Tuning Iron(II) Excited States with Bulky Ligands and Investigating Chromium(III) Photocatalytic Mechanisms for Earth-Abundant Photocatalysis

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Tuning Iron(II) Excited States with Bulky Ligands and
Investigating Chromium(III) Photocatalytic Mechanisms for Earth-Abundant Photocatalysis

by

Steven M. Fatur
B.S., Tufts University, 2008

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written by Steven M. Fatur

has been approved for the Department of Chemistry and Biochemistry

by:

_____________________________
Niels H. Damrauer

_____________________________
Oana R. Luca

Date________________________

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

Photocatalysis opens up new synthetic pathways and is a potential method for storing solar energy in chemical bonds. Many transition metal photocatalysts utilize long-lived metal-to-ligand charge transfer (MLCT) states as the catalytically active state. However, earth-abundant Fe(II) analogues of successful Ru(II) photocatalysts are plagued by ultrafast relaxation. Decreased ligand-field splitting in these first-row metal complexes opens new relaxation pathways via low-lying metal-centered states. To design potential photocatalysts with Fe(II) centers we chose to exploit the decreased ligand-field splitting by destabilizing the singlet state until the lowest energy quintet state became the ground state, opening up a distinct dynamical picture and lengthening the MLCT excited-state lifetime. In general, this class of complexes displays a >100-fold improvement relative to the ~100 fs MLCT lifetime of the low-spin parent, Fe(II) bis-terpyridine. This is accomplished using a sterically demanding bis-terpyridyl ligand framework in which interligand repulsion destabilizes lower spin states to force the quintet ground state. Furthermore, this framework is easily altered synthetically by employing substituents with either steric or electronic effects, allowing for substantial tunability. We have systematically synthesized a range of these compounds and investigated them using x-ray crystallography, electrochemistry, magnetic measurements, and transient absorption spectroscopy. Through this effort, we highlight a novel approach to controlling excited-state dynamics and ground-state absorption in Fe(II) polypyridines with potential photocatalysis applications.
A secondary project explores the mechanisms of Cr(III) photocatalyzed [4+2] cycloadditions. Cr(III) polypyridyl complexes have been found to serve as replacements for more expensive Ru(II) photocatalysts in these reactions. However, their application to a wider scope of reactions is limited by a lack of mechanistic understanding. With static and time-resolved photoluminescence spectroscopy and Stern-Volmer quenching studies, we show that [Cr(Ph$_2$phen)$_3$]$^{3+}$ (Ph$_2$phen = 4,7-diphenyl-phenanthroline) is a potent photooxidant for promoting radical cation Diels-Alder reactions. Further experiments show that atmospheric oxygen is critical for turning over the catalyst. Finally, the mechanistic study of a related reaction with the same catalyst suggests that an energy transfer mechanism is also feasible in certain cases. This broader understanding of mechanistic pathways uncovers a rich vein for further mechanistic studies and Cr(III) catalyst development.
# Table of Contents

Chapter 1. Introduction

1.1. Motivation ..........................................................................................................................1

1.2. Platinum Group Metal Photocatalysts ........................................................................3

1.3. Iron(II) Polypyridines as Photocatalysts .................................................................6

1.4. Strong-Field Ligand Approach ....................................................................................8

1.5. Research Plan: Sterically Hindered Weak-Field Ligands ........................................11

1.6. Overview of Chapters .....................................................................................................14

1.7. Chromium(III) Photocatalytic Mechanisms ..............................................................16

1.8. References .......................................................................................................................17

Chapter 2. Experimental Procedures

2.1. General Synthesis ...........................................................................................................23

2.2. Ligand Synthesis ............................................................................................................23

2.3. Complex Synthesis .........................................................................................................28

2.4. X-Ray Crystallography ................................................................................................32

2.5. Magnetic Measurements ..............................................................................................36

2.6. Electrochemistry and Spectroelectrochemistry ..........................................................37

2.7. Emission Studies on Cr(III) and Ru(II) Complexes ..................................................38

2.8. Other Experimental Details ..........................................................................................39

2.9. $^1$H NMR Spectra for New Ligands ............................................................................40

2.10. References ....................................................................................................................43

Chapter 3. Iron(II) 6,6”-Dichloroterpyridine: Accessing the Quintet Excited State Manifold

3.1. Introduction .....................................................................................................................45
3.2. Synthesis of dctpy and [Fe(dctpy)\(_2\)]\(^{2+}\) .................................................................46
3.3. Magnetic Measurements and X-Ray Crystallography .................................................49
3.4. Electronic Transitions and the Quintet MLCT State ..................................................51
3.5. Photophysical Exploration of the \(^5\)MLCT ..............................................................55
3.6. Conclusions ..................................................................................................................60
3.7. References ....................................................................................................................60

Chapter 4. Using Steric Strain to Manipulate the Spin States and Photophysics of High-Spin Iron(II) Terpyridines

4.1. Introduction and Motivation .........................................................................................63
4.2. [Fe(dbtpy)\(_2\)]\(^{2+}\) Electronic Absorption ..........................................................................65
4.3. Structural Data for [Fe(dbtpy)\(_2\)]\(^{2+}\) .........................................................................66
4.4. [Fe(dfpy)\(_2\)]\(^{2+}\) Electronic Absorption ...........................................................................68
4.5. SQUID Magnetometry .................................................................................................71
4.6. Deconvolving the Temperature-Dependent Absorption ..............................................73
4.7. Structural Data for [Fe(dfpy)\(_2\)](BF\(_4\))\(_2\) .....................................................................76
4.8. Cyclic Voltammetry .....................................................................................................78
4.9. Excited-State Dynamics ...............................................................................................79
4.10. Conclusions ...............................................................................................................90
4.11. References .................................................................................................................92

Chapter 5. Highly-Strained Iron(II) Terpyridines Containing Electron-Donating and -Withdrawing Substituents

5.1. Introduction and Motivation .........................................................................................96
5.2. Synthesis of 4'-Substituted Ligands and Complexes ..................................................99
5.3. Electronic Absorption and Magnetic Susceptibility of 4'-Substituted Complexes ..........103
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.4</td>
<td>Electrochemistry of 4’-Substituted Complexes</td>
<td>108</td>
</tr>
<tr>
<td>5.5</td>
<td>X-Ray Crystallography of 4’-Substituted Complexes</td>
<td>110</td>
</tr>
<tr>
<td>5.6</td>
<td>Excited-State Dynamics of 4’-Substituted Complexes</td>
<td>112</td>
</tr>
<tr>
<td>5.7</td>
<td>A Computational Model for Understanding the Dynamics</td>
<td>115</td>
</tr>
<tr>
<td>5.8</td>
<td>Conclusion and Future Directions</td>
<td>118</td>
</tr>
<tr>
<td>5.9</td>
<td>References</td>
<td>119</td>
</tr>
</tbody>
</table>

Chapter 6. Diquinolinylpyridyl Ligands to Increase Visible Absorption and Control Excited-State Charge Localization in High-Spin Iron(II) Complexes

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Introduction and Motivation</td>
<td>122</td>
</tr>
<tr>
<td>6.2</td>
<td>Synthesis of Diquinolinylpyridyl Ligands and Complexes</td>
<td>125</td>
</tr>
<tr>
<td>6.3</td>
<td>Magnetic and Structural Characterization of [Fe(dqp)_2]^{2+} and [Fe(decdqp)_2]^{2+}</td>
<td>128</td>
</tr>
<tr>
<td>6.4</td>
<td>Lowering the Energy of the MLCT Transition in [Fe(dqp)_2]^{2+} and [Fe(decdqp)_2]^{2+}</td>
<td>130</td>
</tr>
<tr>
<td>6.5</td>
<td>Charge Localization in [Fe(dqp)_2]^{2+} and [Fe(decdqp)_2]^{2+}</td>
<td>134</td>
</tr>
<tr>
<td>6.6</td>
<td>MLCT Lifetimes and Photophysical Picture for [Fe(dqp)_2]^{2+} and [Fe(decdqp)_2]^{2+}</td>
<td>136</td>
</tr>
<tr>
<td>6.7</td>
<td>Conclusions on the Broader State of High-Spin Iron(II) Chromophores</td>
<td>138</td>
</tr>
<tr>
<td>6.8</td>
<td>Potential Applications</td>
<td>141</td>
</tr>
<tr>
<td>6.9</td>
<td>References</td>
<td>143</td>
</tr>
</tbody>
</table>

Chapter 7. Mechanisms of Cr(III) Photoredox Catalysis

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Introduction and Motivation</td>
<td>146</td>
</tr>
<tr>
<td>7.2</td>
<td>General Cr(III) Photophysics</td>
<td>149</td>
</tr>
<tr>
<td>7.3</td>
<td>Cr(III) Photoredox Behavior with Electron-Rich Substrates</td>
<td>151</td>
</tr>
<tr>
<td>7.4</td>
<td>The Role of Oxygen</td>
<td>157</td>
</tr>
</tbody>
</table>
7.5. Chromium Photocatalysis with Electron-Poor Substrates ........................................163
7.6. Conclusions ........................................................................................................167
7.7. References .........................................................................................................168

Bibliography .............................................................................................................171
List of Tables

Table 1.1. Properties of Prominent PGM Photoredox Catalysts ................................................................. 4

Table 2.1. Structural and Diffraction Data Relevant to Chapters 3 and 4 ............................ 34

Table 2.2. Structural and Diffraction Data Relevant to Chapters 5 and 6 ............................ 35

Table 3.1. X-Ray Structural Data for [Fe(dctp)₂]^2+ ................................................................. 49

Table 3.2. Electrochemical Data for [Fe(dctp)₂]^2+ Collected in MeCN versus SCE ................................................................. 55

Table 4.1. X-Ray Structural Data for [Fe(dctp)₂]^2+ and [Fe(dbtp)₂]^2+ .......................... 68

Table 4.2. Temperature-Dependent Structural Data for [Fe(dft)₂](BF₄)₂ ............................ 77

Table 4.3. Cyclic Voltammetry Data for Halogenated Complexes in MeCN versus SCE ................................................................. 79

Table 4.4. Global Fit Lifetimes Collected in Room-Temperature Acetonitrile ............... 86

Table 5.1. Magnetic Susceptibility and Effective Magnetic Moment of 4’-Substituted Complexes ................................................................. 103

Table 5.2. Cyclic Voltammetry Data Collected in Acetonitrile versus SCE ............................ 108

Table 5.3. X-Ray Structural Data for 4’-Substituted Complexes ................................................................. 111

Table 5.4. Time Constants for the Thermalization (τ₁) and MLCT Excited-State Relaxation (τ₂) of 4’-Substituted Complexes ................................................................. 115

Table 5.5. DFT Spin Density Results for [Zn(MeCN)₃(L)]⁺ ................................................................. 117

Table 6.1. Selected X-Ray Structural Parameters for [Fe(decq)₂](BF₄)₂ ................................................................. 129

Table 6.2. Cyclic Voltammetry Data versus SCE for [Fe(dq)₂]^2+ and [Fe(decq)₂]^2+ ................................................................. 132

Table 6.3. DFT Spin Density Results for [Zn(MeCN)₃(L)]⁺ for L = dq, decq ................................................................. 136

Table 6.4. Time Constants for the Thermalization (τ₁) and MLCT Excited-State Relaxation (τ₂) of Fe(II) bis-(diquinolinylpyridyl) Complexes ................................................................. 137

Table 7.1. Substrates for Quenching Studies and their Oxidation Potentials .......... 156
List of Figures

Figure 1.1. Latimer diagram for a generalized photoredox catalyst (PC) acting as a photooxidant .................................................................3
Figure 1.2. Abundance of elements in the Earth’s crust ..................................................5
Figure 1.3. UV-visible absorption spectra for [Ru(bpy)₃]²⁺ and [Fe(bpy)₃]²⁺ .......................6
Figure 1.4. Potential energy surface cartoons for a Ru(II) polypyridyl and an Fe(II) polypyridyl ........................................................................8
Figure 1.5. Potential energy surface cartoon for a typical iron(II) polypyridine showing the effect of increasing the ligand field ........................................9
Figure 1.6. Fe(II) complexes containing strong-field ligands ........................................10
Figure 1.7. Structure of btz ligand and [Fe(btz)₃]²⁺/³⁺ ................................................................11
Figure 1.8. Structure of [Ru(dbtpy)₂]²⁺ and constrained-DFT results ..............................12
Figure 1.9. Representative orbital occupancy diagrams for the multielectronic ground states in high-spin (⁵T) and low-spin(¹A) octahedral complexes complexes ........13
Figure 1.10. Potential energy surface cartoons for low- and high-spin iron(II) complexes ........................................................................14
Figure 1.11. Overview of ligands used throughout this thesis for high-spin Fe(II) polypyridyl complexes .................................................................16
Figure 2.1. ¹H NMR of dctpy ..................................................................................40
Figure 2.2. ¹H NMR of dftpy ..................................................................................40
Figure 2.3. ¹H NMR of mc-dctpy ...........................................................................41
Figure 2.4. ¹H NMR of Ph-dctpy ...........................................................................41
Figure 2.5. ¹H NMR of NH₂-dctpy ...........................................................................42
Figure 2.6. ¹H NMR of decdqp ..............................................................................42
Figure 3.1. Synthesis of dctpy ligand using Suzuki coupling methodology ..............47
Figure 3.2. Synthesis of [Fe(dctpy)₂](BF₄)₂ ..............................................................47
Figure 3.3. $^1$H NMR spectrum of [Fe(dctpy)$_2$]$^{2+}$ taken in CD$_3$CN .................................................48

Figure 3.4. Crystal structure of [Fe(dctpy)$_2$](BF$_4$)$_2$ .................................................................50

Figure 3.5. UV-Visible absorption spectra of free dctpy, [Zn(dctpy)$_2$]$^{2+}$, and [Fe(dctpy)$_2$]$^{2+}$ .............................................................................................................52

Figure 3.6. TD-DFT generated spectra of free dctpy, [Zn(dctpy)$_2$]$^{2+}$, and [Fe(dctpy)$_2$]$^{2+}$ .............................................................................................................53

Figure 3.7. Natural transition orbitals of [Fe(dctpy)$_2$]$^{2+}$ for the transition at 343 nm ..........53

Figure 3.8. Natural transition orbitals of [Fe(dctpy)$_2$]$^{2+}$ for the transition at 410 nm ..........54

Figure 3.9. TA spectroscopy and quantitative spectrotelectrochemical analysis of [Fe(dctpy)$_2$]$^{2+}$ .............................................................................................................56

Figure 3.10. Reductive and oxidative spectrotelectrochemistry of [Fe(dctpy)$_2$]$^{2+}$ ..........58

Figure 3.11. Shift kinetics of the 370 nm band ...........................................................................59

Figure 4.1. Structures of 6,6”-dihaloterpypyridyl ligands and complexes .................................64

Figure 4.2. UV-vis absorption spectra for [Fe(dftpy)$_2$]$^{2+}$, [Fe(dctpy)$_2$]$^{2+}$, [Fe(dbtpy)$_2$]$^{2+}$ ........65

Figure 4.3. Crystal structure of [Fe(dbtpy)$_2$](BF$_4$)$_2$ .................................................................67

Figure 4.4. UV-visible absorption spectra of a solution of [Fe(dftpy)$_2$]$^{2+}$ at
  temperatures between 277-334 K ........................................................................................70

Figure 4.5. Temperature dependence of magnetic susceptibility data ......................................71

Figure 4.6. Molar absorptivities of the high-spin and low-spin states of [Fe(dftpy)$_2$]$^{2+}$
determined from global analysis of T-dependent data .........................................................74

Figure 4.7. Measured molar absorptivities of the high-spin states of [Fe(dftpy)$_2$]$^{2+}$, [Fe(dctpy)$_2$]$^{2+}$, [Fe(dbtpy)$_2$]$^{2+}$ .................................................................................................76

Figure 4.8. Overlaid crystal structures of [Fe(dftpy)$_2$](BF$_4$)$_2$ collected at 300 K and
  120 K ........................................................................................................................................78

Figure 4.9. TA spectroscopy of [Fe(dbtpy)$_2$]$^{2+}$ ...........................................................................81

Figure 4.10. TA spectroscopy of [Fe(dftpy)$_2$]$^{2+}$ ...........................................................................83
Figure 4.11. TA spectra of [Fe(dftpy)₂]²⁺ following 515 nm excitation.........................................................84

