameters from device characterization of F2X- and F3X-TiO<sub>2</sub> devices<sup>a,b</sup>

<sup>a</sup>Electrolyte contained 0.5M LiI, 0.05M I<sub>2</sub>, and 0.3M 4-*tert*-butylpyridine dissolved in acetonitrile. <sup>b</sup>Data collected by Dr. Christopher Tichnell.

about 13% for F2CA and 5% for F3CA.<sup>4</sup> Considering the lower APCE values across the entire visible spectrum for F3CA, it should not be surprising that the cell efficiencies are similarly affected. In a separate study, Ferrere measured the oxidation potential of the Fe(II/III) couple for both F3CA and F2CA in acetonitrile: +638 mV and -77 mV versus ferrocene, respectively.<sup>13</sup> Although these values are based on the dye in solution, rather than bound to TiO<sub>2</sub>, with F3CA at a more positive value than F2CA (which is already strained when the energetics of the excited state are compared to the conduction band edge of TiO<sub>2</sub>), the photocurrent is bound to suffer. The more positive Fe(II/III) couple for F3CA may also hurt the rate of dye regeneration as well. As for whether hydroxamic acid or carboxylic acid is a better linker for cell efficiency, improvements in the short-circuit current density are seen with the hydroxamic acid, but the overall efficiencies are within error (at least for F2CA and F2HA). Based on results from Chapter 4, testing these solar cells without the 4-*tert*-butylpyridine additive may result in better performing devices for all dyes.

#### 5.3.2 Excited state dynamics of dyes in solution

To get an idea of the inherent relaxation dynamics associated with these dyes, they were studied in methanol. Since the degree of protonation for dyes with acidic protons is known to influence the kinetics of the complex,<sup>14</sup> additional complexes were prepared by Dr. Christopher Tichnell where the acidic proton on the anchoring group was replaced with a methyl group – resulting in esters (-COMe) instead of carboxylic acid (-CA) groups and *N*-methoxy-carboxamides

(-HOMe) in lieu of hydroxamic acid (-HA) groups. Replacement of the acidic protons with methyl groups is not expected to significantly affect the lifetimes of these complexes since the electronic effects should be similar, so they should represent reasonable standards for the 'fully protonated' version of the dyes. Ideally, the lifetimes between the acidic version and the methyl version of each pair of reciprocal chromophores will be similar, indicating that all dyes exhibit similar levels of protonation. Additionally, dyes with -HA groups were modified to *N*-methyl-hydroxamic acid (-HAM) for improved solubility.



**Figure 5-3.** Time-resolved data displaying the ground state recovery dynamics of different Fe(II)-polypyridyl complexes in methanol. F2X complexes were excited at 610 nm. F3X complexes were excited at 550 nm.

As seen in Figure 5-3, faster rates of ground state recovery (GSR) are observed for the F2X complexes compared to the F3X series. This reflects the stronger ligand field effect of the -CN groups. No effect on the rate of GSR is observed when pumping at the higher energy MLCT band versus the lower energy MLCT band for each complex. When comparing the GSR time constants between -HAM and -CA anchoring groups, complexes with -CA groups exhibit slightly shorter lifetimes than -HAM groups in methanol for both the F2X and F3X series. This could be due to

slight changes in the energetics of these systems between the two anchoring groups, but it could also be a reflection of a difference in molecular volume, where complexes with -HAM are slightly larger than -CA and so it may take more time to undergo the Fe-N bond length changes to return to the ground state. This idea is based on findings from Chapter 3.

The results from Figure 5-3 highlight how long the molecule is excited, but it does not reflect the amount of time the complex has to inject an electron. Since this class of Fe(II) complexes relaxes to lower energy, metal-centered ligand field states from the initially populated, MLCT state which is capable of injection, the MLCT deactivation lifetime is a key piece of information for IET studies. This was measured by fitting the transition from a positive transient absorption (TA) feature to a negative one, probing at the red edge of the MLCT<sub>1</sub> band.<sup>15</sup> While these results (in Table 5-2) are in solution rather than bound to a semiconductor substrate (and so should not be taken as the actual lifetimes occurring in a fully operational cell), by comparison, longer lifetimes are observed for the F2X series relative to the F3X complexes. This suggests that F2X dyes (especially F2HAM) should have increased injection yields compared to F3X dyes. Although these results provide qualitative comparisons, repeating these studies when bound to an inert substrate should disclose the true excited state dynamics as they are in DSSCs. The purpose of this is discussed in more detail in Chapter 6.

	<b>MLCT Deactivation (fs)</b>
F3CA	$210 \pm 15$
F3HAM	$215 \pm 10$
F3COMe	$210 \pm 10$
F3HOMe	$215 \pm 25$
F2CA	$530 \pm 30$
F2HAM	$785 \pm 125$

**Table 5-2.** Excited state dynamics of complexes in methanol<sup>a</sup>

<sup>a</sup>F2X complexes were excited at 610 nm. F3X complexes were excited at 550 nm.

#### 5.3.3 Studying interfacial electron transfer of Fe(II) dye-TiO<sub>2</sub> assemblies

For the time-resolved measurements of half-cells, the redox mediator was excluded from the electrolyte in order to simplify the number of processes taking place. This prevented any signal loss due to dye regeneration or back electron transfer. A few of the same redox-inert electrolyte mixtures from Chapter 4 were used in studying these F2X- and F3X-TiO<sub>2</sub> devices: Li' (0.5M LiClO<sub>4</sub> in acetonitrile), Li + DTBP' (0.5M LiClO<sub>4</sub> and 0.3M 2,6-di-*tert*-butylpyridine in acetonitrile), and Li + TBP' (0.5M LiClO<sub>4</sub> and 0.3M 4-*tert*-butylpyridine in acetonitrile). Recall that Li<sup>+</sup> cations intercalate into the semiconductor substrate which shifts the conduction band edge to more positive potentials, whereas the pyridyl additives are able to passivate the semiconductor surface which has the end result of shifting the band edge to more negative potentials – this effect is stronger for TBP than DTBP. Results shown here will compare between dyes with and without cyano groups and whether swapping one linker for another impacts the qualitative injection yield. The -COMe and -HOMe complexes were not a part of this study as they should not bind to TiO<sub>2</sub>.