Figure 4.12. Single-exponential fit at the peak wavelength of the thermalized TA spectra .................................................................................................................87

Figure 4.13. Cartoon of potential energy surfaces and orbital occupancy diagrams for states used to describe the dynamics in the series of Fe(II) dihaloterpyridine complexes ..................................................................................89

Figure 5.1. Potential energy surfaces showing the effect of lowering the MLCT energy in a hypothetical low-spin and high-spin iron(II) complex..........................97

Figure 5.2. Structures of 4’-substituted ligands and the related Fe(II) complexes ..................98

Figure 5.3. Retrosynthesis of 4’-substituted ligands .................................................................................100

Figure 5.4. Synthesis of 4-amino-2,6-dibromopyridine .........................................................................100

Figure 5.5. Synthesis of 4-phenyl-2,6-dibromopyridine .........................................................................100

Figure 5.6. Resonance structures of 2,6-dibromopyridine N-oxide .......................................................101

Figure 5.7. General synthetic scheme for 4’-substituted terpyridyl ligands .............................................102

Figure 5.8. UV-vis absorption spectra of the [Fe(mc-dctpy)₂]²⁺, [Fe(Ph-dctpy)₂]²⁺, and [Fe(NH₂-dctpy)₂]²⁺ complexes .................................................................105

Figure 5.9. UV-vis absorption spectra of mc-dctpy, NH₂-dctpy, and Ph-dctpy .................................106

Figure 5.10. UV-vis absorption spectra of the [Fe(mc-dctpy)₂]²⁺, [Fe(Ph-dctpy)₂]²⁺, and [Fe(NH₂-dctpy)₂]²⁺ complexes focusing on 400-600 nm .................................................107

Figure 5.11. Crystal structures and average Fe-N_central bond lengths .................................................111

Figure 5.12. Thermal ellipsoid plot of [Fe(Ph-dctpy)₂]²⁺ with π-π interactions ......................................112

Figure 5.13. Transient absorption spectra of [Fe(mc-dctpy)₂]²⁺ .................................................................114

Figure 5.14. Spin density plot for [Zn(dctpy)(MeCN)₃]¹⁺ .........................................................................116

Figure 5.15. Selected structures showing DFT spin density results for [Zn(MeCN)₃(L)]⁺ where L = dctpy, 4’-COOH-dctpy, NH₂-dctpy ...........................................117

Figure 6.1. Structure of dqp and decdqp ligands and the related iron(II) complexes ..................122

Figure 6.2. Synthesis of dqp ligand .................................................................................................125
Figure 6.3. Three step procedure for the synthesis of decdqp ligand ........................................126
Figure 6.4. Mechanism for the first of two Pfitzinger reactions to form the 2,6-di(quinolin-2-yl)pyridinyl framework ..........................................................127
Figure 6.5. Crystal structure of [Fe(decdqp)2](BF4)2 ..............................................................130
Figure 6.6. UV-vis spectra of [Fe(dqp)2]2+ and [Fe(decdqp)2]2+ ........................................131
Figure 6.7. Oxidative electrochemistry of [Fe(dqp)2]2+ ......................................................132
Figure 6.8. Cyclic voltammograms of [Fe(decdqp)2]2+ ......................................................134
Figure 6.9. Selected structures showing DFT spin density results for [Zn(MeCN)3(L)]+ where L = dctpy, 4’-COOH-dctpy, and decdqp .....................135
Figure 6.10. Example orbital occupancy diagrams to facilitate discussion of the multielectron states .................................................................139
Figure 6.11. Potential energy surface cartoons displaying the two possible scenarios for the 5E state .................................................................140
Figure 6.12. Modified Jablonski diagram for [Fe(NHC)2]2+-sensitized TiO2 .......................142
Figure 6.13. Hypothetical complex for creating charge-separated excited states ............143
Figure 7.1. Thermally-driven versus visible light photocatalyzed Diels-Alder cycloadditions .................................................................146
Figure 7.2. Structures and selected properties relevant to photocatalysis for [Ru(bpz)3]2+ and [Cr(Ph2phen)3]3+ ......................................................148
Figure 7.3. Reaction scheme for the [Cr(Ph2phen)3]3+ photocatalyzed Diels-Alder cycloaddition of trans-anethole and isoprene ......................149
Figure 7.4. Visible absorption and emission spectra for [Cr(Ph2phen)3]3+ .......................149
Figure 7.5. Modified Jablonski diagram for relevant transitions in Cr(III) polypyridyl complexes .................................................................151
Figure 7.6. Initially proposed mechanism for Cr(III) photocatalyzed [4+2] cycloadditions .................................................................152
Figure 7.7. Raw TRPL data showing emission of [Cr(Ph2phen)3]3+ in at various concentrations of trans-anethole .................................................................154
Figure 7.8. Stern-Volmer plot for the quenching of [Cr(Ph₂phen)₃]³⁺ by trans-anethole ..... 154

Figure 7.9. Measured quenching rate constants for three Cr(III) catalysts with five substrates plotted versus the oxidation potential of each substrate ....................... 157

Figure 7.10. Oxygen dependence of the emission quenching of [Cr(Ph₂phen)₃]³⁺ by trans-anethole ..................................................................................... 159

Figure 7.11. Photographs of the initial reaction mixture and after 24 hours of irradiation in a nitrogen atmosphere ................................................................. 160

Figure 7.12. Electronic absorption difference spectrum after a 40 hour photoreaction in which oxygen was excluded and a simulated spectrum ..................... 161

Figure 7.13. Computationally determined free energies for reactions relevant to the mechanism ..................................................................................................... 161

Figure 7.14. Proposed mechanism for Cr(III) photocatalysis of [4+2] cycloadditions .......... 162

Figure 7.15. Reaction scheme for the [Cr(Ph₂phen)₃]³⁺ photocatalyzed Diels-Alder cycloaddition of 4-methoxychalcone and isoprene ........................................ 163

Figure 7.16. Stern-Volmer plot for the quenching of [Cr(Ph₂phen)₃]³⁺ by 4-methoxychalcone ........................................................................................................ 164

Figure 7.17. Stern-Volmer plot for the quenching of [Cr(dmcbpy)₃]³⁺ by 4-methoxychalcone ........................................................................................................ 165

Figure 7.18. Emission spectra from successive additions of 4-methoxychalcone to a solution of [Cr(Ph₂phen)₃]³⁺ ........................................................................ 166
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>4’-COOH-dctpy</td>
<td>4’-(carboxylic acid)-6,6”-dichloro-2,2’;6’,2”-terpyridine</td>
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<td>ΔA</td>
<td>change in absorbance</td>
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<td>ε</td>
<td>molar extinction coefficient</td>
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</tr>
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</tr>
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<tr>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>dqp</td>
<td>2,6-(diquinolin-2-yl)-pyridine</td>
</tr>
</tbody>
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DSSC  dye-sensitized solar cell

E_{1/2}  half-wave potential

ESA  excited-state absorption

ESI-TOF  electrospray ionization – time of flight

Fc  ferrocene

GS  ground state

HOMO  highest occupied molecular orbital

HRMS  high-resolution mass spectrometry

HS  high-spin

IL  intraligand

ISC  intersystem crossing

k_{q}  quenching rate constant

L  ligand

LIESST  light-induced excited-state spin trapping

LLCT  ligand-to-ligand charge transfer

LMCT  ligand-to-metal charge transfer

LS  low-spin

LUMO  lowest unoccupied molecular orbital

M  metal

MC  metal-centered

mc-dctpy  4’-methylcarboxylate-6,6”-dichloro-2,2’;6’,2”-terpyridine

MeCN  acetonitrile

MLCT  metal-to-ligand charge transfer
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-N-N</td>
<td>N_{terminal}-N_{central}-N_{terminal} angle</td>
</tr>
<tr>
<td>NH$_2$-dctpy</td>
<td>4’-amino-6,6”-dichloro-2,2’;6’,2”-terpyridine</td>
</tr>
<tr>
<td>NHC</td>
<td>N-heterocyclic carbene</td>
</tr>
<tr>
<td>NTO</td>
<td>natural transition orbital</td>
</tr>
<tr>
<td>OTTLE</td>
<td>optically transparent thin layer electrode</td>
</tr>
<tr>
<td>PC</td>
<td>photoredox catalyst</td>
</tr>
<tr>
<td>Ph-dctpy</td>
<td>4’-phenyl-6,6”-dichloro-2,2’;6’,2”-terpyridine</td>
</tr>
<tr>
<td>Ph$_2$phen</td>
<td>4,7-diphenyl-1,10-phenanthroline</td>
</tr>
<tr>
<td>phen</td>
<td>1,10-phenanthroline</td>
</tr>
<tr>
<td>ppy</td>
<td>2-phenylpyridine</td>
</tr>
<tr>
<td>R(Fe-N)</td>
<td>iron-nitrogen bond distance</td>
</tr>
<tr>
<td>R(Ru-N)</td>
<td>ruthenium-nitrogen bond distance</td>
</tr>
<tr>
<td>R$_f$</td>
<td>retention factor</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>SCO</td>
<td>spin crossover</td>
</tr>
<tr>
<td>SQUID</td>
<td>superconducting quantum interference device</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>TA</td>
<td>transient absorption</td>
</tr>
<tr>
<td>TBA</td>
<td>tetrabutylammonium</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>time-dependent density functional theory</td>
</tr>
<tr>
<td>TIP</td>
<td>temperature-independent paramagnetism</td>
</tr>
<tr>
<td>TLC</td>
<td>thin-layer chromatography</td>
</tr>
<tr>
<td>tpy</td>
<td>2,2’;6’,2”-terpyridine</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>TRPL</td>
<td>time-resolved photoluminescence</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>ultraviolet-visible</td>
</tr>
<tr>
<td>X-pyridyl</td>
<td>halogen to central pyridyl ring distance</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1. Motivation

Sunlight is an abundant, clean, inexpensive energy source available in all parts of the world. However, devising methods for harnessing this energy to do useful work by providing electricity, chemical potential, or energy storage is one of the most important challenges of the 21st century.\(^1\)\(^-\)\(^4\) One possible utilization strategy for solar energy is photocatalysis, in which visible light provides access to a new reaction pathway and/or the energy needed to surmount a reaction barrier.\(^5\) The concept of harnessing sunlight as an unlimited, nonpolluting source of energy to perform chemical reactions has existed for over a century since it was first proposed by Giacomo Ciamician in 1912.\(^6\) Despite this long history, a number of obstacles have limited the industrial utilization of photocatalysis, which has only begun to grow recently.\(^7\)\(^-\)\(^9\) Nevertheless, it remains a particularly appealing goal given that sunlight-driven photocatalytic reactions for organic synthesis could be cleaner, more economical, and more efficient than conventional synthetic pathways which often rely on thermal energy sourced from fossil fuels.\(^5\)

With these goals in mind there has been a significant revival in the field since the late 2000s spearheaded by Yoon, Stephenson, MacMillan, and others.\(^5\)\(^,\)\(^10\)\(^-\)\(^15\) Photochemical reactions often utilize highly reactive species formed \textit{in situ} where they can attack otherwise inert substrates. Due to this, photocatalysis can promote processes such as C-H activation and selective coupling of moieties by harnessing reactive radical\(^16\)\(^-\)\(^18\) and triplet\(^19\) species. These tools open up new approaches which synthetic organic chemists can use in the pursuit of ever more complicated targets.\(^20\) In light of these benefits, the development of new photocatalytic
reactions is proceeding rapidly with applications such as the production of fine chemicals, active pharmaceutical ingredients, and high-performance polymers.

In nearly all of these reactions, it is necessary to utilize either a photoredox catalyst, which absorbs light and directly oxidizes or reduces a substrate, or a photosensitizer that absorbs light and activates a substrate or co-catalyst through energy transfer. While both options have potential uses, in the present work we will focus primarily on photoredox catalysts.

The roles of a photoredox catalyst in a catalytic cycle can be understood by considering the generalized Latimer diagram presented in Figure 1.1. Since the first step is for the catalyst to absorb a photon, strong molar absorptivities in the visible portion of the electromagnetic spectrum (400-800 nm) are desirable. Following visible absorption, the photoredox catalyst should form a long-lived state with a high quantum yield. This serves to limit the amount of wasted energy since more photoexcited molecules will have enough time to diffuse through solution and react with a substrate. Finally, reversible oxidations or reductions at low potentials maximize the thermodynamic driving force for photoexcited electron transfer reactions.

Transition metal complexes are ideal candidates for meeting all of these requirements. First, the metal centers often have highly-absorptive metal-to-ligand charge transfer (MLCT) excitations which fall in the visible portion of the spectrum. Second, the heavy-atom effect can encourage intersystem crossing (ISC) to long-lived states with different spin multiplicities, where radiative relaxation is a spin-forbidden process. Third, the complexes often have multiple stable oxidation states, enabling highly reversible redox processes that can lead to large turnover numbers for these catalysts.
Figure 1.1. Latimer diagram for a generalized photoredox catalyst (PC) acting as a photooxidant. The PC can absorb light (blue arrow) then undergo ISC (blue wavy line) to a long-lived state. The photoexcited catalyst in its long-lived state ($^3\text{PC}^*$) can then oxidize a substrate (red arrows) with an excited state reduction potential ($E_{1/2}^{\text{red}} = h\nu + E_{1/2}^{\text{red}}$, where $h\nu$ in eV is equivalent to $V$ for the one electron process). Finally, the reduced catalyst PC, can then be oxidized back to its starting state by some acceptor (A).

1.2. Platinum Group Metal Photocatalysts

The most commonly used photoredox catalysts are iridium(III) and ruthenium(II) polypyridyl complexes. These photocatalysts possess many of the desirable traits described above for transition metal complexes including strong visible absorption, long excited-state lifetimes, and potent excited state redox potentials. Two of the most common platinum group metal photocatalysts, $[\text{Ir(ppy)}_3]^3+$ (ppy = 2-phenylpyridine) and $[\text{Ru(bpy)}_3]^2+$ (bpy = 2,2′-bipyridine), are shown in Table 1.1 along with some properties that are pertinent to photoredox catalysis.
Table 1.1. Properties of Prominent Platinum Group Metal Photoredox Catalysts

<table>
<thead>
<tr>
<th></th>
<th>[Ir(ppy)$_3$]$^{3+}$</th>
<th>[Ru(bpy)$_3$]$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excited state lifetime ($\tau$)</td>
<td>1.9 $\mu$s</td>
<td>1.1 $\mu$s</td>
</tr>
<tr>
<td>MLCT absorption peak ($\lambda_{\text{max}}$)</td>
<td>375 nm</td>
<td>452 nm</td>
</tr>
<tr>
<td>Molar absorptivity ($\varepsilon$)</td>
<td>$\sim$8,000 M$^{-1}$cm$^{-1}$</td>
<td>$\sim$12,000 M$^{-1}$cm$^{-1}$</td>
</tr>
<tr>
<td>Excited-state reduction potential</td>
<td>$E_{1/2}^{3+/2+} = +0.31$ V</td>
<td>$E_{1/2}^{2+/1+} = +0.81$ V</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^{4+/3+} = -1.73$ V</td>
<td>$E_{1/2}^{3+/2+} = -0.77$ V</td>
</tr>
</tbody>
</table>

Potentials are versus SCE. Data for [Ir(ppy)$_3$]$^{3+}$ and [Ru(bpy)$_3$]$^{2+}$ were obtained from the listed references.

Both of these complexes have high absorptivities in the visible or near-UV and long excited-state lifetimes, which allow for a large number of excited-state species (the active catalyst) to exist in solution at a given time under sufficient irradiation. The long lifetimes also allow for the excited-state species to diffuse through solution and collide with a substrate prior to relaxing. Once they encounter a substrate, they are strong excited-state reductants ([Ir(ppy)$_3$]$^{3+}$, [Ru(bpy)$_3$]$^{2+}$) and oxidants ([Ru(bpy)$_3$]$^{2+}$). This combination of features is desirable for many different photocatalytic reaction schemes.