**Figure 5-4.** Electronic absorption spectra for dye-TiO<sub>2</sub> assemblies with the Li + TBP' electrolyte: F2CA-TiO<sub>2</sub> (green trace), and F3CA-TiO<sub>2</sub> (purple trace). The absorption spectra are normalized to the maximum of the lower energy MLCT band. The absorption of bare TiO<sub>2</sub> has been subtracted from each, prior to normalization.

To start, half-cells incorporating F2CA and F3CA adsorbed to  $TiO_2$  were compared in the more traditional electrolyte, Li + TBP'. The absorption spectra for these half-cells (presented in Figure 5-4) show that the MLCT bands for the F3CA complex are rather blue-shifted relative to the F2CA complex. Therefore, to prevent inaccuracies in the qualitative injection yield as a result of excitation wavelength, samples were excited at their MLCT band maxima for the TA measurements. As the data in Figure 5-5 show, both dyes exhibit an offset, albeit small, that persists beyond the timescale of ground state recovery following excitation into either MLCT band; thus, this offset should represent the signal that remains due to the oxidized dye. In comparing the magnitude of the offset, the F2CA complex has an increased injection yield compared to its F3CA counterpart. Although part of the problem may be that the energetics for the F3CA complex do not overlap well with the TiO<sub>2</sub> conduction band, even excitation into the MLCT<sub>2</sub> band is worse off than that of F2CA. A larger issue probably stems from the shortened MLCT



**Figure 5-5.** TA data representing the qualitative injection yield following excitation into the MLCT<sub>1</sub> band (red triangles) versus MLCT<sub>2</sub> (blue squares) of (a) F2CA- and (b) F3CA-TiO<sub>2</sub> cells with the Li + TBP' electrolyte. All data are normalized at t = 6 ps.



**Figure 5-6.** Electronic absorption spectra of (a) F2HA-TiO<sub>2</sub> and (b) F2HAM-TiO<sub>2</sub> with the following electrolyte: Li' (red trace), Li + DTBP' (yellow trace), and Li + TBP' (green trace). The absorption spectra are normalized to the maximum of the lower energy MLCT band. The absorption of bare TiO<sub>2</sub> has been subtracted from each, prior to normalization.

As discussed in Chapter 4, the additives present in the electrolyte are able to shift the conduction band of the semiconductor to either more positive or more negative energies. Since the -CA and -HA anchoring groups have different donor states that will interact with the density of states on the TiO<sub>2</sub>, adjusting the conduction band edge may improve (or potentially worsen) the injection yield for one group more than another. One way to check this is by studying how the qualitative injection yield changes across the different dyes as the electrolyte is modified. And so, this was done with the Li', Li + DTBP', and Li + TBP' electrolytes for the F2CA, F2HA, and F2HAM dyes on TiO<sub>2</sub>. The remainder of the half-cells discussed in this chapter were prepared by Karl C. Nielsen of the McCusker group. Extra F2CA-TiO<sub>2</sub> cells were also included in these studies (although they are not reported here) to make sure that any differences in personal cell fabrication techniques did not have a noticeable impact on the results. It also served to show that the results were remarkably reproducible from sample-to-sample and day-to-day laser idiosyncrasies.

From the absorption spectra shown in Figure 5-6, it is possible to see that the F2HA-TiO<sub>2</sub> half-cells exhibit slightly blue-shifted MLCT transitions in the different electrolyte conditions compared to the F2HAM-TiO<sub>2</sub> cells. It is also interesting to note that the MLCT<sub>2</sub> band of the



**Figure 5-7.** TA data representing the qualitative injection yield following excitation into the MLCT<sub>1</sub> band (red triangles) versus MLCT<sub>2</sub> (blue squares) of (a) F2HA-TiO<sub>2</sub> and (b) F2HAM-TiO<sub>2</sub> with the Li' electrolyte. All data are normalized at t = 6 ps.



**Figure 5-8.** TA data displaying the qualitative injection yield following excitation into the MLCT<sub>1</sub> band (red triangles) versus MLCT<sub>2</sub> (blue squares) of (a) F2HA-TiO<sub>2</sub> and (b) F2HAM-TiO<sub>2</sub> with the Li + DTBP' electrolyte. All data are normalized at t = 6 ps.



**Figure 5-9.** TA data portraying the qualitative injection yield following excitation into the MLCT<sub>1</sub> band (red triangles) versus MLCT<sub>2</sub> (blue squares) of (a) F2HA-TiO<sub>2</sub> and (b) F2HAM-TiO<sub>2</sub> with the Li + TBP' electrolyte. All data are normalized at t = 6 ps.

	Redox-Inert Electrolyte			
	Li'	Li + DTBP'	Li + TBP'	
Exciting MLCT <sub>1</sub> band	$-0.111 \pm 0.004$	$-0.047 \pm 0.002$	$-0.039 \pm 0.003$	
Exciting MLCT <sub>2</sub> band	$-0.416 \pm 0.031$	$-0.351 \pm 0.013$	$-0.181 \pm 0.012$	

**Table 5-3.** Qualitative injection yields for F2CA-TiO<sub>2</sub> in various electrolytes<sup>a</sup>

<sup>a</sup>These results are plotted and discussed in Chapter 4, and represent the offset that remains from biexponential fits for TA data normalized at t = 6 ps.

F2HA-based cells appears to shift with each change in the electrolyte, although the reasoning behind this is not clear. Also, if the goal is to excite all samples at the  $\lambda_{max}$  of each MLCT band, having the MLCT<sub>2</sub> band shift to such blue wavelengths makes it more difficult to study since neither laser system is able to generate much in that region (i.e. fourth-harmonic generation). What I was able to collect can be found in Figures 5-7 thru 5-9 (with Table 5-3 included as a reference to the F2CA-based results). Similar to what was observed in Chapter 4, the offset increases as the passivating pyridyl removed from the electrolyte source is in the order of Li + TBP' < Li + DTBP' < Li', regardless of which F2X dye-TiO<sub>2</sub> device was examined by time-resolved spectroscopic measurements. However, there is no discernable difference between

the offsets measured for binding through -CA versus -HA (or -HAM). If anything, F2HAMsensitized devices were worse off than F2CA or F2HA in most cases. These findings agree with the results from the J-V curve measurements discussed above (Table 5-1), although they do not have to match considering these TA measurements only examine the injection process while J-V curves are also impacted by other solar cell processes.

#### 5.4 Conclusions

The goal of this work was to examine the effect of different linkers (carboxylic acid versus hydroxamic acid) and different ligand coordination geometries (bpy-L versus cyano) on interfacial electron transfer in Fe(II)-sensitized solar cells. There is computational work by the Jakubikova group that suggests that the hydroxamic acid should result in better cell efficiencies over the carboxylic acid anchoring group. Thus far, however, experimental results based on device characterization and time-resolved spectroscopic measurements do not exhibit a preference for one over the other in terms of cell efficiency or injection yield, respectively. There is, however, a notable difference between the injection yield of F2X and F3X dyes. This most likely stems from poor energetic matching between the excited states of F3X and conduction band of TiO<sub>2</sub>. The cyano ligands also help by increasing the ligand field strength relative to bpy, and thus, the F2X chromophores have longer MLCT lifetimes than the F3X complexes, resulting in more time for the injection process. Alternative electrolyte conditions may assist in improving the devices discussed here, but shifting from TiO<sub>2</sub> to a semiconductor with a more positive conduction band edge (i.e. SnO<sub>2</sub>) may also have a positive impact on the photocurrent for both F2X and F3X complexes. Other anchoring groups should be explored as well to test how well these computational results predict real changes in cell efficiency.

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# **6** Conclusions and future directions

# 6.1 Dissertation results

Transient absorption (TA) spectroscopy represents the means by which the discoveries presented throughout my dissertation were made possible. During my tenure at Michigan State University, the ultrafast laser lab of the McCusker group acquired a laser system with 35 femtosecond (fs) pulses (Road Runner) and upgraded the existing 130-fs laser system (Wile E) to include a 1035-mm translation stage (see Chapter 2 for more information about these laser systems). Both advancements have been invaluable for completing the work shown here.

Without the 13-ns delay line on the Wile E laser system, it would not have been possible to distinguish how different solvents affected the ground state recovery (GSR) lifetime of tris(2,2'-bipyridine)iron(II),  $[Fe(bpy)_3]^{2+}$ , and related derivatives (see discussion in Chapter 3). Additionally, the extended stage delay on Wile E made it possible to verify that signal offsets for the Fe(II) complexes adsorbed to titanium dioxide (TiO<sub>2</sub>) films extended well beyond the expected excited state lifetimes of those Fe(II) dyes. These studies also gave credence to previously published results, highlighting how changes in excitation wavelength and electrolyte solution are critical to the performance of solar cells incorporating Fe(II) sensitizers. It is with the newer system, Road Runner, that I have been able to quantify the ultrafast metal-to-ligand charge transfer (MLCT) state lifetimes for bis(cyano)bis(4,4'-dicarboxylic acid-2,2'-bipyridine)iron(II) (referred to as F2CA in Chapters 4 and 5) and related dyes in solution. Also with Road Runner, first steps have been taken to identify signals associated with interfacial electron transfer (IET) between F2CA and TiO<sub>2</sub> by probing in the near-infrared region.

In studying Fe(II) complexes for their use in dye-sensitized solar cells (DSSCs), the focus has predominately been on understanding the competition between IET and MLCT deactivation,

where the challenge stems from them both occurring on similar timescales. There are still a number of questions to answer as a result of the work within this dissertation as well as new directions to pursue with recent synthetic advancements that will be discussed in the following sections.

## 6.2 Studying interfacial electron transfer in dye-sensitized solar cells

#### 6.2.1 Distinguishing between electron transfer and excited state dynamics

At this time, only one study has been published regarding the injection dynamics of F2CA bound to  $TiO_2$ .<sup>1</sup> The work by Lian and co-workers represents the first experiment to demonstrate that the injection dynamics of an Fe(II) complex were able to rival relaxation to lower-lying ligand field (LF) excited states, and thus, generate the current first observed by Ferrere.<sup>2</sup> Following photoexcitation at 400 nm, a pump wavelength which excites the higher energy MLCT band, a rise time that matched the instrument response function (IRF) of the laser system being used was observed while probing at 5000 nm. Comparison of these results with an exponential rise function generated from a 100-fs time constant led them to conclude that IET occurs on a timescale faster than 100 fs. It should be noted that for these time-resolved spectroscopic measurements, Asbury et al. examined an F2CA-sensitized TiO<sub>2</sub> nanocrystalline thin film without a supporting electrolyte, contrary to the 'half-cells' described in Chapters 4 and 5. Given that the injection yield can change based on the additives present in the electrolyte,<sup>3</sup> the upper limit of the IET rate they report may not match what is actually taking place in a fully operational DSSC. However, it does underscore the importance of using an ultrafast laser system with fs resolution for these studies.

Although the Road Runner laser system affords shorter pulses (35 fs) than what is described in the study from the previous paragraph, the accurate measurement of lifetimes associated with IET of Fe(II) dye-TiO<sub>2</sub> assemblies still remains to be done. Preliminary work presented in Chapter 4 sought to identify probe wavelengths which monitor TA signals due solely

to electrons being added to the conduction band of TiO<sub>2</sub>. Interestingly, both positive and negative change in absorbance ( $\Delta A$ ) signals were observed while probing the F2CA-TiO<sub>2</sub> assembly in the near-IR wavelength region. Recall from Chapter 2 that a negative feature in TA spectroscopy is indicative of either emission or an excited state (ES) that absorbs less than the ground state (GS), since more photons are reaching the photodiode in the ES than in the GS. Given that these Fe(II) complexes are not emissive and the near-IR represents a region where the electronic absorption spectrum of these dyes is not expected to absorb, this is unexpected. However, it is possible that vibrational overtones or combinations of F2CA are being detected in this region. Whatever the case, it is clear that the absorption spectra of other possible signal sources need to be identified in order to get a better handle on where to probe in order to measure the electrons being transferred into the semiconductor conduction band.