Despite the highly desirable properties for these complexes, their applicability is limited since platinum group metals are rare. Figure 1.2 shows the abundance of elements in the Earth’s crust as provided by the United States Geological Survey.
Figure 1.2. Abundance of elements in the Earth’s crust, United States Geological Survey.\textsuperscript{25}

As seen in Figure 1.2, ruthenium and iridium are some of the rarest naturally-occurring elements with abundances 4-6 orders of magnitude lower than all the first-row transition metals. These metals are expensive due to their rarity; thus it is highly desirable to develop photocatalysts using more abundant elements. Some more common metals have already found success as photocatalysts on the lab scale. Examples in the literature include: copper,\textsuperscript{26–28} zirconium,\textsuperscript{29} molybdenum\textsuperscript{30}, and chromium.\textsuperscript{16,17,31} Additionally, some organic molecules have shown photocatalytic activity by replicating the high ISC yields needed for long-lived active catalysts.\textsuperscript{14} Research into organic photocatalysts is ongoing and their development complements the progress in transition-metal based complexes, both of which may offer their own unique reactivities. Despite the clear success of some of these photocatalysts, Ru(II) and Ir(III)-based photocatalysts remain the most prominent photocatalysts in the synthetic toolbox and finding a drop-in replacement that replicates all the desired reactivities remains challenging.
1.3. Iron(II) Polypyridines as Photocatalysts

Fe(II) would seem to be an ideal candidate to replace Ir(III)- or Ru(II)-based catalysts since it also possesses a $d^6$ metal center and many of the same traits that make Ru(II) catalysts so appealing. The iron-containing analogue of a common ruthenium-based catalyst, $[\text{Fe(bpy)}_3]^{2+}$, has a strongly absorptive $1\text{MLCT} \leftarrow 1\text{GS}$ transition in the visible range as seen in Figure 1.3.

![Graph](image.png)

**Figure 1.3.** UV-visible absorption spectra for $[\text{Ru(bpy)}_3]^{2+}$ and $[\text{Fe(bpy)}_3]^{2+}$ in room-temperature acetonitrile.

Furthermore, $[\text{Fe(bpy)}_3]^{2+}$ undergoes reversible oxidation and reduction at potentials similar to $[\text{Ru(bpy)}_3]^{2+}$. In fact, oxidation of the Fe$^{2+}$ core actually occurs at a lower potential (1.05 V vs. SCE in water) than the oxidation of the Ru$^{2+}$ core (1.27 V vs. SCE in water). This suggests that $[\text{Fe(bpy)}_3]^{2+}$ could be a more potent photoreductant and be utilized in a wider scope of reactions.

However, the critical area where iron-based complexes do not compare favorably with their ruthenium analogues is in excited-state lifetimes. Following excitation to the excited state, $[\text{Fe(bpy)}_3]^{2+}$ has been found to relax into a low-lying quintet state on a subpicosecond timescale with more recent measurements clocking the time constant to between 50 and 150 fs. While there have been some reports of Fe(II) photocatalysis in the literature, the sub-picosecond
lifetimes of the MLCT states suggest that the catalytic mechanism must be quite different from that of Ru(II) systems. Furthermore, it is unknown whether observed catalytic activity in one setting can translate to broader applicability involving a variety of substrates. These points were explicitly noted by Collins et al. in explaining their observed photochemical synthesis of carbazoles with [Fe(phen)$_3$]$^{2+}$ (phen = 1,10-phenanthroline).$^{37}$

Ultrafast MLCT relaxation in Fe(II) polypyridines has been attributed to lower-lying metal-centered (MC) excited states, which provide crossing points and energy-wasting pathways on the potential energy surfaces. As opposed to MLCT states where charge density relocates from the metal to the ligand, effectively forming [M$^{3+}$L(L$^-$)], these metal-centered states have similar charge distributions as the ground state. Instead, metal-ligand anti-bonding orbitals (the eg$^*$ set in an octahedral field) have been populated in MC excited states, as would be seen following a d-d excitation. It is convenient to conceptualize the interplay of these states and the photophysical relaxation pathway using a potential energy surface plot. In this type of plot energy is represented on the vertical axis and the metal-ligand bond distance (often an important geometric parameter in these systems) is displayed on the x-axis. Figure 1.4 displays such potential energy surface plots for prototypical Fe(II) and Ru(II) polypyridines. Populating the $^3$MC state is a critical step in the relaxation pathway for both species.$^{35,39}$ As Figure 1.4 suggests, the higher multiplicity MC states in iron(II) complexes are closer in energy to the ground state than in their ruthenium(II) counterparts, effectively reducing the barrier to relaxation from the long-lived MLCT states.
Figure 1.4. Potential energy surface cartoons depicting typical photodynamics for a Ru(II) polypyridyl, left, and an Fe(II) polypyridyl, right. The x-axis shows the metal-ligand bond length, which is generally a critical geometric parameter. The purple arrow shows photoexcitation, the red arrows show the nonradiative relaxation pathways. Note the substantial barrier for $^{1,3}\text{MLCT} \rightarrow ^3\text{MC}$ relaxation in the ruthenium diagram that is absent in the iron diagram.

These metal-centered state energy effects can be attributed to the smaller size of the 3$d$ frontier orbitals in Fe(II) relative to the 4$d$ frontier orbitals in Ru(II) (and 5$d$ in Ir$^{3+}$), which leads to reduced metal-ligand orbital overlap and a reduction in ligand-field splitting for these pseudoocathedral complexes. Therefore, in order to make Fe(II) polypyridines behave more like Ru(II) polypyridines, one could attempt to increase the ligand-field splitting to destabilize triplet and quintet MC states.

1.4 Strong-Field Ligand Approach

Concurrent with the work presented in this thesis, other research groups have exploited strong-field carbene ligands in order to increase the octahedral field splitting attempting to mimic the state energies of Ru(II) complexes in an Fe(II) system. This approach is displayed graphically in Figure 1.5. Increasing the octahedral field splitting strongly affects the higher
multiplicity metal-centered states (\(^3\)MC and \(^5\)MC). Since these states require populating \(e_g^*\) orbitals which are destabilized in stronger ligand fields, the \(^3\)MC and \(^5\)MC are significantly raised in energy, ideally above the \(^1,3\)MLCT states so that they no longer serve as relaxation pathways.

![Potential energy surface cartoon](image)

**Figure 1.5.** Potential energy surface cartoon for a typical iron(II) polypyridine showing the effect of increasing the ligand field (red arrows). The blue arrow shows photoexcitation.

There have been many synthetic approaches to increasing the ligand field strength of polypyridyl ligands. One of the first approaches used an expanded coordination geometry to more closely approach true octahedral coordination.\(^{40}\) While the overall MLCT lifetime did not increase, it was argued that the \(^5\)MC was destabilized such that the \(^3\)MC became the lowest energy excited state.\(^{40}\) In another approach, a heteroleptic complex was synthesized to increase the overall ligand field while still using a common polypyridyl ligand. This approach proved successful in \([\text{Fe(CN)}_4(bpy)]^{2-}\) where the MLCT excited state was found to have a lifetime of 20 ps.\(^{41}\) However, the most successful strong ligand-field schemes have utilized N-heterocyclic carbene (NHC) ligands to exploit the potent \(\sigma\)-donation abilities of this class of ligands.\(^{42-54}\) Two particularly important examples of Fe(II) complexes using NHC ligands are shown in Figure 1.6. In 2013, the groups of Sundström and Wärnmark reported on the Fe(II) bis-NHC complex shown on the left in Fig. 1.6 which was found to have a 9 ps MLCT lifetime.\(^{42}\) To put this in context,
recall that the parent, $[\text{Fe(bpy)}_3]^{2+}$, has an MLCT excited state lifetime of 50-150 fs.$^{34,35}$ Following this exciting result, NHC ligands with electron-withdrawing groups were found to further increase the MLCT excited state lifetime as exemplified by the complex on the right in Figure 1.6 with a measured MLCT lifetime of 26 ps.$^{51}$

![Fe(II) complexes containing strong-field ligands from Liu et al.$^{42}$ and Pastore et al.$^{51}$](image)

**Figure 1.6.** Fe(II) complexes containing strong-field ligands from Liu et al.$^{42}$ and Pastore et al.$^{51}$

Beyond lengthening the excited-state lifetime, these carboxylic acid groups served a secondary purpose: they provide an attachment point to a semiconductor such as TiO$_2$. When attached to such a semiconductor, it was found that electron injection was quite efficient with quantum yields of injection as high as 92%, albeit with rapid recombination.$^{46}$ This was especially significant to the dye-sensitized solar cell (DSSC) community since it provided the first indication that Fe(II)-based chromophores could potentially replace the Ru(II) complexes, the scarcity of which serves to limit any widespread use of DSSCs.

Very recent work out of the Persson, Wärnmark, and Sundström groups show significant lengthening in charge-transfer lifetimes of closely related iron(II) and iron(III) complexes.$^{55,56}$ The researchers were able to achieve these results by designing ligands with even stronger σ-donor and π-acceptor properties which could bind an iron(II) or iron(III) center in a tris-bidentate coordination geometry. This new ligand is named btz (3,3’-dimethyl-1,1’-bis(p-tolyl)-4,4’-bis(1,2,3-triazol-5-ylidene)) and is shown along with $[\text{Fe(btz)}_3]^{2+/3+}$ in Figure 1.7.
The tricationic version of this complex was shown to contain a true Fe$^{3+}$ metal center and a doublet ground state ($^2$T). Following excitation to a $^2$LMCT, a 100 ps lifetime was observed along with luminescence of the spin-allowed radiative return to the ground state.$^{55}$ This was the first luminescent iron complex,$^{57}$ indicating a substantial improvement from the sub-picosecond charge transfer lifetimes of traditional iron(II) polypyridines. Following up on this success, the iron(II) complex was synthesized, boasting an impressive 528 ps lifetime.$^{56}$ This advance is attributed to the extremely strong ligand field which arises from the nearly octahedral coordination geometry of the tris-bidentate motif along with the extremely strong $\sigma$-donating and $\pi$-accepting abilities of the ligands themselves. The ~0.5 ns MLCT lifetime of [Fe(btz)$_3$]$^{2+}$ presents exciting new opportunities for utilizing iron(II) complexes in both photosensitization and photocatalysis schemes where diffusion times can compete with relaxation.

1.5 Research Plan: Sterically Hindered Weak-Field Ligands

The work presented throughout this thesis highlights the concurrent development of an alternate approach to Fe(II) chromophore MLCT lifetime extension where we can change the nature of the dynamics themselves using specifically designed structural and electronic
perturbations. This work is rooted in the use of sterically hindered weak-field ligands rather than the strong-field NHC approach detailed above. The original impetus for this approach was our group’s investigation of a Ru(II) complex: [Ru(dbtpy)₂]²⁺ (where dbtpy = 6,6”-dibromo-2,2’;6’2”-terpyridine). This complex utilized substitution at the 6 and 6” positions of the terpyridine to add intramolecular steric strain which distorted the state geometries and energies resulting in a nesting of the ³MLCT and ³MC state and with it a ~6x longer MLCT lifetime relative to [Ru(tpy)₂]²⁺ (Fig. 1.8).

![Figure 1.8](image.png)

**Figure 1.8.** Left: Structure of [Ru(dbtpy)₂]²⁺. Right: Constrained-DFT results showing ground and excited state energies at various geometries for [Ru(tpy)₂]²⁺ (blue) and [Ru(dbtpy)₂]²⁺ (red). Figure reprinted from Vallett, P. J. and Damrauer, N. H.

Since Fe(II) polypyridyl complexes relax via a similar ¹³MLCT → ³MC pathway, we hypothesized that introducing steric strain would similarly alter the relevant state geometries and allow us to avoid the barrierless crossing, thereby extending the MLCT excited-state lifetime. However, instead of introducing a subtle geometric perturbation, the relevant ground and excited states were altered significantly. When employing these strained ligands, the ligand field is much weaker since interligand repulsion prevents shorter metal-ligand bond distances. With this reduced octahedral field splitting, populating the antibonding orbitals becomes more
favorable than pairing two electrons in the same orbital (Fig. 1.9). The end result of these perturbations is that the $^5\Gamma$ state becomes the ground state with its four unpaired electrons and longer metal-ligand bond lengths.

![Figure 1.9. Representative orbital occupancy diagrams for the multielectronic ground states in high-spin ($^5\Gamma$) and low-spin($^1\Delta$) octahedral complexes.](image)

This result was generally unexpected since almost all known Fe(II) polypyridyl complexes are found to be low-spin due to the relatively strong ligand fields of N-donor atoms and the possibility of $\pi$-backboning enabled by the aromatic pyridyl ligands resulting from the mixing of their empty $\pi^*$ molecular orbitals with occupied Fe(II) d orbitals. However, iron(II) bis-6,6’-dimethylterpyridine, a related complex synthesized by Constable et al., showed that steric strain could force a high-spin ground state. These researchers also attempted to use extremely bulky phenyl groups at the 6 and 6” positions, but this led to bidentate coordination of the ligands and a four-coordinate iron(II) complex.

The predominance of the quintet ground state provided us the opportunity to explore excited-state dynamics that are distinct from those associated with low-spin Fe(II) polypyridines (Figure 1.10). In principle, this could allow us to escape the pitfalls that limit MLCT excited-state lifetimes in the parent low-spin complexes. We hypothesized that a $^5$MLCT state exists for these complexes, and we wondered if a $^5$MLCT $\rightarrow$ $^5$GS would allow us to access the MLCT manifold in these high-spin complexes. Following excitation, relaxation into a long-lived $^7$MLCT may be possible, analogous to the $^1$MLCT $\rightarrow$ $^3$MLCT transition in Ru(II) polypyridines. If we could gain control over the $^5$MLCT excited-state lifetimes, we could potentially utilize
these complexes as inexpensive replacements for Ru(II) photocatalysts or in novel photoredox catalysis schemes unique to these iron(II) complexes.

Figure 1.10. Potential energy surface cartoons for the low- and high-spin iron(II) complexes shown above the graphs. The blue arrow shows photoexcitation, the red dashed arrow shows relaxation.

1.6. Overview of Chapters

Chapter 2 describes the experimental methods used throughout this work including detailed synthetic procedures for all the chromophores. With these methods in hand, we examine the molecular structure, ground-state properties, and the photophysics of an initial member of this class of high-spin Fe(II) polypyridyl complexes, [Fe(dctpy)$_2$]$^{2+}$ (dctpy = 6,6”-dichloro-2,2’,6’,2”-terpyridine) in Chapter 3. Interestingly, this chromophore is found to contain a high-spin MLCT state that is accessible through visible light excitation. Furthermore, a time constant of 16 ps is extracted for the $^5$MLCT, a > 100-fold improvement over [Fe(bpy)$_3$]$^{2+}$, the low-spin parent.

Chapter 4 follows up on the initial success of [Fe(dctpy)$_2$]$^{2+}$ by examining a series of iron(II) bis-6,6”-dihaloterpyridines (Figure 1.11) where larger halogens are expected to introduce
greater intramolecular steric strain. This tuning of the steric-strain is highlighted in the x-ray crystallography of the structures including the fluorinated complex – [Fe(dftpuy)2]2+ – which is found to exhibit room-temperature spin-crossover properties. A thorough investigation of the electronic absorption, magnetism, electrochemistry, and excited state dynamics of this series of complexes provides a more detailed picture of the potential energy surfaces that are relevant to the photodynamics of these compounds. Furthermore, it is found that the excited-state lifetime can be tuned as a direct result of altering the intramolecular steric strain and providing a design principle that could be applied to other first-row transition metal chromophores.

The use of electron-withdrawing and -donating groups is explored in Chapter 5 as a method for altering the excited state energies in an attempt to raise the barrier to relaxation. Although electrochemical and electronic absorption studies show a lower energy MLCT state suggesting a higher barrier to relaxation, we find that the excited lifetime is actually shorter in one of these complexes: [Fe(mc-dctpy)2]2+, where mc-dctpy = 4’-methylcarboxylate-6,6’-dichloroterpyridine. This leads us to utilize density functional theory to model localization of electron density in the excited state. Our findings suggest that charge localization and coupling between the MLCT and MC states is an important parameter for understanding the observed excited-state lifetimes.

Finally, Chapter 6 investigates an alternate ligand framework (dqp and decdqp, Figure 1.11) where we incorporate the coupling principles highlighted in Chapter 5. A combination of geometric, electronic and coupling concepts leads to the longest 5MLCT lifetime to date along with a significant increase in absorption across the visible spectrum. This chapter ends by proposing a path forward to superior high-spin iron(II) chromophores and schemes for utilization of these complexes in photocatalysis.
1.7. Cr(III) Photocatalytic Mechanisms

In addition to the investigation of a new class of Fe(II) chromophores, this thesis examines the mechanistic pathways of Cr(III) photocatalysis. While much more limited in scope than the chapters devoted to Fe(II), these focused experiments highlight both the uniqueness of Cr(III) photo-oxidants and their utility in promoting [4+2] cycloadditions for a variety of substrates. A more detailed introduction to this class of photoredox catalysts and the studied reactions will be given within Chapter 7.
1.8. References


Chapter 2

Experimental Procedures

2.1. General Synthesis

All solvents and reagents were obtained from Sigma-Aldrich and used without further purification unless otherwise noted. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. NMR spectra were acquired on a Bruker Avance-III 300 MHz spectrometer or a Varian INOVA 500 MHz spectrometer, mass spectrometry was performed at the University of Colorado Central Analytical Laboratory, and elemental analysis was performed by Robertson Microlit Laboratories Inc., Ledgewood, NJ.

2.2. Ligand Synthesis

6,6''-dichloro-2,2':6',2''-terpyridine (dctpy). Using standard Schlenk techniques, 2,6-dibromopyridine (118.5 mg, 0.50 mmol, 1.0 eq.) was combined with 6-chloropyridine-2-boronic acid pinacol ester (Synthonix, 297 mg, 1.24 mmol, 2.5 eq.), and palladium(0) tetrakis-triphenylphosphine (60 mg, 10 mol. %) in 60 mL of nitrogen-sparged 1,4-dioxane. An additional solution of 264 mg of sodium carbonate in 10 mL of deionized (DI) water (0.25 M) was sparged with nitrogen and added to the reaction vessel. The reaction mixture was refluxed for ~48 hours with stirring until 2,6-dibromopyridine was consumed. The organic layer was extracted with 2:1 water:ethyl acetate, then dried with magnesium sulfate and evaporated to dryness. The crude solid was purified by column chromatography using a gradient of hexanes/ethyl acetate (90/10 to 50/50) on silica. Yield: 85 mg, 57% \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 8.52 (dd, J = 7.7, 0.9 \text{ Hz}, 2\text{H}), 8.47 (d, J = 7.9 \text{ Hz}, 2\text{H}), 7.96 (dd, J = 8.1, 7.7 \text{ Hz}, 1\text{H}), 7.82 (t, J = 7.8 \text{ Hz}, 2\text{H}), 7.37 (dd, J = 7.7, 0.9 \text{ Hz}, 2\text{H}), 7.23 (t, J = 7.7 \text{ Hz}, 1\text{H})\).
= 7.9, 0.9 Hz, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 156.7, 153.9, 151.0, 139.4, 138.1, 124.3, 121.9, 119.4. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{15}$H$_9$N$_3$Cl$_2$Na 324.0071; Found 324.0071.

6,6''-difluoro-2,2':6',2''-terpyridine (dftpy). Using standard Schlenk techniques, 2,6-dibromopyridine (168 mg, 0.71 mmol, 1.0 eq.) was combined with 6-fluoropyridine-2-boronic acid (Combi-Blocks, 300 mg, 2.13 mmol, 3.0 eq.), and palladium(0) tetrakis-triphenylphosphine (123 mg, 15 mol. %) in 72 mL of nitrogen-sparged 1,4-dioxane. An additional solution of 375 mg (5 eq.) of sodium carbonate in 24 mL of deionized water (0.15 M) was sparged with nitrogen and added to the reaction vessel. The reaction mixture was heated to reflux for 24 hours with stirring until the 2,6-dibromopyridine was consumed, as monitored by TLC. A mixture of water and ethyl acetate (2:1, 75 mL) was added and the organic layer was washed with water three times, then dried with magnesium sulfate, filtered, and evaporated to dryness. The crude solid was purified by column chromatography using chloroform on silica gel ($R_f = 0.7$). Yield: 151 mg, 79%. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.49 (ddd, $J = 7.6$, 2.4, 0.8 Hz, 2H), 8.40 (d, $J = 7.8$ Hz, 2H), 8.01-7.89 (m, 3H), 6.98 ppm (ddd, $J = 8.1$, 3.0, 0.8 Hz, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 163.15 (d, $J = 238.7$ Hz), 154.77 (d, $J = 13.0$ Hz), 153.88, 141.78 (d, $J = 7.6$ Hz), 138.14, 121.70, 118.17 (d, $J = 4.0$ Hz), 109.61 ppm (d, $J = 37.4$ Hz). HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{15}$H$_9$N$_3$F$_2$Na 292.0662; Found 292.0660.

4'-methylcarboxylate-6,6''-dichloro-2,2':6',2''-terpyridine (mc-dctpy). Using standard Schlenk techniques, 2,6-dibromo-4-methylesterpyridine (Combi-blocks, 52 mg, 0.18 mmol, 1.0 eq.) was combined with 6-chloropyridine-2-boronic acid pinacol ester (Synthonix, 121 mg, 0.51 mmol, 2.9 eq.), potassium phosphate tribasic (117 mg, 0.55 mmol, 3.1 eq.), and palladium(0) tetrakis-triphenylphosphine (42 mg, 20 mol. %) in 5 mL of nitrogen-sparged
toluene and 0.5 mL of nitrogen-sparged water. The reaction mixture was heated to 125 °C for 72 hours with stirring. A mixture of water and toluene (1:1, 40 mL) was added and the organic layer was washed twice with water and once with brine, then dried with magnesium sulfate, filtered, and evaporated to dryness. The crude solid was purified by column chromatography using chloroform on silica gel ($R_f = 0.5$). Yield: 43 mg, 68%. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.97 (s, 2H), 8.51 (dd, $J = 7.8$, 0.9 Hz, 2H), 7.83 (t, $J = 7.8$ Hz, 2H), 7.40 (dd, $J = 7.9$, 0.9 Hz, 2H), 4.04 ppm (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 165.69, 156.00, 155.34, 151.33, 140.22, 139.65, 124.99, 121.36, 119.75, 52.97 ppm. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for C$_{17}$H$_{11}$N$_3$O$_2$Cl$_2$Na 382.0126; Found 382.0120.

4'-Phenyl-6,6''-dichloro-2,2':6',2''-terpyridine (Ph-dctpy). Using standard Schlenk techniques, 2,6-dibromo-4-phenylpyridine (55 mg, 0.18 mmol, 1.0 eq., prepared from literature procedures$^{1,2}$) was combined with 6-chloropyridine-2-boronic acid pinacol ester (Synthonix, 122 mg, 0.51 mmol, 2.8 eq.), potassium phosphate tribasic (124 mg, 0.57 mmol, 3.2 eq.), and palladium(0) tetrakis-triphenylphosphine (30 mg, 14 mol. %) in 5 mL of nitrogen-sparged toluene and 0.5 mL of nitrogen-sparged water. The reaction mixture was heated to 125 °C for 48 hours with stirring. A mixture of water and toluene (1:1, 40 mL) was added and the organic layer was washed twice with water and once with brine, then dried with magnesium sulfate, filtered, and evaporated to dryness. The crude solid was purified by column chromatography first with chloroform on silica ($R_f = 0.6$), then by dry-loading on silica and using 10/90 ethyl acetate/hexanes on silica gel ($R_f = 0.3$). Yield: 46 mg, 67%. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.71 (s, 2H), 8.57 (dd, $J = 7.8$, 0.9 Hz, 2H), 7.90-7.86 (m, 2H), 7.83 (t, $J = 7.8$ Hz, 2H), 7.57-7.44 (m, 3H), 7.39 ppm (dd, $J = 7.9$, 0.9 Hz, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 156.92, 154.68, 151.13,
151.00, 139.57, 138.33, 129.38, 127.57, 124.55, 119.97, 119.79 ppm. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C_{21}H_{13}N_{3}Cl_{2}H 378.0565; Found 378.0552.

4'-amino-6,6''-dichloro-2,2':6',2''-terpyridine (NH_{2}-dctpy). Using standard Schlenk techniques, 2,6-dibromo-4-aminopyridine (56 mg, 0.22 mmol, 1.0 eq., prepared from literature procedures) was combined with 6-chloropyridine-2-boronic acid pinacol ester (Synthonix, 153 mg, 0.64 mmol, 2.9 eq.), potassium phosphate tribasic (138 mg, 0.65 mmol, 3.0 eq.), and palladium(0) tetrakis-triphenylphosphine (44 mg, 17 mol. %) in 5 mL of nitrogen-sparged toluene and 0.5 mL of nitrogen-sparged water. The reaction mixture was heated to 125 °C for 48 hours with stirring. A mixture of water and toluene (1:1, 40 mL) was added and the organic layer was extracted, washed twice with 5% K_{3}PO_{4} solution, then dried with magnesium sulfate, filtered, and evaporated to dryness. The crude solid was purified by column chromatography using silica gel. First the silica was pre-treated with 2% triethylamine in hexanes. Then, the crude NH_{2}-dctpy was loaded onto the column with toluene and eluted with a solution of 78/20/2 hexanes/ethyl acetate/triethylamine (R_{f} = 0.24). Yield: 39 mg, 56%. 1H NMR (300 MHz, CDCl_{3}): δ 8.49 (dd, J = 7.7, 0.9 Hz, 2H), 7.78 (t, J = 7.8 Hz, 2H), 7.73 (s, 2H), 7.34 (dd, J = 7.8, 0.9 Hz, 2H), 4.40 (s, 2H). 13C NMR (75 MHz, CDCl_{3}): δ 157.18, 154.90, 154.76, 150.80, 139.48, 124.23, 119.69, 107.56 ppm. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C_{15}H_{10}N_{4}Cl_{2}H 317.0361; Found 317.0360.

Diethyl 2,2’-(pyridine-2,6-diyl)diquinoline-4-carboxylate (decqdp). Isatin (1.100 g, 7.48 mmol, 2.0 eq.) was combined with 2,6-diacetylpyridine (0.605 g, 3.71 mmol, 1.0 eq) and ground together with a mortar and pestle. The mixed solids were then added to a 50 mL round bottom flask and 3.75 g of cold (0°C) 33% NaOH was added with manual stirring. The mixture slowly congealed during 15 minutes of mixing to form a reddish-purple solid. Next, 3.75 mL of
ice-cold (0°C) H₂O were added and the solid was removed by vacuum filtration and washed with a copious amount of acetone (~250 mL). After drying on the filter, the dark pink solid was dissolved in 90 mL of water and acidified with 10% HCl to pH 2-3. Upon acidification, the solution became a thick orange suspension reminiscent of tomato soup. This mixture was filtered to produce a thick orange/red cake and allowed to dry on the filter. The wet orange cake was mixed with ethanol and then evaporated to remove residual water and produce a free flowing orange powder. Instead of purifying at this step, we decided to proceed with esterification to facilitate separation on a silica column.

For the esterification the crude product from the previous step was used in 200 mg portions. 18 mL of concentrated sulfuric acid was combined with 36 mL of ethanol and then 200 mg of the crude product was added and the solution was heated to reflux for 24 hours (~125°C). While refluxing, the color of the mixture became darker and less cloudy. The reaction mixture was then cooled to room-temperature, 60 mL of H₂O (0°C) was added, and the solution was neutralized to pH 13 with 25% NaOH. The resulting solid was filtered and washed with copious amounts of water to dissolve remaining salt and left to dry. The crude solid was purified by column chromatography on silica gel. First the silica was pre-treated with 1% triethylamine in hexanes. Then, the crude product was dry-loaded onto silica with 1% triethylamine in chloroform. The elution was performed using a solution of 84/15/1 hexanes/ethyl acetate/triethylamine and the pure product was collected as a white solid that appeared blue under UV-light. (Rᵣ = 0.3) A yellow compound eluted afterward, which was discarded. Beginning with 605 mg of 2,6-diacetylpyridine, the final yield was 245 mg, 14%. ¹H NMR (500 MHz, CDCl₃) δ 9.29 (s, 2H), 8.79 (d, J = 8.3 Hz, 2H), 8.76 (d, 2H), 8.27 (d, J = 8.4 Hz, 2H), 8.10 (t, J = 7.8 Hz, 1H), 7.81 (ddd, J = 8.3, 6.8, 1.4 Hz, 2H), 7.68 (ddd, J = 8.3, 6.8, 1.3 Hz, 2H), 4.61
(q, J = 7.1 Hz, 4H), 1.56 (t, J = 7.2 Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 166.8, 155.7, 155.0, 148.9, 138.3, 136.6, 130.5, 130.0, 128.4, 125.7, 125.2, 122.5, 120.4, 62.0, 14.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{29}$H$_{23}$N$_3$O$_4$H 478.1767; Found 478.1765.

2.3. Complex Synthesis

[Fe(dctpy)$_2$](BF$_4$)$_2$. Using standard Schlenk techniques, iron(II) tetrafluoroborate hexahydrate (Strem Chemical, 24 mg, 0.071 mmol, 1.0 eq.) was combined with dctpy (47 mg, 0.16 mmol, 2.2 eq.) in 25 mL of nitrogen-sparged 1,4-dioxane. The solution was heated to reflux with continuous stirring for 24 hours. The resulting solution was evaporated to dryness, then dissolved in acetonitrile and filtered. The filtrate was crystallized from slow diffusion of diethyl ether into acetonitrile and the product was recovered as orange needles. Crystals suitable for x-ray diffraction were grown from vapor diffusion of tetrahydrofuran into a benzonitrile solution. Yield: 30 mg, 51%. $^1$H NMR (300 MHz, CD$_3$CN) δ 71.64 (br. s, 4H), 63.05 (br. s, 4H), 49.27 (br. s, 4H), 13.28 (br. s, 4H), -28.53 (br. s, 2H). Anal. Calcd. for C$_{30}$H$_{18}$N$_6$Cl$_4$FeB$_2$F$_8$: C, 43.22; H, 2.18; N, 10.08. Found: C, 43.25; H, 1.99; N, 9.89. HRMS (ESI-TOF) m/z: M$^{2+}$ Calcd for C$_{30}$H$_{18}$N$_6$Cl$_4$Fe 329.9836; Found 329.9841.

[Zn(dctpy)$_2$](BF$_4$)$_2$. The same synthetic procedure was used as for [Fe(dctpy)$_2$](BF$_4$)$_2$. Zinc(II) tetrafluoroborate hydrate (Strem Chemical, 21 mg, 0.059 mmol) was combined with dctpy (40 mg, 0.13 mmol) to produce white crystalline plates. Yield: 12 mg, 30%. $^1$H NMR (300 MHz, CD$_3$CN) δ 8.80 – 8.63 (m, 6H), 8.56 (dd, J = 8.0, 0.9 Hz, 4H), 8.16 (t, J = 8.0 Hz, 4H), 7.50 (dd, J = 8.0, 0.9 Hz, 4H). HRMS (ESI-TOF) m/z: M$^{2+}$ Calcd for C$_{30}$H$_{18}$N$_6$Cl$_4$Zn 333.9806; Found 333.9804.
[Fe(dftpy)$_2$](BF$_4$)$_2$. Using standard Schlenk techniques, Fe(II) tetrafluoroborate hexahydrate (29 mg, 0.086 mmol, 1.0 eq.) was combined with dftpy (45 mg, 0.17 mmol, 2.0 eq.) in 24 mL of nitrogen-sparged 1,4-dioxane. The solution was heated to reflux with stirring for 24 hours, whereupon the resulting mixture was evaporated to dryness, then dissolved in acetonitrile and filtered through glass wool paper. The filtrate was concentrated in vacuo and crystallized from slow diffusion of diethyl ether into acetonitrile, where the product was collected as red-orange blocks. Crystals suitable for x-ray diffraction were obtained via slow evaporation of acetonitrile. Yield: 20 mg, 30%. $^1$H NMR (300 MHz, CD$_3$CN) δ 70.79 (br. s, 4H), 70.37 (br. s, 4H), 52.06 (br. s, 4H), 14.96 (br. s, 4H), -24.60 ppm (br. s, 2H). A reproducible sub-spectrum was observed corresponding to a diamagnetic species which is assigned to the low-spin state of the same molecule. The integration values reported for this state have been scaled by 12.5 times relative to the integration values listed above in order to facilitate comparison of the diamagnetic peaks to one another. Assigned to singlet ground state: δ 8.88 – 8.67 (m, 4H), 8.64 – 8.46 (m, 4H), 8.42 – 8.25 (m, 4H), 8.19 – 7.99 (m, 2H), 7.32 – 7.05 ppm (m, 4H). Anal. calcd for C$_{30}$H$_{18}$N$_6$FeB$_2$F$_{12}$: C, 46.92; H, 2.36; N, 10.94. Found: C, 46.64; H, 2.21; N, 10.68. HRMS (ESI-TOF) m/z: M$^{2+}$ Calcd for C$_{30}$H$_{18}$N$_6$F$_4$Fe 297.0439; Found 297.0436.