One way of discerning which features are specific to excited state dynamics is with time-resolved spectroscopic measurements of these complexes in solution. To start, spectroelectrochemical measurements can aid in establishing what features to expect in a differential absorption spectrum which are indicative of MLCT excited states.<sup>4</sup> Combining this with time-resolved absorption data will allow features specific to LF states to then be identified. Should an isosbestic point be revealed in the time-resolved data, any signal observed when probing at that wavelength while studying an Fe(II) dye-TiO<sub>2</sub> assembly should be representative of either the oxidized dye or electrons in the conduction band. Either of these signal sources would help to quantify the timescale of injection. However, it should come as no surprise that the solvent choice plays a role, not only in the lifetimes of MLCT and LF states (see Chapter 3) for Fe(II) complexes, but also in the absorption spectrum of complexes such as F2CA due to the presence of the –CN groups, which induce solvatochromism.<sup>3</sup> While it is possible that any trends observed between
different Fe(II) dyes in the same solvent may be qualitatively similar to what is occurring in the corresponding DSSC, that may not be a good assumption to make considering how changes in the electrolyte additives have been shown to impact the injection yield by shifting the energetics of the dye and semiconductor, alike; therefore, a more appropriate intermediate is desired rather than relying solely on solution-based results to address excited state dynamics. This discussion serves to show how important it is to measure the excited state dynamics of the dye as it would be found in the solar cell – bound to a semiconductor surface with the appropriate surrounding electrolyte.

The desire to mimic the same conditions as when bound to TiO<sub>2</sub> with the same electrolyte solution as in a full solar cell, while only studying the excited state dynamics, speaks to the need to prepare dye-semiconductor assemblies which employ an 'inert' semiconductor, meaning that injection from the excited dye to the semiconductor is not possible. These kinds of studies have been implemented before with traditional ruthenium dyes, such as *cis*-bis(isothiocyanato)bis(4,4'dicarboxylic acid-2,2'-bipyridine)ruthenium(II) (also known as N3) with films made from zirconium dioxide (ZrO<sub>2</sub>) and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>).<sup>5-7</sup> The band gap associated with these materials is larger (ZrO<sub>2</sub> is ~5 eV<sup>8,9</sup> and Al<sub>2</sub>O<sub>3</sub> is ~10 eV<sup>5,10</sup>) than that observed for TiO<sub>2</sub>  $(\sim 3.2 \text{ eV}^{11,12}$  for anatase), but the more relevant parameter to consider here is where the conduction band edge sits relative to the energetics of the excited dye. These energy levels will shift slightly based on the surrounding electrolyte due to the dependence of the conduction band edge of metal oxides on the pH of the solution,<sup>13</sup> but for context, the work by Durrant and co-workers measured the conduction band edge potentials for TiO<sub>2</sub>, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> versus the saturated calomel electrode (SCE) to be -0.42 V, -1.24 V, and -4.45 V, respectively, in a 1:1 solution of ethylene carbonate/propylene carbonate.<sup>10</sup> Given that the conduction band edge for  $ZrO_2$  is only ~1 V more negative than that of TiO<sub>2</sub>, electron injection has been shown to be possible from N3 following excitation at bluer wavelengths.<sup>14</sup> Thus, the significantly higher conduction band edge makes  $Al_2O_3$  a more desirable option to prevent injection while looking at the pump dependence of excited state dynamics for Fe(II) dyes.



**Figure 6-1.** F2CA bound to Al<sub>2</sub>O<sub>3</sub> with 0.5M LiBF<sub>4</sub> in acetonitrile after excitation at 525 nm and probing at 570 nm.

Unfortunately, initial attempts by Dr. Christopher Tichnell (of the McCusker group) to prepare a colloidal Al<sub>2</sub>O<sub>3</sub> paste resulted in opaque films which did not allow for effective transmission of the probe beam, and thus, hindered the signal-to-noise response. As for the TA signal that was detected from the F2CA-Al<sub>2</sub>O<sub>3</sub> assembly, it persisted out to time delays that were considerably longer than the expected lifetime of the dye in solution (see Figure 6-1). This lasting offset is most likely a result of defects which form trap states that are present at energy levels within the band gap, both at the surface and in the bulk of semiconductor thin films.<sup>15–18</sup> These trap states are generally due to oxygen vacancies present in the nanocrystalline framework. In an effort to diminish the presence of oxygen deficiencies, a thin film of Al<sub>2</sub>O<sub>3</sub> was prepared by atomic layer deposition (ALD) with help from the Hamann group at Michigan State University;<sup>19</sup>

bypass this issue may be to apply a few layers of  $Al_2O_3$  by ALD over the homemade alumina paste. Now, as trap states are also known to negatively impact the performance metrics of DSSCs utilizing TiO<sub>2</sub>, methods that have been shown to diminish the density of trap states include introducing the TiO<sub>2</sub> to an oxygen plasma source,<sup>20</sup> flowing oxygen over the surface during the annealing process,<sup>21</sup> or treating it with TiCl<sub>4</sub>,<sup>22</sup> all prior to soaking the semiconductor in the dye solution. Similar efforts may be carried out with the inert semiconductor films. If the number of trap states cannot be reduced, then ZrO<sub>2</sub> may represent a more desirable inert substrate to utilize for these studies, because the surface properties of ZrO<sub>2</sub> match that of TiO<sub>2</sub> well;<sup>23</sup> therefore, the binding motifs and the effects of electrolyte should be similar to that observed in a functional DSSC.

# 6.2.2 Probing in the mid-IR to increase signal associated with injected electrons

As mentioned in the previous section, when studying excited dye molecules that are adsorbed to a semiconductor surface, probing in the visible region generally detects the absorptions of the dye molecule and can assist in determining whether it is in a ground, excited, or oxidized state. However, there is evidence illustrating that there can be significant spectral overlap of the absorption bands of these different states, making it more challenging to separate interfacial electron transfer (IET) from the additional dynamics at a particular wavelength.<sup>7,14,24–28</sup> Moreover, as was discussed in Chapters 4 and 5, probing in the visible region represents 'indirect' measurements of injection, where the data correspond to the loss of the excited state or the formation of the oxidized dye rather than a direct assessment of the electron injecting into the conduction band of the semiconductor. It has been shown, however, that probing in the infrared (IR) region allows for the direct measurement of IET.<sup>5,6,16,29–36</sup>

Signal from the electron injected into the semiconductor has been observed in the near-IR region (700 to 5000 nm); however, there can still be additional and significant contributions from other species in this wavelength region.<sup>5,35,37</sup> Probing even farther in the red, out to the mid-IR (approximately 5 to 25  $\mu$ m), can detect vibrational transitions of the dye, but more importantly, there is a significant increase in the TA signal from electrons injected into the conduction band of the semiconductor.<sup>5,6,16,29–36</sup> This increased signal from injected electrons is caused by free carrier absorption with an absorption coefficient that increases as a function of the probe wavelength.<sup>38</sup> This effect can be exploited regardless of the semiconductor used. Considering how the competition between injection and MLCT state deactivation of Fe(II) polypyridyl dyes diminishes the injection yield compared to their Ru(II) analogues, any increase in the amount of signal generated from injection would be helpful for detection purposes.