[Fe(dbtpy)$_2$](BF$_4$)$_2$. The same synthetic procedure was used as for [Fe(dftpy)$_2$](BF$_4$)$_2$. Fe(II) tetrafluoroborate hexahydrate (34 mg, 0.10 mmol, 1.0 eq.) was combined with dbtpy (86 mg, 0.22 mmol, 2.2 eq.) to produce orange crystalline plates. Crystals suitable for x-ray diffraction were obtained by vapor diffusion of diethyl ether into an acetonitrile solution. Yield: 40 mg, 40%. $^1$H NMR (300 MHz, CD$_3$CN) δ 71.19 (br. s, 4H), 60.60 (br. s, 4H), 47.05 (br. s, 4H), 11.09 (br. s, 4H), -28.39 ppm (br. s, 2H). Anal. Calcd. for C$_{30}$H$_{18}$N$_6$Br$_4$FeB$_2$F$_8$: C, 35.62; H,
Iron(II) tetrafluoroborate hexahydrate was dried in a vacuum oven at 100 °C overnight to remove water and stored in a nitrogen-filled glove box. Iron(II) tetrafluoroborate (9 mg, 0.04 mmol, 1.0 eq) was combined with mc-dctpy (32 mg, 0.089 mmol, 2.2 eq) in 15 mL of acetonitrile. The resulting solution was stirred and heated to 70 °C overnight under a slight positive pressure of nitrogen. The following day, the solution was concentrated in vacuo, filtered through glass wool paper, and crystallized by slow diffusion of diethyl ether into the acetonitrile solution. The product was collected as vibrant orange blocks, which were suitable for x-ray diffraction. Yield: 25 mg, 65%. ¹H NMR (300 MHz, CD₃CN) δ 69.73 (br. s, 4H), 62.84 (br. s, 4H), 51.34 (br. s, 4H), 10.58 (br. s, 4H), 2.88 ppm (br. s, 6H). Anal. Calcd for C₃₀H₁₈N₆Br₄Fe 418.8820; Found 418.8823.

[Fe(mc-dctpy)₂](BF₄)₂. The same procedure was used as for [Fe(mc-dctpy)₂](BF₄)₂ above. Iron(II) tetrafluoroborate (9 mg, 0.04 mmol, 1.0 eq) was combined with Ph-dctpy (33 mg, 0.089 mmol, 2.2 eq). Crystals suitable for diffraction were obtained by slow diffusion of diethyl ether into an acetonitrile solution. Yield: 15 mg, 38%. ¹H NMR (300 MHz, CD₃CN) δ 70.80 (br. s, 4H), 62.23 (br. s, 4H), 48.96 (br. s, 4H), 14.28 (br. s, 4H), 7.63 (t, J = 7.2 Hz, 4H), 2.08 (t, J = 7.4 Hz, 2H), 0.71 (d, J = 7.7 Hz, 4H). Anal. Calcd for C₃₄H₂₂N₆Cl₄FeO₄B₂F₈: C, 42.99; H, 2.37; N, 8.85. Found: C, 43.03; H, 2.33; N, 8.69. HRMS (ESI-TOF) m/z: M²⁺ Calcd for C₃₄H₂₂N₆Cl₄FeO₄ 387.9892; Found 387.9896.

[Fe(NH₂-dctpy)₂](BF₄)₂. A similar procedure was used as for [Fe(mc-dctpy)₂](BF₄)₂ above. Iron(II) tetrafluoroborate (15 mg, 0.065 mmol, 1.0 eq) was combined with NH₂-dctpy (45
mg, 0.14 mmol, 2.2 eq). The recrystallization step was performed by slow diffusion of chloroform into an acetonitrile solution. Crystals suitable for diffraction were obtained by slow diffusion of tetrahydrofuran into a benzonitrile solution. Yield: 36 mg, 64%. $^1$H NMR (300 MHz, CD$_3$CN) δ 67.44 (br. s, 4H), 59.22 (br. s, 4H), 46.97 (br. s, 4H), 17.49 (br. s, 4H), -14.43 (br. s, 1H). Anal. Calcd for C$_{42}$H$_{26}$N$_6$Cl$_4$FeB$_2$F$_8$: C, 41.71; H, 2.33; N, 12.97. Found: C, 41.68; H, 2.17; N, 12.82. HRMS (ESI-TOF) m/z: M$^{2+}$ Calcd for C$_{30}$H$_{20}$N$_6$Cl$_4$Fe 344.9945; Found 344.9965.

[Fe(dqp)$_2$](BF$_4$)$_2$. Iron(II) tetrafluoroborate hexahydrate was dried in a vacuum oven at 100 °C overnight to remove water and stored in a nitrogen-filled glove box. Iron(II) tetrafluoroborate (6.5 mg, 0.065 mmol, 1.0 eq) was combined with dqp (50 mg, 0.150 mmol, 2.3 eq, prepared following a procedure adapted from literature$^3$) in 15 mL of acetonitrile. The resulting solution was heated to reflux overnight under a slight positive pressure of nitrogen. The following day, the solution was concentrated in vacuo, filtered through glass wool paper and crystallized by slow diffusion of diethyl ether into the acetonitrile solution. The product was collected as red needles. Yield: 23 mg, 39%. $^1$H NMR (500 MHz, CD$_3$CN) δ 75.08 (br. s), 63.19 (br. s), 31.05 (br. s), 10.60 (br. s), 9.88 (br. s), 9.10 (br. s), -12.96 ppm (br. s). Anal. Calcd for C$_{46}$H$_{30}$FeN$_6$B$_2$F$_8$: C, 61.65; H, 3.37; N, 9.38. Found: C, 61.67; H, 3.22; N, 9.36. HRMS (ESI-TOF) m/z: M$^{2+}$ Calcd for C$_{40}$H$_{30}$FeN$_6$ 361.0941; Found 361.0947.

[Fe(decdqp)$_2$](BF$_4$)$_2$. Iron(II) tetrafluoroborate hexahydrate was dried in a vacuum oven at 100 °C overnight to remove water and stored in a nitrogen-filled glove box. Iron(II) tetrafluoroborate (15 mg, 0.028 mmol, 1.0 eq) was combined with decdqp (30 mg, 0.063 mmol, 2.2 eq) in 12 mL of acetonitrile. The resulting solution was heated to reflux overnight under a slight positive pressure of nitrogen. The following day, the solution was concentrated in vacuo, filtered through glass wool paper and crystallized by slow diffusion of diethyl ether into the
acetonitrile solution. The product was collected as dark red blocks (almost black), which were suitable for x-ray diffraction. Yield: 18 mg, 54%. Anal. Calcd for C$_{58}$H$_{46}$FeN$_6$O$_8$B$_2$F$_8$: C, 58.81; H, 3.91; N, 7.10. Found: C, 58.85; H, 4.09; N, 7.14. HRMS (ESI-TOF) m/z: M$^{2+}$ Calcd for C$_{58}$H$_{46}$FeN$_6$O$_8$ 505.1364; Found 505.1363.

2.4. X-Ray Crystallography

Crystals were mounted under a stream of nitrogen on a cryoloop with Paratone-N oil. Data collection was performed at 100 K, 120 K, or 300 K as noted using a Bruker D8-Quest Eco diffractometer, Mo K$\alpha$ radiation, and a graphite monochromator. Data integration and absorption correction were performed using the APEX 3 software suite (Bruker) and structures were solved by direct methods and refined in OLEX2 using SHELXS, SHELXT, and SHELXL.$^5$ Thermal parameters for all non-hydrogen atoms were refined anisotropically by full matrix least-squares on F$^2$. Hydrogen atoms were placed in calculated positions and refined using a riding model with U(H) = 1.5 × U$_{eq}$ (bonded carbon atom) for methyl groups and U(H) = 1.2 × U$_{eq}$ (bonded carbon atom) for all others. Errors shown throughout this thesis are given by $\sigma_{avg} = \sqrt{\sum(\sigma_i)^2} / n$, with n measurements where $\sigma_i$ is the e.s.d. of an individual distance or angle.

The structure of [Fe(dctpy)$_2$(BF$_4$)$_2$] was investigated for possible missed symmetry, however, solving in centrosymmetric $C_2/c$ gave significantly worse agreement values. It was finally refined as a two-component inversion twin. The 300 K structure of [Fe(dftpy)$_2$(BF$_4$)$_2$] was found to have very disordered BF$_4^-$ groups, likely due to the high temperature of data collection. While some of the disorder was modeled, additional attempts did not improve the agreement between the model and the data. The B-F bond lengths were restrained to sensible values since they were found to be much longer or shorter than typical when left unrestrained. The disorder
was diminished in the 120 K structure of the same crystal. [Fe(dbtpy)₂](BF₄) was refined as a two-component twin, with the ratio of the components being 90:10. The largest residual Q-peak is located in a solvent void and is likely to be additional solvent disorder. It is possible that this is a water molecule with a partial occupancy and modeling it in this manner slightly improved the agreement values. But in the end, there was insufficient evidence to make the assignment and it wasn’t modeled.

[Fe(mc-dctpy)₂](BF₄)₂ was found to exhibit extensive solvent disorder in separate data sets collected from three distinct single crystals. In the data set we chose to model, the solvent molecules that have been placed are in positions which match the highest electron density, although significant amounts of unmodeled electron density remain. Due to this, hydrogens were not added to the solvent molecules, which had relatively large thermal ellipsoids as well. Using a solvent mask to account for electron density not attributed to [Fe(mc-dctpy)]²⁺ or the two (BF₄)⁻ ions improved agreement values significantly (R₁ < 5%) but the geometric parameters of the Fe-containing complex remained largely unaffected. Therefore, we decided to model the solvent as best we could despite the worse overall agreement values expecting that the geometric parameters of the Fe(II) complex would be valid for comparison to other complexes and we would not have altered the underlying data. We note that in the metal complex, C17 has rather strange anisotropic parameters. We expect this is a reflection of the range of the movement of the entire ester group contributing to a variety of positions sampled in the diffraction data.

[Fe(am-dctpy)₂](BF₄)₂ has three carbon atoms (C2, C3, and C4) which have thermal ellipsoids which are all elongated in the same direction. Modeling of these as two separate parts was found to lead to minimal improvement in the agreement values. It is possible that this is an artifact of the two ligands which are being modeled as crystallographically equivalent in fact
being slightly dissimilar. For the structure of \([\text{Fe}(	ext{decdqp})_2](\text{BF}_4)_2\), SADI, RIGU, and SIMU restraints were used for the diethyl ether molecule to maintain a reasonable geometry in spite of the significant disorder. Additionally, one of the ethyl ester substituents on the ligands was found to be disordered over two positions and was modeled as such.

**Table 2.1. Structural and Diffraction Data Relevant to Chapters 3 and 4**

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<td>90</td>
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<td>γ (°)</td>
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<td>90</td>
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<td>&gt; 2\sigma])</td>
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\(a\) \(R_1 = \Sigma||F_o||-||F_c||/\Sigma||F_o||\). \(b\) \(wR_2 = (\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}\) for \(F_o > 4\sigma(F_o)\).
Table 2.2. Structural and Diffraction Data Relevant to Chapters 5 and 6

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<th><a href="%5BBF$_4$%5D">Fe(mc-dctpy)$_2$</a>$_2$</th>
<th><a href="%5BBF$_4$%5D">Fe(Ph-dctpy)$_2$</a>$_2$</th>
<th><a href="%5BBF$_4$%5D">Fe(NH$_2$-dctpy)$_2$</a>$_2$</th>
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<td>tetrahydrofuran</td>
<td>acetonitrile, diethyl ether</td>
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<td>C$<em>{46}$H$</em>{52}$B$_2$Cl$_4$FeN$_8$O$_4$</td>
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<td>100(2)</td>
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<td>99.9% ($\theta = 29.131$)</td>
<td>99.9% ($\theta = 28.283$)</td>
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$^a R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$.  
$^b wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$ for $F_o > 4\sigma(F_o)$.  

35
2.5. Magnetic Measurements

The mass susceptibility ($\chi_g$) and effective magnetic moment ($\mu_{eff}$) for all paramagnetic compounds were determined via the Evans method.\textsuperscript{6,7} Following this method, \(~1-2\) mL of solution was prepared with a concentration of \(~5\) mg of analyte per mL of acetonitrile (CH$_3$CN). This solution was transferred into a coaxial insert (New Era) and then placed inside of a 5 mm NMR tube containing deuterated acetonitrile (CD$_3$CN) and spiked with three drops of acetonitrile (CH$_3$CN). The chemical shift difference of CH$_3$CN in the inner and outer tube was measured at 25.0 °C in a 500.37 MHz Varian Inova NMR Spectrometer. Diamagnetic corrections were applied using the values tabulated by Bain and Berry.\textsuperscript{8} The gram susceptibility was calculated using Equation 2.1,

$$\chi_g = -\frac{3\Delta f}{4\pi fc}$$

Equation 2.1

where $\Delta f$ is the chemical shift difference in Hz of the two acetonitrile peaks, $f$ is the frequency of the spectrometer (also in Hz), $c$ is the concentration of the paramagnetic substance in g/mL, and $\chi_g$ is the gram susceptibility of the compound in emu/g. This value was converted into an observed molar susceptibility observed and used to determine the paramagnetic contribution ($\chi_p$) by subtracting the diamagnetic correction ($\chi_D$). An effective magnetic moment in Bohr magnetons was obtained using Equation 2.2 where $T$ is the temperature in K.

$$\mu_{eff} = \sqrt{8\chi_p T}$$

Equation 2.2

SQUID data were collected using a Quantum Design MPMS XL SQUID magnetometer. All sample preparations were performed on the bench top. Powdered microcrystalline samples
were dissolved in acetonitrile and placed into a straw, whereupon the straw was sealed. The compounds [Fe(dftpy)_2](BF_4)_2 and [Fe(dctpy)_2](BF_4)_2 were measured at concentrations of 0.077 and 0.053 M, respectively. For solid state measurements, powdered microcrystalline samples were placed into polyethylene bags, sealed and inserted into a straw. Ferromagnetic impurities were probed through a variable field (H) analysis (0 to 10 kOe) of the magnetization (M) at 100 K: no curvature was observed in the M vs H plot, indicating that there are no significant ferromagnetic impurities in these samples. Magnetic susceptibility data were collected at temperatures ranging from 2 to 315 K for [Fe(dctpy)_2](BF_4)_2 in acetonitrile, 100 to 315 K for [Fe(dftpy)_2](BF_4)_2 in acetonitrile, and 2 to 315 K for [Fe(dftpy)_2](BF_4)_2 in the solid state. The samples that were dissolved in acetonitrile were inserted into the magnetometer at ~30-50 K essentially flash-freezing them. They were then warmed to 100 K for the M vs H scan, and then cooled to 2 K to begin the susceptibility sequence. After warming to 315 K, the samples were immediately cooled back down to 2 K. Data were corrected for the diamagnetic contributions of the sample holder and solvent by subtracting empty containers; corrections for the sample were calculated from Pascal’s constants. The SQUID measurements were performed by Robert F. Higgins at Colorado State University. Additional details are provided in the associated manuscript in which this experiment originally appeared.9

2.6 Electrochemistry and Spectroelectrochemistry

Cyclic voltammetry (CV) was performed using an electrochemical analyzer (CH Instruments 601C) and a 3-electrode setup with a 1.6 mm diameter Pt disc working electrode (BASi), Pt wire counter electrode, and freshly prepared 0.01M Ag/AgNO_3 reference electrode. All measurements were taken on freshly prepared solutions of the analyte (~2 mM) in
acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) electrolyte and
degassed with Ar for 2 minutes, then blanketed with Ar for the duration of the experiment.
Ferrocene was used as an internal standard. Prior to the experiment, the working electrode was
polished using a 1µm diamond slurry and alumina, and cleaned with methanol between runs. The
scan rate was set to 100 mV/s. Peak separations were ~70 mV for all measurements except for
the oxidation of some iron complexes, which had larger peak separations due to their proximity
to the edge of the solvent window.

Spectroelectrochemistry experiments utilized a home-built glass optically transparent
thin-layer electrode (OTTLE) cell with a 2 mm path length and a Pt mesh working electrode, a Pt
wire counter electrode, and the Ag/AgNO$_3$ reference electrode described above. As in the CV
measurements, the analyte was dissolved in acetonitrile with 0.1M TBAPF$_6$ and degassed with
Ar then blanketed with Ar for the duration of the experiment. Throughout the bulk electrolysis,
electronic absorption spectra were taken on a Hewlett-Packard diode array spectrophotometer
(HP8452A). Additional details are available elsewhere.$^{10}$

2.7. Emission Studies on Cr(III) and Ru(II) Complexes

Emission lifetime measurements were conducted in nitromethane solutions of the catalyst
at 0.1 absorbance and the indicated concentration of quencher. The solutions were irradiated at
400 nm or 450 nm for the 4-methoxychalcone quenching experiments. Irradiation at 400 nm
used the frequency doubled output from a 1kHz repetition rate Ti:Sapphire laser system. To
irradiate the samples at 450 nm, a pulsed Nd:YAG laser (Continuum Surelite II) with a 10 Hz
repetition rate, ~5 ns pulse width, and centered at 355 nm was used to pump a Continuum
Surelite optical parametric oscillator to obtain 450 nm light and the power was attenuated as
needed using neutral density filters. Emission was measured through a ~15 nm bandpass filter centered at 750 nm (chromium complexes) or 600 nm (ruthenium complexes) using a Hamamatsu H9305-02 photomultiplier tube (PMT) operating at – 900 Vdc. The PMT response was recorded using a LeCroy 9384L Oscilloscope and averaged over 1000 scans. The resulting decays were fit using a single exponential decay function. For static emission experiments, a xenon arc lamp was used in conjunction with an SLM 8000C spectrofluorometer. Quenching rate constants were obtained from the measured emission intensity or $\tau$ values using the Stern-Volmer equation. Air-free photochemical measurements were performed on samples prepared in a nitrogen-filled glovebox and placed in a 1 cm × 1 cm cuvette and sealed with a Teflon valve. Additional details of these measurements are available elsewhere.\textsuperscript{11,12}

2.8. Other Experimental Details

UV-Visible absorption spectra were collected on a Hewlett-Packard diode array spectrophotometer (HP8452A) or an Agilent Cary 5000 UV-Vis-NIR spectrometer. Samples were prepared using HPLC-grade acetonitrile (EMD Millipore) in a 1 cm pathlength cuvette. Temperature control of samples was performed using a refrigerated constant temperature circulator (VWR 1145). Information regarding transient absorption and computational experiments have been collected elsewhere.\textsuperscript{9,10,13,14}
2.9. $^1$H NMR Spectra for New Ligands

Figure 2.1. $^1$H NMR of dctpy.

Figure 2.2. $^1$H NMR of dftpy.
Figure 2.3. $^1$H NMR of mc-dctpy.

Figure 2.4. $^1$H NMR of Ph-dctpy.
Figure 2.5. $^1$H NMR of NH$_2$-dctpy.

Figure 2.6. $^1$H NMR of decdq.
2.10. References


Chapter 3

Iron(II) 6,6”-Dichloroterpyridine: Accessing the Quintet Excited State Manifold


3.1. Introduction

We became interested in a different strategy for metal-to-ligand charge transfer (MLCT) lifetime extension based on previous work in our group involving Ru(II) bis-terpyridyl systems where the ligands (dbtpy = 6,6”-dibromo-2,2’:6’,2”-terpyridine) contain significant steric bulk at positions enhancing inter-ligand repulsion.¹ In this work, it was argued based on constrained density functional theory results that these inter-ligand interactions hinder the kinds of motions that engender coupling between the MLCT and metal-centered (MC) manifolds.¹ By applying this same strategy to an iron(II) complex, we thought that it would be possible to limit the rapid loss of the MLCT state by limiting motions along surfaces that offer low barriers to relaxation. However, as will be described below, bis-tridentate Fe(II) complexes of the related ligand 6,6”-dichloro-2,2’:6’,2”-terpyridine (dctpy) do not adopt a low-spin ground state structure. Rather, analogous to what has been seen by Constable and coworkers in related methyl and phenyl-substituted systems,² inter-ligand repulsions push [Fe(dctpy)₂]²⁺ into a quintet ground state with no evidence of singlet character at room temperature. This situation presented an opportunity to investigate the photophysics of a high-spin Fe(II) system which had not been previously considered in the literature. Namely, can the ⁵MLCT manifold (which has been discussed in theoretical work³–⁶ and in low-temperature crystal work⁷) be directly accessed from a quintet
ground state, and do the structural properties within the Franck-Condon state significantly alter its subsequent non-radiative decay dynamics? X-ray crystallography, electrochemistry, UV-vis spectroscopy, density functional theory (DFT), and transient absorption (TA) spectroscopy are employed to show that MLCT excitation is indeed feasible and that the 5,7 MLCT lifetime, determined from our exploration of this initial system, effectively matches the longest that was known for an Fe(II) polypyridyl system at the time of publication.8,9

3.2. Synthesis of dctpy and [Fe(dctpy)2]2+

The dctpy ligand was synthesized using a Suzuki-Miyaura cross-coupling protocol shown to be effective for similar systems.10–12 In the synthesis of dctpy, two equivalents of 2-chloropyridyl-6-boronic acid pinacol ester couple to a central 2,6-dibromopyridine to form the terpyridyl framework (Fig. 3.1). This has the advantage of introducing the chloro groups prior to forming the terpyridyl framework where substituting only the 6 and 6’ positions could prove challenging using standard aromatic substitution reactions. Furthermore, this reaction takes advantage of the relative reactivity of halogens in Suzuki couplings, I > Br >> Cl,10 such that the coupling occurs at both bromine sites on the dibromopyridine prior to any reaction with the chlorine sites on the boronic acid pinacol esters. While running this reaction, an intermediate was observed via TLC that was assumed to be the singly reacted 6-bromo-6’-chloro-2,2’-bipyridine, an assignment which was later confirmed by NMR. When the reaction was stopped, some of the 6-bromo-6’-chloro-2,2’-bipyridine intermediate remained, but there was no evidence of any quaterpyridines, a side product we wished to avoid which would result from additional coupling reactions occurring at chlorine sites. This control is thought to be possible due both to the lower
reactivity of Cl compared to Br and the chosen conditions such as lower temperatures and limited equivalents of the boronic acid pinacol ester.

**Figure 3.1.** Synthesis of dctpy ligand using Suzuki coupling methodology.

The complex [Fe(dctpy)₂]²⁺ was prepared in refluxing 1,4-dioxane from the tetrafluoroborate salt of iron(II) and two equivalents of the dctpy ligand (Fig. 3.2). Weakly-coordinating counterions and solvent were found to be important for avoiding competitive coordination to the metal ion since the steric bulk on the ligand promotes lability. This is emphasized by the sensitivity of the complex to polar protic solvents such as water and methanol which likely form an iron(II)-solvento species. Purification of this compound was attempted using column chromatography, but the compound decomposed on silica in the highly polar solvents necessary for elution. Instead, the complex was dissolved in acetonitrile and filtered to remove the mostly insoluble dctpy. Following filtration, the filtrate was crystallized by slow diffusion of diethyl ether to produce pure product. A d¹⁰ metal complex, [Zn(dctpy)₂]²⁺ was similarly prepared and used for assigning electronic transitions (described below).

**Figure 3.2.** Synthesis of [Fe(dctpy)₂](BF₄)₂.
Confirmation of the identity of this compound proved to be challenging. $^1$H NMR spectra of the complex showed significant peak broadening and splitting patterns were not discernible. Furthermore, Fermi-contact shifting caused the hydrogen nuclei peaks to shift extremely far downfield to positions between $\delta = 80$ and $-30$ ppm, far beyond the normal spectroscopic region (Fig. 3.3). Instead, elemental analysis, mass spectrometry, and x-ray crystallography were used to confirm sample identity and purity.

![1H NMR spectrum of [Fe(dctpy)$_2$]$^{2+}$ taken in CD$_3$CN.](image)

**Figure 3.3.** $^1$H NMR spectrum of [Fe(dctpy)$_2$]$^{2+}$ taken in CD$_3$CN.
3.3. Magnetic Measurements and X-Ray Crystallography

An initial indication of a high-spin ground state in [Fe(dctpy)₂]²⁺ comes from room-temperature NMR experiments in CD₃CN where the ^1H resonances are found at chemical shifts far beyond the normal region suggesting proximity to a paramagnetic site (Fig. 3.3). Quantitative measurement of the magnetic susceptibility by NMR reveals an effective magnetic moment of 5.3, consistent with other iron(II) species with four unpaired electrons in a distorted octahedral geometry.²,¹³ From these measurements, and the fact that [Fe(tpy)₂]²⁺ is low spin in its ground state, it is apparent that the dctpy ligand has sufficient steric bulk to weaken the ligand field via interligand repulsion, leading to a room temperature quintet ground state. A deeper look at the geometric effects of this steric strain is provided by X-ray crystallography.

Table 3.1. X-Ray Structural Data for [Fe(dctpy)₂]²⁺

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<th>complex</th>
<th>Fe-N$_{\text{central}}$ (Å)</th>
<th>Fe-N$_{\text{terminal}}$ (Å)</th>
<th>θ N-N-N (°)</th>
<th>Θ (°)</th>
<th>X-pyridyl (Å)</th>
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<td>[Fe(tpy)₂]²⁺</td>
<td>1.890(4)</td>
<td>1.988(3)</td>
<td>102.8(2)</td>
<td>1.5(3)</td>
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<td>2.080(2)</td>
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<td>4.1(1)</td>
<td>3.074(1)</td>
</tr>
</tbody>
</table>

" Structural data from Baker et al.¹⁴ Data taken at 295 K for [Fe(tpy)₂]²⁺, 120 K for [Fe(dctpy)₂]²⁺.

X-ray diffraction data for [Fe(dctpy)₂](BF₄)₂ were collected at 120 K and selected geometric parameters are displayed in Table 3.1. The resulting structure displays a geometry consistent with a quintet ground state and highlights the steric strain that encourages the electronic configuration of four unpaired electrons in metal-derived orbitals, two of which are antibonding in nature. This latter point about steric strain is highlighted in Figure 3.4, which presents thermal ellipsoid plots for [Fe(dctpy)₂]²⁺. Viewed along the axis containing the central Fe-N bonds (left-hand image), the distortion of the terpyridyl planes is immediately noticeable. The vertical dctpy ligand is twisted about the two inter-ring C-C bonds, so that the two chlorine atoms are pointing towards opposite sides of the central pyridyl group with the C-Cl bonds at a pseudo-dihedral angle of 28.0(2)°. A similar effect is seen in the horizontal dctpy ligand but is
less pronounced at only 10.1(2)°. The overall twisting distortion is likely occurring because of repulsion between the chlorine atoms and the π-system of the central pyridine on the opposing ligand, especially the more electronegative nitrogen atom. This steric interaction is undoubtedly critical in the determination of the ground spin state in [Fe(dctpy)$_2$]$^{2+}$. To limit electronic repulsion, these molecules adopt a geometry where Fe–N bonds are elongated and where the terpyridyl $N_{\text{terminal}}$-$N_{\text{central}}$-$N_{\text{terminal}}$ (N-N-N) angle is consequentially increased, thus serving to extend the distance of the halogen from the π-system of the second ligand relative to what is seen in low-spin analogues such as [Fe(tpy)$_2$]$^{2+}$. For example, in [Fe(dctpy)$_2$]$^{2+}$ the Fe-$N_{\text{central}}$ bond elongates to 2.080(2) compared to a typical low-spin value of ~1.9 Å. There is also a substantial deviation from a true octahedral coordination geometry as evidenced by the average $N_{\text{terminal}}$-Fe-$N_{\text{central}}$ bond angle of ~75° in the halogenated complex, even smaller than the ~81° seen in [Fe(tpy)$_2$]$^{2+}$.

Figure 3.4. Crystal structure of the Fe-containing complex in [Fe(dctpy)$_2$](BF$_4$)$_2$ shown from two distinct points of view with thermal ellipsoids rendered at 50% probability. C = gray, Cl = green, Fe = orange, N = blue. Hydrogen atoms have been removed for clarity.

Despite the Fe–N bond elongation, the [Fe(dctpy)$_2$]$^{2+}$ structure still shows short distances between the halogen substituent and the central pyridyl ring of the opposing ligand. The value is tabulated in Table 3.1 (X-pyridyl) and is ~0.35 Å shorter than the sum of the Bondi radii of the
halogen and carbon$^{15,16}$ The fact that these distances are still short despite the significant geometric distortions described above underscores the even greater unfavorable steric interactions that would exist in a hypothetical low-spin complex with these ligands. A final tabulated metric for these is the so-called “rocking angle” $\Theta$, which represents the angular deviation from $180^\circ$ for $N_{\text{central}}$-Fe-$N_{\text{central}}'$. We note this quantity by way of connecting to work by Jakubikova and coworkers who have shown that the quintet state of [Fe(tpy)$_2$]$^{2+}$ exhibits a substantial ($10^\circ$) value for $\Theta$ and a soft potential in this rocking direction whereas the singlet ground state is locked into a linear arrangement.$^5$ In [Fe(dctpy)$_2$]$^{2+}$ we observe a value of 4.1(1)$^\circ$, suggesting only an intermediate distortion along this coordinate relative to [Fe(tpy)$_2$]$^{2+}$.

Although it is relatively rare, we have looked for evidence of a spin-crossover equilibrium at the temperature of our measurements. No spectral changes are observed in NMR data over the temperature range 20 °C to -45 °C and no change is observed in the UV-Vis spectrum of [Fe(dctpy)$_2$]$^{2+}$ (whose features are discussed below) upon cooling to 77K in glass forming 2-methyl-tetrahydrofuran. Finally, the crystallographic data above shows that a high-spin geometry is retained in the solid state even upon cooling to 120 K. For the static and time-resolved spectroscopic experiments that follow, it is clear that the quintet state is the dominant state subjected to photoexcitation.

3.4. Electronic Transitions and the Quintet MLCT State

Molar absorptivities of dctpy, [Zn(dctpy)$_2$]$^{2+}$, and [Fe(dctpy)$_2$]$^{2+}$ have been measured in room temperature MeCN and are shown in Figure 3.5. For all three species, the intense feature at ~290 nm is expected to be $\pi^* \leftarrow \pi$ in nature. Upon complexation with Zn(II) or Fe(II), a second feature emerges to the red with a peak at ~340 nm. Time-dependent density functional theory
(TD-DFT) results shown in Figure 3.6 nicely reproduce this observation and the associated natural transition orbitals (NTOs) for those transitions indicate participation by both ligands (Fig. 3.7). This suggests that the metal center either plays a role as an electronic coupling center for ligand-to-ligand charge transfer (LLCT) or the metal center provides a scaffold for constraining the ligand geometry and altering intraligand transitions. A notable difference between the Fe(II) and Zn(II) species is the red-shifting of the lower energy transition and the appearance of a broad absorptive feature tailing into the visible upon substitution of Zn(II) with the redox-active Fe(II) center (Fig. 3.5, right-hand spectra). It’s likely that this broad feature is partially responsible for the red-shifting of the more intense band. This feature is replicated in the TD-DFT results in the form of several low-intensity and low-energy transitions in the region from 400-480 nm.

![Graph of Molar Absorptivity vs. Wavelength](image)

**Figure 3.5.** UV-Visible absorption spectra in room temperature MeCN of free dctype, [Zn(dctype)₂]²⁺, and [Fe(dctype)₂]²⁺. The right-hand figure focuses on spectral differences observed above 350 nm.
Figure 3.6. TD-DFT generated spectra of dctpy (blue), [Zn(dctpy)]$^{2+}$ (red), and [Fe(dctpy)]$^{2+}$ (green). Transitions of interest have been numbered for clarity.