If one of the goals is to be able to probe in the mid-IR region, Road Runner, which is currently able to produce wavelengths as red as 2600 nm but can only detect wavelengths up to 1800 nm, would require a number of modifications. At present, neither of the optical parametric amplifiers (OPAs) on the laser table (Coherent, OPerA Solo) is configured to generate pulses in the mid-IR region. One alternative to sending an OPA to Coherent for a costly upgrade would entail steering and mixing the signal and idler beams from a single OPA into a crystal made of silver-gallium-sulfide (AgGaS<sub>2</sub>).<sup>33</sup> This results in the generation of a new pulse through a nonlinear process known as difference-frequency generation (DFG), where the frequency produced is the difference between the frequencies of the two beams combined in the crystal. Tuning the output of the signal and idler beams would allow beams ranging in wavelength from 2.6 to 16  $\mu$ m to be generated. As an alternative to reworking the exits for the signal and idler beams from the same OPA, another solution allows the output from the regenerative amplifier to be used directly by

generating a mid-IR continuum as a product of third-harmonic generation.<sup>39,40</sup> Additionally, this route would allow one to select the desired wavelength range from the continuum as needed rather than necessitating that the signal and idler beams be tuned and realigned in order to produce the desired mid-IR probe wavelength.



**Figure 6-2.** Example of experimental set-up for generating a mid-IR continuum by focusing the beams from third-harmonic generation and filtering out shorter wavelengths. Based on figures from references 39 and 40.

Following the configuration in Figure 6-2, Tokmakoff and co-workers were able to produce an IR continuum that ranged from 3000 to 25,000 nm from an 800-nm pulse with a 35-fs pulse duration and an energy of 400  $\mu$ J – conditions which are similar to those available on the Road Runner laser system. To achieve this, the doubling crystal was used to double the frequency of the 800-nm pulse, generating 400-nm light. Next, the purpose of the delay plate is to correct for temporal discrepancies between the 800-nm light and the 400-nm light. This is achieved by taking advantage of the orthogonal polarizations between the two beams such that they are affected differently by the fast and slow axes of the delay plate. Following that, the waveplate is used to set the polarizations between the 800-nm and 400-nm beams at 45° from one another before they enter the tripling crystal to produce 267-nm light. After the tripling crystal, a spherical mirror is used to focus the spatially- and temporally-aligned beams to such a point where fs pulse filamentation occurs in air. It is at this point that the mid-IR continuum is created. A second spherical mirror then collimates the laser, before a filter selectively transmits only the mid-IR range of wavelengths along the laser table.

While the folded prism compressor on the pump beam line of the Road Runner laser system is able to compress pump pulses to a duration where resolving injection dynamics is feasible, that represents only half of the equation for the temporal resolution, as it is a convolution of both the pump and probe pulses; thus, a short probe pulse is also needed to analyze the IET process in order to reasonably quantify ultrafast IET dynamics. Recall from Chapter 2 the relationship between pulse duration and bandwidth, where the energy required to maintain a fs pulse then translates to a significantly larger bandwidth in mid-IR, thus the continuum. To ensure that these probe pulses are as short as possible, a germanium window should be introduced.<sup>41</sup> This window can also act as a long pass filter to remove the UV and visible light required to generate the mid-IR beam. After the mid-IR pulse reaches the sample, it would need to be detected by something other than the current spectrometers and photodiodes in the McCusker ultrafast laser lab, as they are not suitable for this wavelength range. A mercury-cadmium-telluride (MCT) detector would meet these needs. Then it is just a matter of collecting and analyzing data. Once the film preparation for an inert semiconductor has been refined, discerning between excited state dynamics and interfacial electron transfer and quantifying the associated rates should be straightforward.

# 6.3 Optimization of solar cell components for iron(II)-based chromophores

Solar cells incorporating iron(II)-based chromophores have been studied more as a proof of concept up to this point, utilizing components that have been optimized for ruthenium(II)-based chromophores. Since the limiting factor for Fe(II) dyes stems from the lifetime of the injecting state, the conditions that work well to optimize solar cells with Ru(II) dyes are not necessarily the same that need to be considered for Fe(II) dyes. Unfortunately, it is difficult to identify what changes are going to be the most effective considering how inter-related the forward (favorable) and backward (unfavorable) processes are. Keeping that in mind, here are some recommendations of components to examine.

# 6.3.1 Test injection efficiency with new semiconductor surfaces

As has been discussed extensively in Chapter 4, the rate of IET is impacted by the conduction band of the semiconductor, both in terms of its energetics and the density of states that affect the electronic coupling with the dye. And so, while adjustments to the additives in the electrolyte can be used to drive the conduction band either up or down in energy in order to optimize cell performance, those changes to the electrolyte will also impact the energetics of the



**Figure 6-3.** Potential semiconductors to study with Fe(II) dyes such as F2CA in order to increase the overall injection yield, most notably from the lower energy MLCT band.