Figure 3.7. Natural transition orbitals of [Fe(dctpy)]$^{2+}$ ($\alpha$ above, $\beta$ below) plotted for the transition (#17) at 343 nm.
While [Fe(dctpy)₂]²⁺ lacks the visible extinction of its parent [Fe(tpy)₂]²⁺,¹⁷ it has a tailing visible feature that is also seen in other high-spin systems.²,¹⁸⁻²⁰ The molar absorptivity of 1200 M⁻¹cm⁻¹ at 400 nm is suggestive of a symmetry-allowed transition (i.e. not metal-centered d-d) with the possibility of MLCT originating in the quintet spin manifold: ⁵MLCT ← ⁵GS. While still significantly stronger than a typical MC transition, the reduced molar absorptivity of this MLCT transition relative to [Fe(tpy)₂]²⁺ (12,000 M⁻¹cm⁻¹)¹⁷ can be rationalized since a high-spin complex will have longer metal-ligand bond distances and less orbital overlap between the metal d and ligand π* orbitals. We have looked for additional support of this assignment in both TD-DFT calculations and electrochemical data. NTOs corresponding to the transitions in this range uniformly show beta electron density on the metal relocating to the ligand, indicative of an MLCT transition. Figure 3.8 shows an origin orbital that is primarily Fe dₓᵧ in nature with minor contributions from the π system on the terminal pyridines, specifically at the 1,4, and 6 positions. The destination orbital for this transition on the other hand, shows significant electron density spread throughout the π system on both ligands with a node along the z-axis. It is interesting to note that in the origin orbital, the chlorine atom seems to lower the energy of the adjacent carbon, leading to additional electron density on the 6 position versus the 2 position.

Figure 3.8. Natural transition orbitals of [Fe(dctpy)₂]²⁺ plotted for the transition (#11) at 410 nm.
Moving to the electrochemistry, we note that there is commonly a strong correlation between MLCT energies and the difference in the first one-electron oxidation and reduction potentials of coordination complexes.\(^{21}\) Table 3.2 shows potentials measured for \([\text{Fe(dctpy)}_2]^{2+}\) and \([\text{Fe(tpy)}_2]^{2+}\) versus SCE. Focusing on the halogen-substituted molecule relative to the parent, the one-electron reduction potential undergoes a significant positive shift due to the electron withdrawing character of the Cl atoms and their impact stabilizing unoccupied ligand \(\pi^*\) orbitals. At the same time, electron density at the metal center is expected to decrease through a halogen-derived inductive effect and because interligand steric repulsions limit the \(\sigma\) donation from the ligands. With comparable positive shifts in the 3+/2+ couple and the 2+/1+ couple, the calculated \(\Delta E_{1/2}\) for \([\text{Fe(dctpy)}_2]^{2+}\) is similar to that seen in \([\text{Fe(tpy)}_2]^{2+}\), thus suggesting that an MLCT state should be energetically attainable in the substituted complex.

**Table 3.2. Electrochemical Data for \([\text{Fe(dctpy)}_2]^{2+}\) Collected in MeCN versus SCE**

<table>
<thead>
<tr>
<th>complex</th>
<th>(3+/2+)</th>
<th>(2+/1+)</th>
<th>(\Delta E_{1/2})^b (V)</th>
<th>(\Delta E_{\text{MLCT}})^c (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe(tpy)}_2]^{2+})</td>
<td>1.10</td>
<td>-1.26</td>
<td>2.36</td>
<td>2.2</td>
</tr>
<tr>
<td>([\text{Fe(dctpy)}_2]^{2+})</td>
<td>1.60</td>
<td>-0.83</td>
<td>2.43</td>
<td>~2.5</td>
</tr>
</tbody>
</table>

\(^{a}\)\(E_{1/2}\) potentials measured versus \(\text{Fc/Fc}^+\) with 0.38 V added to obtain values vs. SCE. \(^{b}\)\(\Delta E_{1/2} = E(3+/2+) - E(2+/1+)\). \(^{c}\)\(\Delta E_{\text{MLCT}}\): energy derived from absorption spectrum in Fig. 3.2 or for \([\text{Fe(tpy)}_2]^{2+}\).\(^{17}\)

### 3.5. Photophysical Exploration of the \(\text{^5MLCT}\)

Having established the relevance of the \(\text{^5MLCT}\) manifold in the visible light absorption of \([\text{Fe(dctpy)}_2]^{2+}\), we now employ TA spectroscopy to investigate the excited-state dynamics. As expected based on literature involving polypyridyl \(\text{Fe(II)}\) species,\(^{22}\) the complex is non-emissive at room temperature, suggesting that a non-radiative decay pathway is dominant. This pathway is explored following excitation at 400 nm in the 2D intensity plot of TA dynamics as a function of white-light continuum probe wavelength (Fig. 3.5A) with a time window of 50 ps. The dominant
features of the spectra are an intense absorption peak at ~370 and the broad, lower intensity feature spanning the visible range. A cursory view of the data suggests minor spectral evolution in the first few picoseconds and then decay to baseline of these spectral features within the 50 ps window.

Figure 3.9. A. TA spectroscopy of [Fe(dctpy)₂]²⁺ in room temperature MeCN with several individual spectra shown in the inset (the white stripe indicates where pump scatter has been removed). B. Quantitative spectroelectrochemical analysis of [Fe(dctpy)₂]²⁺ in room temperature MeCN based on measurement of faradaic current. Full experimental details are available elsewhere.²³

Before describing a quantitative analysis of the dynamics, we first consider assignment of the observed spectral features. First, we believe it is possible to rule out formation of a singlet excited state (¹A) with a configuration comparable to what is found in the ground state of
[Fe(tpy)_2]^2+ (t_{2g}^6 in an pseudo-octahedral approximation). In such a state we would expect to see the strong 1MLCT ← 1A transition that gives many low-spin iron(II) complexes their characteristic purple color. Although, we note that the steric bulk of the halogen substituents may raise the energy of the 1A and/or diminish the oscillator strength, thereby making the 1MLCT ← 1A feature less obvious. Further evidence that the 1A is not formed is provided by the near-UV excited-state absorption (ESA). In a 1A state, we would expect to see a bleach feature in the near UV due to the blue-shifting of the LLCT absorption akin to the difference between [(Fedctpy)_2]^2+ and [Zn(dctpy)_2]^2+ (Fig. 3.5), and not the ESA at 370 nm, which is actually observed. A further example of the features of the 1A state will be provided in Chapter 4 when a spin-crossover complex is discussed. Overall, these features are inconsistent with the TA spectra of [Fe(dctpy)_2]^2+.

We have also ruled out the observation of a triplet ligand field state 3MC (for simplicity: t_{2g}^5 e_g^1). Such a state has been definitively observed as an intermediate in the spin-crossover dynamics of [Fe(bpy)_3]^{2+}. Notably, however, its observation required x-ray fluorescence as the spectral features of the 3MC and 5MC are too similar for distinction in ultrafast TA measurements by several groups. Given the significant spectral differences observed in our 5MC absorption (Fig. 3.5) versus our TA (Fig. 3.9; inset), it is highly unlikely that the latter heralds the formation of a 3MC state.

Spectroelectrochemical methods are commonly used to identify electronic transitions relevant to MLCT states by highlighting absorptions generated due to reduction of polypyridyl systems. Using faradaic current we have quantified the change in molar extinction of UV and visible features produced in [Fe(dctpy)_2]^2+ during the measurement (See Chapter 2 for details). Upon one-electron oxidation, the principal observation is an enhancement of the ~350 nm
absorption (Fig. 3.10). This supports the assignment of this band as LLCT since the intensity of such a transition would be enhanced through increased inter-ligand electronic coupling accompanying metal oxidation and the resultant decrease of metal-ligand bond distances. Upon one-electron reduction, that same band is lost, concomitant with the growth of visible and near-UV features characteristic of the polypyridyl ligand radical anion. Superposing these redox spectra leads to a predicted difference spectrum characterized by a strong transition at ~ 380 nm and a broad absorption throughout the visible. The qualitative similarity of these data with the TA difference spectra shown in the inset of Figure 3.9 is striking and suggests an assignment of those transient features to a MLCT excited state.

**Figure 3.10.** Reductive (left) and oxidative (right) spectroelectrochemistry of [Fe(dctpy)$_2$]$^{2+}$ in 0.1 M TBAPF$_6$ in MeCN with the potential vs. 0.01 M Ag/AgNO$_3$ held constant at -1.3 V (reduction) and 1.5 V (oxidation).

Focusing on $\Delta t = 1$ ps and beyond, the collected transient spectral data can be cleanly reproduced by a global model with only two exponential components with time constants $\tau_1 = 3.6 \pm 0.6$ ps and $\tau_2 = 16 \pm 1$ ps (error bars are $2\sigma$ for three separate data sets). To understand the components it is first instructive to consider the time evolution of the bright UV TA feature. A comparison of normalized spectra reveals no isosbestic point, but rather a smooth evolution of the band to a spectral position that decays with the longer time constant. In other words, there is no evidence for two distinct electronic states that interconvert on the short time scale. This
indicates that ~4 ps are needed for photoexcited $\text{[Fe(dctpy)₂]}^{2+}$ to thermalize within a $^5\text{MLCT}$ or $^7\text{MLCT}$ (after ultrafast intersystem crossing (ISC)), including the expected inner and outer-sphere nuclear reorganization accompanying formation of the polar state. Such an assignment has been made for early components in the excited state dynamics of both $\text{[Fe(CN)₄(bpy)]}^{2-}$ and $\text{[Os(bpy)₃]}^{2+}$.²⁷,²⁸

The second component, 16 ps, reflects the time needed for ground state recovery with no evidence of an intermediate. It can therefore be assigned as the lifetime of the $^5\text{MLCT}$ or $^7\text{MLCT}$ produced upon photoexcitation. Figure 3.11 offers support for this assignment by showing the time evolution of the maximum TA feature in the UV. This signal decays exponentially to baseline with a time-constant of $17.7 \pm 1$ ps, similar to the $\tau_2$ value discussed above. Analysis of the time-evolution of the spectral shift ($4 \pm 1$ ps) captures the shorter time constant (Fig. 3.11). Together these provide conclusive evidence that there is a faster blue shift (assigned to thermalization) and slower overall decay (ground state recovery).

**Figure 3.11.** Shift kinetics of the 370 nm band. Top: time-evolution of the maximum $\Delta A$ value. Bottom: Wavelength evolution of the maximum $\Delta A$ as determined by a polynomial fit.
3.6. Conclusions

In summary, we have synthesized and studied an iron(II) bis-dihaloterpyrdyl complex, [Fe(dctpy)$_2$]$^{2+}$, where inter-ligand repulsive interactions produce a high-spin quintet ground state. This complex can be excited with visible light to access the high-spin MLCT manifold where the lifetime is measured to be 16 ps or ~320-times longer than in the parent, [Fe(bpy)$_3$]$^{2+}$. This $^5$MLCT (or $^7$MLCT) lifetime matches the longest known at the time of discovery, competing with low-spin ground state systems ($^3$MLCT) where strong ligand fields have been exploited. We believe this result opens new design and utilization opportunities for charge-transfer lifetime enhancement in Fe(II) coordination complexes. Next generation systems will explore whether MLCT lifetimes can be systematically tuned by variation of steric bulk (Chapter 4), the use of electron-withdrawing and -donating ligand substituents (Chapter 5), and selective excited-state electronic localization (Chapter 6).

3.7. References


Chapter 4

Using Steric Strain to Manipulate the Spin States and Photophysics of High-Spin Iron(II) Terpyridines


RFH and MPS performed SQUID magnetometry measurements and contributed insight into spin-crossover phenomena. SGS performed and analyzed the TA experiments and the T-dependent data. All contributed to writing the original manuscript and designing the study.

4.1. Introduction and Motivation

In Chapter 3 a new design for Fe(II) chromophores was introduced in which accessing the quintet manifold enabled us to attain a significantly longer MLCT excited-state lifetime of 16 ps. This original complex utilized a sterically demanding ligand, 6,6”-dichloroterpyidine (dctpy) and a bis-tridentate binding motif. We argued that interligand steric repulsion raised the energy of the lower spin states (singlet and triplet) resulting in a quintet ground state and optically accessible $^5$MLCT state.

We hypothesize that these extended MLCT lifetimes relative to low-spin Fe(II) polypyridines are based on one or both of two possible effects. First, it is conceivable that compared to the $^1$MLCT or $^3$MLCT of prototypical low-spin Fe(II) polypyridyl complexes, the $^5$MLCT happens to be more poorly coupled to states such as the $^3$MC that can provide non-radiative pathways. Second, the size of the substituents driving the interligand steric interactions may serve to diminish the conformational freedom of the system within the excited-state manifold, thus preventing motions necessary for intersystem crossing events within the relaxation process. In this chapter, we seek to explore these ideas by virtue of exploring the
sensitivity of high-spin MLCT lifetimes to the size of substituents that drive the interligand steric interactions in the first place. In an effort to minimize other potential perturbations, we explore a halogen series of molecules (Figure 4.1), bookending the aforementioned [Fe(dctpy)₂]²⁺ with bromine- and fluorine-containing analogues, [Fe(dbtpy)₂]²⁺ and [Fe(dftpy)₂]²⁺. Preparation of the ligands and complexes was performed following similar procedures to those described in Chapter 3 for dctpy and [Fe(dctpy)₂]²⁺. Full synthetic details for the new complexes and ligands are given in Chapter 2.

![Diagram](image)

**Figure 4.1.** Structures of 6,6”-dihaloterpyridyl ligands and complexes.

Within this work, it is important to recognize that the parent [Fe(tpy)₂]²⁺ has a singlet ground state (¹A), suggesting that for substituent sizes smaller than Cl, the interconversion from ⁵MC to ¹A may become thermally allowed. Should this occur, it would be an interesting addition to the body of literature on light-induced excited-state spin trapping (LIESST)¹,² where a low driving force and a high-barrier for ⁵MC → ¹A interconversion (as would be expected given the steric constraints in dftpy) results in extended lifetimes of the ⁵MC. Given that [Fe(dctpy)₂]²⁺ has an optically bright ⁵MLCT ← ⁵MC transition, but relaxes back to the ⁵MC state in 16 ps, we became curious about the possibility that a lower-lying ¹A in [Fe(dftpy)₂]²⁺ might alter that pathway, perhaps enabling a reverse-LIESST effect³ and creating a long-lived transient singlet population. In summary the work herein considers optical, crystallographic, and magnetic data, in order to explore how halogen size impacts ⁵,⁷MLCT lifetimes as well as spin crossover.
4.2. [Fe(dbtpy)]^{2+} Electronic Absorption

The UV-Vis absorption spectrum of [Fe(dbtpy)]^{2+} is displayed in Figure 4.2, where the features closely match those of [Fe(dctpy)]^{2+} discussed in the previous chapter and elsewhere.\(^4\)

**Figure 4.2.** UV-vis absorption spectra in room-temperature acetonitrile for [Fe(dftpy)]^{2+}, [Fe(dctpy)]^{2+}, and [Fe(dbtpy)]^{2+} with inset to highlight redder transitions.

For both molecules, there are two transitions appearing at ~ 220 nm and ~ 295 nm that are also observed in the free ligand spectra. These are assumed to be ligand-based \(\pi^* \leftrightarrow \pi\) in nature. Moving to the red, intense transitions are observed at ~ 350 nm, that by contrast are absent in the free ligand spectra. On the basis of this observation as well as TD-DFT explorations of [Fe(dctpy)]^{2+}, observations concerning the model complex [Zn(dctpy)]^{2+}, and spectroelectrochemical data for [Fe(dctpy)]^{2+}, the feature in [Fe(dbtpy)]^{2+} is assigned as being a ligand-based transition with ligand-to-ligand charge transfer (LLCT) being the most likely.\(^4\)

From our perspective, the most important feature that is observed in the [Fe(dbtpy)]^{2+} spectrum is a long tail that extends from 400-500 nm. In Chapter 3, it was argued that a similar feature in the [Fe(dctpy)]^{2+} spectrum is evidence for a \(^5\)MLCT \(\leftrightarrow\) \(^5\)GS transition. There, the transition is blue-shifted and less absorptive relative to the parent [Fe(tpy)]^{2+} (562 nm, 12,000 M\(^{-1}\)cm\(^{-1}\)).\(^5\)

65
This is consistent with the assignment of $^5\text{MLCT}$ in the halogen-substituted molecule where longer Fe-N bond lengths reduce metal-ligand orbital overlap and raise the energy of the charge transfer state by Coulombic arguments. Given that the larger size of the bromine substituents in $[\text{Fe(dbtpy)}_{2}]^{2+}$ will only serve to increase interligand repulsions compared to $[\text{Fe(dctpy)}_{2}]^{2+}$, we readily make the same spectral assignment for this new molecule.