dye. An alternative would be to study these Fe(II) dyes when bound to a different semiconductor surface. Although TiO<sub>2</sub> represents one of the most widely studied materials, other examples of wide band gap semiconductors that have been used as the mesoporous oxide layer in the past include ZnO, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, and Nb<sub>2</sub>O<sub>5</sub>.<sup>42-44</sup> The semiconductor being selected to replace TiO<sub>2</sub> should exhibit a conduction band edge which is more positive than TiO<sub>2</sub> in an effort to increase the injection yield from an Fe(II) dye. In that case, ZnO and Nb<sub>2</sub>O<sub>5</sub> do not represent reasonable substitutes since the conduction band of ZnO matches the energetic level of TiO<sub>2</sub>, while that of Nb<sub>2</sub>O<sub>5</sub> is even more negative. And although the conduction band for In<sub>2</sub>O<sub>3</sub> is significantly lower in energy than TiO<sub>2</sub>, it has an indirect band gap of ~2.6 eV which, unfortunately, could absorb light itself at wavelengths blue of 475 nm.<sup>45</sup> Thus, SnO<sub>2</sub> and Sb<sub>2</sub>O<sub>3</sub> are shown as potential test subjects in Figure 6-3 which showcases their energetics relative to the F2CA dye in a cell with 0.5M Li<sup>+</sup> but no pyridyl source. Given that the open-circuit photovoltage (V<sub>OC</sub>) of a solar cell is tied to its power conversion efficiency, using a semiconductor with a lower conduction band edge will inherently lower the maximum possible V<sub>oc</sub>. So, in order to improve the efficiency of a cell, the photocurrent (which relates to the injection yield) will have to increase.

### 6.3.2 Modifying electrolyte composition

It has become increasingly clear that additive selections made based on the excited state dynamics associated with Ru(II) dyes are not necessarily the best options for Fe(II) dyes. This stems from the fact that injection from Fe(II) polypyridyl dyes competes with relaxation to lower-lying LF states. And so, simply changing the semiconductor may not afford the maximum possible injection efficiency of an iron(II)-based dye. There most likely would also be a need to adjust the concentration of additives in the electrolyte solution to optimize the cell's operating conditions. The effects of solvent choice and additives present in the solution on F2CA and similar

dyes are evidenced in work by Ferrere,<sup>3</sup> and have been followed up by myself and Dr. Christopher Tichnell, as discussed in Chapters 4 and 5. Beyond that, improvements may be found by changing the redox shuttle present in the solution, as the maximum possible  $V_{OC}$ , mentioned above, is also dependent on the reduction potential of the redox mediator. DSSCs with Ru(II)-based dyes tend to employ the  $\Gamma/I_3^-$  system as the redox shuttle. In addition to adjusting the reduction potential, the desire for an alternative redox shuttle to the  $\Gamma/I_3^-$  system is driven by the complex dye regeneration process (which reduces the oxidized dye through a multi-electron, inner-sphere process), the fact that this particular redox couple absorbs light in the same regions as sensitizers, and the volatile nature of iodine. Recent studies have shown that Co(II/III) polypyridyl systems may represent possible redox shuttles to replace the  $\Gamma/I_3^-$  system where simple modifications to the ligand substituents allow for reduction potential tunability.<sup>46-48</sup> As always, there is a balance to the solar cell system, where modifying one component helps or hurts the reverse process. The suggestions made in this section are done with the assumption that improvements in the injection yield should offset any losses that are incurred. The only way to know for sure is to test them.

#### 6.4 Extending MLCT state lifetimes of Fe(II) complexes

When thinking of how to improve the performance metrics of solar cells incorporating Fe(II) dyes adsorbed to a semiconductor surface such as titania, the majority of the discussion throughout this dissertation has been on making modifications to these systems in an effort to make the IET process faster (e.g. swap the anchoring group on the dye or tweak the electrolyte additives to modulate the  $TiO_2$  conduction band edge). While increasing the rate of IET to the semiconductor may improve the overall efficiency of a solar cell, the injection rate of Fe(II) polypyridyl-based sensitizers is already ultrafast.<sup>1</sup> Since poor photon-to-current conversion efficiencies for solar cells with Fe(II) polypyridyl complexes originate from the competition between injection and relaxation

to lower-lying LF states, another course of action would be to find a way to increase the lifetime of the MLCT states. Since IET occurs on the 100-fs timescale, simply prolonging the MLCT lifetime to 10 ps would be sufficient to produce an injection yield of ~99%. As straightforward as that sounds in theory, this approach has proven to be rather synthetically challenging. Avenues being pursued to address this will now be described.

#### 6.4.1 Disrupting the vibrational modes involved in the MLCT-to-LF conversion

If an Fe(II) complex was synthesized where changes to the ligand structure were able to inhibit the intersystem crossing process to a LF state, the lifetime of the injecting, MLCT state should increase. To do this, it would be necessary to have a handle on the reaction coordinate associated with the MLCT-to-LF deactivation process. One technique that can be used to identify this coordinate is variable-temperature transient absorption spectroscopy, where the data collection and subsequent analysis are similar to that described in Chapter 2, but with an optical Dewar that allows for data to be collected at different temperature points. Using Marcus theory, described in Chapter 3, the reorganization energy ( $\lambda$ ) can be parsed out and used to calculate the relevant vibrational modes through computational means.

Unfortunately, the MLCT state lifetime of Fe(II) polypyridyl complexes is too short for variable-temperature TA measurements to obtain the reorganization energy associated with the MLCT-to-LF transition directly. Instead, the value for the molecule of interest will need to be estimated as the difference between the reorganization energy of the MLCT-to-GS transition of a Ru(II) analog and that of the LF-to-GS transition of the Fe(II) complex. However, once the desired variable-temperature measurements are collected, like in Chapter 3, there are still three unknowns in the Marcus equation to solve for. To simplify this, any molecules studied should be genuine Fe(II) spin-crossover complexes, exhibiting a thermal equilibrium between the low-spin,  ${}^{1}A_{1}$  state

and the high-spin,  ${}^{5}T_{2}$  state. This should allow for the change in free energy ( $\Delta G^{0}$ ) to be measured via magnetic susceptibility measurements. From here, the reorganization energy associated with the MLCT-to-LF transition can be estimated, and the vibrational modes calculated.

Another method to discern the vibrational modes associated with MLCT state deactivation relies on vibronic coherence. Coherence in not an unfamiliar area in the McCusker group, as it has been used by others to study the active vibrational modes involved in the excited state dynamics of LF states in Cr(III) complexes.<sup>49,50</sup> While measuring the MLCT state lifetime of Fe(II) complexes described throughout this dissertation, oscillatory features were observed in some of the data sets. To explain the science behind this phenomenon, it is important to remember that for transform-limited pulses, as the pulse duration decreases, the pulse bandwidth increases as a result of the time-bandwidth product (refer to the discussion in Chapter 2 for more information). Thus, with a sufficiently short pulse, the increased bandwidth may excite multiple vibrational levels. As



**Figure 6-4.** Single wavelength kinetic trace of F2COMe in methanol (left) with the resulting power spectrum after LPSVD fit of data (right). The left figure displays the following traces: F2COMe (red), methanol (green), exponential fit (black), and the residual (blue). This sample was pumped at 550 nm and probed at 650 nm.

the excited wavepacket moves back and forth across the potential energy surface, oscillations in the signal may appear where the associated frequencies and damping times can provide information about the vibrational modes being activated and their relevance to particular excited state processes.

A MATLAB script written by Dr. Andrey Demidov and Dr. Paul Champion based on linear predictive singular value decomposition (LPSVD) was used to analyze data exhibiting oscillations. An example of typical results from TA measurements and frequency data after LPSVD analysis can be seen in Figure 6-4. Information regarding the observed modes are presented in Table 6-1, where F3CA is tris(4,4'-dicarboxylic acid-2,2'-bipyridine)iron(II), F3HAM is tris(4,4'-di-Nmethyl-hydroxamic acid-2,2'-bipyridine)iron(II), F3COMe is tris(4,4'-dimethoxycarbonyl-2,2'bipyridine)iron(II), F3HOMe is tris(4,4'-di-*N*-methoxy-carboxamide-2,2'-bipyridine)iron(II), and F2HAM is bis(cyano)bis(4,4'-di-N-methyl-hydroxamic acid-2,2'-bipyridine)iron(II). This is not the first time coherence has been seen in Fe(II) complexes. In 2009, Chergui and co-workers reported seeing a 130-cm<sup>-1</sup> mode in  $[Fe(bpy)_3]^{2+,51}$  a frequency that matches well with that listed in Table 6-1. Based on computational work,<sup>52</sup> that frequency was assigned as possibly arising from N-Fe-N bending modes. It is also important to keep in mind that features observed from this type of experiment are not always due to the sample complex. In fact, the frequencies around 500 cm<sup>-1</sup> also appeared in the solvent blanks and are thought to be an artifact from the quartz cuvette itself. Table 6-1. Summary of frequencies observed for Fe(II) complexes in methanol

	<b>Oscillations, cm<sup>-1</sup> (Damping Times, fs)</b>
F3CA	114 (254), 189 (556)
F3HAM	107 (153), 492 (784)
F3COMe	106 (423), 489 (410)
F3HOMe	106 (428), 493 (426)
F2CA	502 (204)
F2HAM	511 (183)
$[Fe(bpy)_3]Br_2$	136 (196)

It should be noted that the pump and probe wavelengths were not optimized for enhanced oscillatory response, nor was the amount of time between data points shortened to improve frequency resolution (as that would require longer periods of data collection). In the future, determining the vibrational modes associated with these frequencies via computational calculations could help establish molecular motions correlated with MLCT state deactivation, and thus which motions to obstruct in future dye design based on the atoms involved in the vibrational mode. Regardless of which of the above methods affords these answers, understanding which modes result in MLCT state deactivation should make it possible to design new molecules meant to inhibit that deactivation.

# 6.4.2 Increasing ligand field strength in Fe(II) complexes: Stabilizing $t_{2g}$ orbitals

Another path being explored to increase the MLCT state lifetime involves inverting the lowest energy excited state from a LF state to a MLCT state. The idea is that with a sufficiently strong ligand field strength, LF states should be destabilized to the point where a MLCT state becomes the lowest energy excited state. Such a feat would mean that these Fe(II) complexes would mimic the order of energetic states in Ru(II) polypyridyl complexes, and perhaps be in a position to replace them in applications that are dependent on the CT states formed following photoexcitation.

One direction to pursue this began by trying to synthesize a complex with improved octahedral symmetry. The majority of the Fe(II) complexes discussed throughout this dissertation represent structures with pseudo-octahedral symmetry. This reduction in symmetry from octahedral results in the degeneracy of the d orbitals being disturbed, causing splitting within the LF states. Achieving a more octahedral coordination environment should therefore decrease the

density of states between MLCT and lower-lying LF states, reducing the coupling between the states and hopefully decreasing the rate of relaxation out of the MLCT manifold.

Based on the structural environment achieved with its Ru(II) analog,<sup>53</sup>  $[Fe(dcpp)_2]^{2+}$ (where dcpp = 2,6-bis(2-carboxypyridyl)pyridine) was prepared by a previous group member.<sup>54</sup> Despite the nearly-perfect octahedral environment that this ligand imposed, this complex, unfortunately, did not exhibit any improvement in the MLCT state lifetime compared to other Fe(II) complexes.<sup>55</sup> However, changes to other optical and electrochemical properties sparked the desire for further investigation. Compared to the structurally-similar  $[Fe(tpy)_2]^{2+}$  (where tpy = 2,2':6',2"-terpyridine) and  $[Fe(bpy)_3]^{2+}$  (which is closer to octahedral symmetry than with the tpy ligand), the oxidation of the Fe(II/III) couple of  $[Fe(dcpp)_2]^{2+}$  was found to be roughly 600 mV more positive. This indicates a stabilization of the  $t_{2g}$  orbitals and may reflect an increase in the ligand field strength relative to the bpy and tpy ligands. Additionally, the electronic absorption spectrum of  $[Fe(dcpp)_2]^{2+}$  is advantageous for solar energy applications as the complex absorbs strongly in the visible with an MLCT absorption band maximum at 610 nm. So began the pursuit of a new class of Fe(II) polypyridyl complexes with a cross-conjugated ligand system, the end goal being to synthesize a ligand with a strong enough ligand field strength to drive the LF states up, above the MLCT states.

In an effort to determine what it is about the dcpp ligand that brought about the  $t_{2g}$  orbital stabilization, a similar complex,  $[Fe(dvpp)_2]^{2+}$  (where dvpp = 2,6-bis(2-vinylpyridyl)pyridine) was synthesized.<sup>56</sup> In this system, the oxygen in the carbonyl is replaced by a =CH<sub>2</sub> group. While the crystal structure of  $[Fe(dvpp)_2]^{2+}$  showed that the two structures were isostructural, the electrochemical data was a better match to  $[Fe(bpy)_3]^{2+}$ . Why would two structurally-similar complexes display such different results? It is possible that the electron-withdrawing effect of the

carbonyl group decreased the amount of electron donation to the metal center when compared to the dvpp ligand, and thus, these differences are a result of each ligand's  $\pi$ -donating ability (or lack thereof). To test this idea, future ligand modifications should be designed to modulate the level of electron donation at the metal center. Although the sensitivity of this ligand's backbone to hydrolysis makes synthetic modifications challenging and limits the solvent options for time-resolved spectroscopic studies, nailing down the specific properties involved in the increased ligand field strength opens up the possibility of an Fe(II) polypyridyl complex achieving a lowest energy excited state that is MLCT in nature.

# 6.4.3 Increasing ligand field strength in Fe(II) complexes: Destabilizing $e_g^*$ orbitals

Attempts to extend the MLCT excited state lifetimes of Fe(II) complexes have been successful in recent years, where, once again, inspiration was drawn from Ru(II) chemistry<sup>57</sup> to prepare ligands with the intent of destabilizing LF states, accomplished here with *N*-heterocyclic carbene (NHC) ligands. While this type of ligand had been used throughout Fe(II) chemistry before, it was primarily used in the field of catalysis, with little study of how the increased electron density on the Fe(II) metal center impacted its photophysics.<sup>58</sup> In 2013, Wärnmark and co-workers reported that the complex [Fe(CNC)<sub>2</sub>]<sup>2+</sup> (where CNC = 2,6-bis(3-methylimidazole-1-ylidine)pyridine) exhibited a <sup>3</sup>MLCT excited state lifetime of  $9 \pm 1$  ps.<sup>59</sup> This change from a traditional polypyridyl ligand (like tpy) resulted in a nearly 100-fold increase in the MLCT state lifetime! Such a dramatic change was attributed to the increase in  $\sigma$ -donation afforded by the ligand which destabilized the  $e_g^*$  orbitals of the Fe(II) metal center. The resulting increase in ligand field strength was then able to significantly destabilize the triplet and quintet LF states relative to other Fe(II) complexes.<sup>60</sup> It should come as no surprise that this finding has led to numerous computational and experimental studies of similar Fe(II) complexes in order to extend the MLCT

state lifetime further,<sup>61–68</sup> with the current record set at 528 ps with  $[Fe(btz)_3]^{2+}$  (where btz = 1,1'-bis(p-tolyl-4,4'-bis(1,2,3-triazol-5-ylidene))).<sup>69</sup>

If the MLCT state lifetime has been the limiting factor associated with solar cell efficiencies in solar energy conversion applications, how does this new complex perform as a sensitizer in a DSSC? In order to investigate this, carboxylate moieties were added as the anchoring group to the pyridine group of the CNC ligand.<sup>65</sup> The addition of the –COOH group led to a red-shift in the MLCT absorption maximum compared to the original molecule, as well as gave a <sup>3</sup>MLCT state lifetime of  $18 \pm 1$  ps in acetonitrile. This was further extended upon adsorption to an Al<sub>2</sub>O<sub>3</sub> film, achieving  $37 \pm 3$  ps. With techniques such as electron paramagnetic resonance, TA spectroscopy, transient terahertz spectroscopy, and computational calculations, Harlang et al. were able to establish that, when bound to TiO<sub>2</sub>, roughly 92% of the light absorbed by [Fe(CNC-COOH)<sub>2</sub>]<sup>2+</sup> was converted to electrons that underwent IET in a matter of a few ps from the <sup>3</sup>MLCT state. Since recent computational work by Jakubikova and co-workers suggests that the rate of IET for [Fe(CNC-COOH)<sub>2</sub>]<sup>2+</sup> should not be noticeably different from that expected by traditional Fe(II) polypyridyl complexes,<sup>66</sup> this finding supports the idea that the high injection yield arises from the Fe(II) NHC complex's extended MLCT state lifetime.

Although the injection yield from  $[Fe(CNC-COOH)_2]^{2+}$  to  $TiO_2$  is extraordinary, it does not speak to how many of those electrons are collected at the back electrode, or how other device metrics fare with this dye in a fully operational solar cell. At the same time that Harlang et al. were measuring the injection yield of the  $[Fe(CNC-COOH)_2]^{2+}$  complex, Duchanois et al. independently prepared and investigated this Fe(II) NHC complex while bound to  $TiO_2$ .<sup>67</sup> Following irradiation under AM1.5, a DSSC containing chenodeoxycholic acid and iodolyte AN-50 (a solution from Solaronix with the  $I^{-}/I_3^{-1}$  redox mediator in acetonitrile) produced an overall efficiency of 0.13%. Efficiency parameters associated with this DSSC only showed slight improvements compared to those published by Ferrere and Gregg when using F2CA as the sensitizer<sup>2</sup> (both of which still lag behind the results presented in Chapter 4). Computational and experimental results discussed earlier indicate that IET is not the limiting factor here, therefore, something else is hindering optimal charge collection at the external load. Results by Harlang et al. do indicate that recombination of the injected electrons from the TiO<sub>2</sub> to the oxidized dye occurs on ultrafast timescales, with roughly 85% of the injected electrons leaving the conduction band within a 149-ps time constant.<sup>65</sup> And so, despite the dramatic shift in excited state lifetime that led to the nearly quantitative yield of injected electrons, it has not led to improvements in solar cell efficiency as of yet. Under the right conditions (e.g. switching the redox couple), however, these advances associated with MLCT state lifetimes definitely suggest that iron complexes may one day be implemented in roles traditionally fulfilled by ruthenium-based systems.

#### 6.5 Closing comments

Although iron represents a natural replacement for ruthenium in the sensitizer of DSSCs, ultrafast deactivation to LF excited states in Fe(II) polypyridyl complexes results in sub-par injection yields and cell efficiencies. Thus, current research efforts have focused on increasing the rate of IET to compete with relaxation, modifying the structure to impede relaxation to LF states, or increasing the ligand field strength such that LF states are energetically higher than the MLCT excited state manifold. Results from studies of novel complexes show promise in the application of solar energy conversion, and also suggest the possibility of replacing ruthenium complexes in other areas where they are commonly used, such as photoredox catalysis.

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