Data from other experiments are consistent with the assignment of a high-spin ground state in $[\text{Fe(dbtpy)}_{2}]^{2+}$. From Evans’ measurements, a magnetic susceptibility value of $\chi_M T = 3.3 \text{ cm}^3 \text{ K mol}^{-1} (\mu_{\text{eff}} = 5.1)$ is obtained, which is a typical value for a high-spin Fe(II) complex with four unpaired electrons, and it is consistent with our previous measurement of $\mu_{\text{eff}} = 5.3$ in $[\text{Fe(dctpy)}_{2}]^{2+}$. Further evidence of a pure high-spin state is found in the $^1\text{H}$ spectrum of $[\text{Fe(dbtpy)}_{2}]^{2+}$, which contains paramagnetically shifted peaks between 80 and -30 ppm and no evidence of low-spin aromatic hydrogen resonances (See Chapter 2 for $^1\text{H}$ NMR chemical shift data).

4.3. Structural Data for $[\text{Fe(dbtpy)}_{2}]^{2+}$

X-ray diffraction data was collected on a single crystal of $[\text{Fe(dbtpy)}_{2}]^{2+}$ at 100 K. The resulting structural model displays a geometry consistent with a quintet ground state, while at the same time highlighting the steric strain that encourages the electronic configuration of four unpaired electrons in metal-centered orbitals, two of which are antibonding in nature. This latter point about steric strain is highlighted in Figure 4.3, which presents thermal ellipsoid plots for $[\text{Fe(dbtpy)}_{2}]^{2+}$ from two different points of view.
Figure 4.3. Crystal structure of the Fe-containing complex in [Fe(dbtpy)$_2$](BF$_4$)$_2$ shown from two distinct points of view with thermal ellipsoids rendered at 50% probability. C = gray, Br = red, Fe = orange, N = blue. Hydrogen atoms have been removed for clarity.

Viewed along the axis containing the central Fe-N bonds (left-hand image), the distortion of the terpyridine planes is immediately noticeable. The vertical dbtpy ligand is twisted about the two inter-ring C-C bonds, so that the two chlorine atoms are pointing towards opposite sides of the central pyridyl group with the C-Br bonds at a pseudo-dihedral angle of 27.8°. A similar effect is seen in the horizontal dctpy ligand but is less pronounced at only 8.2°. The overall twisting distortion is likely occurring because of repulsion between the bromine atoms and the π-system of the central pyridine on the opposing ligand, especially the more electronegative nitrogen atom. This steric interaction is undoubtedly critical in the determination of the ground spin state in [Fe(dbtpy)$_2$]$^{2+}$. To limit its energy-raising effect, the complex adopts an electronic configuration where Fe–N bonds are elongated and where the terpyridine N$_{\text{terminal}}$-N$_{\text{central}}$-N$_{\text{terminal}}$ (N-N-N) angle is consequentially increased, thus serving to extend the distance of the halogen from the π-system of the second ligand relative to what is seen in low-spin analogues such as [Fe(tpy)$_2$]$^{2+}$. In [Fe(dbtpy)$_2$]$^{2+}$, the Fe-N$_{\text{central}}$ bond elongates to 2.074(2) Å compared to a typical low-spin value of ~1.9 Å (Table 4.1). Overall, there is a substantial deviation from a true octahedral coordination geometry as evidenced by the average N$_{\text{terminal}}$-Fe-N$_{\text{central}}$ bond angle of ~75° in the halogenated complexes, even smaller than the ~81° seen in [Fe(tpy)$_2$]$^{2+}$.6
Table 4.1. X-Ray Structural Data for [Fe(dctpy)₂]²⁺ and [Fe(dbtpy)₂]²⁺—Selected Parameters

<table>
<thead>
<tr>
<th>complex</th>
<th>Fe-N_central (Å)</th>
<th>Fe-N_terminal (Å)</th>
<th>∠N-N-N (°)</th>
<th>Θ (°)</th>
<th>X-pyridyl (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(tpy)₂]²⁺</td>
<td>1.890(4)</td>
<td>1.988(3)</td>
<td>102.8(2)</td>
<td>1.5(3)</td>
<td>N/A</td>
</tr>
<tr>
<td>[Fe(dctpy)₂]²⁺</td>
<td>2.080(2)</td>
<td>2.272(1)</td>
<td>111.4(1)</td>
<td>4.1(1)</td>
<td>3.074(1)</td>
</tr>
<tr>
<td>[Fe(dbtpy)₂]²⁺</td>
<td>2.074(2)</td>
<td>2.304(2)</td>
<td>112.65(8)</td>
<td>11.65(8)</td>
<td>3.179(2)</td>
</tr>
</tbody>
</table>

*Structural data from reference.† Data taken at 295 K for [Fe(tpy)₂]²⁺, 120 K for [Fe(dctpy)₂]²⁺ and 100 K for [Fe(dbtpy)₂]²⁺. See Chapter 2 for additional details.

Despite the Fe–N elongation, the [Fe(dbtpy)₂]²⁺ structure shows short distances between the halogen substituent and the central pyridyl ring of the opposing ligand. The values are tabulated in Table 4.1 (X-pyridyl) and are ~0.35 Å shorter than the sum of the Bondi radii of the halogen and carbon for both [Fe(dbtpy)₂]²⁺ and [Fe(dctpy)₂]²⁺. The fact that these distances are still short despite the significant geometric distortions described above underscores the unfavorable steric interactions that would persist in a low-spin complex. A final tabulated metric for these complexes is the so-called “rocking angle” Θ, which represents the angular deviation from 180° for N_central-Fe-N_central. We note this quantity by way of connecting to work by Jakubikova and coworkers who have shown that the quintet state of [Fe(tpy)₂]²⁺ exhibits a substantial (10°) value for Θ and a soft potential in this rocking direction whereas the singlet ground state is locked into a linear arrangement. In [Fe(dbtpy)₂]²⁺ we observe a substantial rocking angle, 11.65(8)°, close to the value determined by Jakubikova et al. for the ⁵MC in [Fe(tpy)₂]²⁺, but much less than the 20.9° they determined for the same compound.

4.4. [Fe(dftpy)₂]²⁺ Electronic Absorption

The absorption spectrum of [Fe(dftpy)₂]²⁺ shown in Figure 4.2 exhibits marked differences from those belonging to [Fe(dctpy)₂]²⁺ and [Fe(dbtpy)₂]²⁺. We first note the higher energy peaks at 288 nm and 332 nm. These mirror features seen in the bromine and chlorine-substituted complexes, but exhibit a blue shift of ~ 10 nm. Given their respective assignments as
$\pi^* \rightarrow \pi$ and LLCT in nature, we anticipate energy shifts in ligand-centered occupied and unoccupied orbitals.

To gain insight into this blue shift, we have considered zinc(II) complexes within the halogen series using density functional theory (DFT). This d$^{10}$ metal was chosen because the metal-centered orbitals of the complexes are stabilized (and filled) such that HOMO and LUMO orbitals are ligand $\pi$ and $\pi^*$ in nature. These ground state calculations therefore afford a cursory view into the origins of energy shifts in bands assigned to LLCT. Calculated energies of the HOMO and LUMO for [Zn(dftpy)$_2$]$^{2+}$, [Zn(dctpy)$_2$]$^{2+}$, and Zn(dbtpy)$_2$]$^{2+}$ show that fluorine substitution serves to stabilize the HOMO while destabilizing the LUMO. This suggests that this complex would be more difficult to oxidize as well as more difficult to reduce compared to its chlorine- and bromine-containing analogues. These orbital energy trends are also observed in mono-substituted halogenated benzenes$^{11}$ and halogenated pyridines. Overall, it appears that stabilization of occupied $\pi$ orbitals has its origin in the increased electronegativity of the F substituent, relative to Cl or Br, which acts through an inductive effect. On the other hand, the fluorine substituent is more effective at destabilizing the LUMO through $\pi$-donation than the larger halogen atoms.$^{12}$ It is noted that HOMO and LUMO orbital energy trends are consistent across the full series of Zn(II) complexes although the perturbations are significantly more subtle in going from Cl to Br then they are upon going from F to Cl.

We next note an even more dramatic spectroscopic change that was first encountered by visual inspection of acetonitrile solutions of [Fe(dftpy)$_2$]$^{2+}$, which have a much redder appearance than the other halogenated complexes (orange-yellow solutions). UV-Vis absorption spectroscopy reveals the emergence of a new prominent transition at 506 nm for the fluorinated
complex, with a molar absorptivity on the order of $10^3 \text{M}^{-1}\text{cm}^{-1}$ (Figure 4.2, inset). This absorptivity is too high to be assigned to a metal-centered d-d transition.

Given the smaller size of the fluorine substituents in $[\text{Fe(dftp}_{2}])^{2+}$ and therefore the potential for increased metal-ligand interactions, we suspected that at room temperature there would be partial population of a singlet ground state and a concomitant $^1\text{MLCT} \leftarrow ^1\text{GS}$ transition. To test this further, we collected UV-Vis absorption spectra as a function of temperature over the range 277 K – 334 K and find the expected result that the visible absorption feature that is peaked at 506 nm increases in intensity as the sample is cooled (Figure 4.4). This temperature dependence heralds an equilibrium between high- and low-spin populations, where the singlet state is favored enthalpically and where the quintet increases in prominence as temperature increases due to entropic contributions to the Gibbs free energy. This same effect on UV-Vis absorption has been observed in Fe(II) bis-4,6-diphenylterpyridine, where temperature-dependence is attributed to spin crossover (SCO).\textsuperscript{13}

\textbf{Figure 4.4.} UV-visible absorption spectra of a solution of $[\text{Fe(dftp}_{2}])^{2+}$ in acetonitrile at temperatures between 277-334 K.
4.5. SQUID Magnetometry

In order to investigate the thermodynamic parameters of the spin-crossover equilibrium, we performed magnetic measurements over a wide temperature range. Magnetic susceptibility data for flash-frozen acetonitrile solutions of [Fe(dftpy)2](BF4)2 and [Fe(dctpy)2](BF4)2, collected via SQUID magnetometry, are shown in Figure 4.5. The chlorine-containing compound [Fe(dctpy)2](BF4)2 displays a $\chi_M T$ value of 3.30 cm$^3$ K mol$^{-1}$ at 315 K, in agreement with the expected spin only value for a non-interacting high-spin Fe(II) species (3.00 cm$^3$ K mol$^{-1}$ for $g = 2$). Upon cooling, the $\chi_M T$ product decreases gradually until ~225 K, at which point a discontinuity in $\chi_M T$ coincides with the melting point of the acetonitrile solvent. Between 200 K and 18 K, the monotonic decrease in $\chi_M T$ may be interpreted as temperature independent paramagnetism (TIP) or possibly (weak) antiferromagnetic coupling between high-spin Fe(II) complexes. The sharper decrease observed below 18 K is likely due to magnetic anisotropy of any remaining high-spin Fe(II) fraction.$^{14}$

![Figure 4.5](image-url)

**Figure 4.5.** Temperature dependence of magnetic susceptibility data collected at 1000 Oe for [Fe(dftpy)2](BF4)2 (red circles, warming and blue circles, cooling) and [Fe(dctpy)2](BF4)2 (green squares) in the presence of acetonitrile. The cyan line corresponds to the best fit of the data which gives parameters of: $g_{HS} = 2.11$, $g_{LS} = 2.00$, $\theta_{HS} = + 2.18$ K, $\theta_{LS} = - 0.001$ K, TIP$_{HS} = 3.0 \times 10^{-3}$ cm$^3$ mol$^{-1}$, TIP$_{LS} = 3.4 \times 10^{-3}$ cm$^3$ mol$^{-1}$ and $\Delta H_{SCO} = 24.5$ kJ/mol assuming $T_{1/2} = 220$ K.
Interestingly, and in alignment with our expectations considering the electronic absorption measurements, [Fe(dftpy)₂](BF₄)₂ shows quite different temperature-dependent magnetic susceptibility behavior. At 315 K, the complex exhibits a $\chi M T$ value of 3.13 cm$^3$ K mol$^{-1}$, also in agreement with other non-interacting high-spin Fe(II) complexes. Upon cooling, however, the $\chi M T$ product decreases, first gradually, then more sharply until ~190 K ($\chi M T = 0.87$ cm$^3$ K mol$^{-1}$) where the change in susceptibility slows. The large change in the $\chi M T$ value between 300 K and 190 K is attributed to a non-hysteretic spin crossover (SCO) event wherein the system converts from $S = 2$ at high temperatures to $S = 0$ at low temperatures. Discontinuities observed in the $\chi M T$ product in the temperature range 200 – 225 K are similar to those observed for the chloride analogue, and perhaps relate to the freezing/thawing of acetonitrile. The non-zero $\chi M T$ values below 190 K show a similar temperature dependence as [Fe(dctpy)₂](BF₄)₂. If this is attributed entirely to TIP, then the admixture of excited states is very large ($\chi_{\text{TIP}} \approx 3.4 \times 10^{-3}$ cm$^3$ mol$^{-1}$). We note that large TIP has been reported in systems where other excited spin-states are accessible,¹⁵–¹⁷ and is evident in frozen solution for Fe(II) triazacyclononane complexes.¹⁸

As depicted in Figure 4.5, this SCO event can be fit to an ideal solution model.¹⁹,²⁰ Assuming a single spin-crossover event ($S = 0 \rightarrow S = 2$) and no cooperativity, the model provides $T_{1/2} = 220$ K and thermodynamic parameters $\Delta H_{\text{SCO}} = 24.5$ kJ mol$^{-1}$ and $\Delta S_{\text{SCO}} = 111$ J K$^{-1}$mol$^{-1}$ (calculated using $\Delta S_{\text{SCO}} = \Delta H_{\text{SCO}}/T_{1/2}$). These thermodynamic parameters are at the higher end of the range reported for Fe(II) SCO complexes, but similar to values measured in pyridine-toluene solutions for salen-type [LFe$^\text{II}$] complexes which bear a N₄O₂ coordination geometry.²¹ The large $\Delta S_{\text{SCO}}$ value suggests a significant entropic benefit due to populating the high-spin state.
The large TIP values and $\chi_M T$ discontinuities in the SCO regime prompted us to perform solid state magnetic measurements on [Fe(dftpy)$_2$](BF$_4$)$_2$. From these measurements, we can conclude that a full SCO event is possible in the solid state ($T_{1/2} \sim 160$ K), and uncommonly large TIP is not observed. However, these data also show a complicated two-step transition in the temperature regime 175-250 K, overlapping with the “solution” data described above. The origins of this behavior are unclear and additional studies are necessary to uncover the origin of the odd solid-state behavior.

4.6. Deconvolving the Temperature-Dependent Absorption

Based on the thermodynamic parameters extracted from SQUID, we can return to the temperature dependent UV-Vis absorption data for [Fe(dftpy)$_2$]$^{2+}$ that were introduced earlier (Figure 4.4). In order to determine molar extinction ($\varepsilon$) values for the high- and low-spin states, we have globally modeled the absorbance of the sample as a function of temperature, $T$, and wavelength, $\lambda$, with a modified Beer’s law shown in Equation 4.1:

$$\text{Absorbance}(T, \lambda) = \ell \cdot c_{\text{total}} \cdot (\gamma_{HS}(T) \cdot \varepsilon_{HS}(\lambda) + (1 - \gamma_{HS}(T)) \cdot \varepsilon_{LS}(\lambda))$$  \hspace{1cm} \text{Equation 4.1}

where $c_{\text{total}}$ is the concentration of all [Fe(dftpy)$_2$]$^{2+}$ species (both high and low spin) and $\gamma_{HS}$ is the mole fraction of the high-spin state. The quantity $\gamma_{HS}$ can be expressed in terms of the equilibrium constant for low-to-high spin conversion, which in turn can be expressed in terms of $\Delta H$ and $\Delta S$ for this process$^{57}$, leading to Equation 4.2:

$$\frac{\exp \left( \frac{\Delta H}{RT} - \frac{\Delta S}{R} \right)}{\exp \left( \frac{\Delta H}{RT} - \frac{\Delta S}{R} \right) + 1} = \gamma_{HS}(T)$$  \hspace{1cm} \text{Equation 4.2}
Using the $\Delta H$ and $\Delta S$ values extracted from SQUID measurements, a global analysis of the temperature-dependent absorption data (Figure 4.4; between 277 K and 334 K) shows that two basis spectra cleanly reproduce the observed behavior which are shown in Figure 4.6.

**Figure 4.6.** Molar absorptivities of the high-spin and low-spin states of [Fe(dftpy)$_2$]$^{2+}$ in acetonitrile determined from global analysis of the temperature-dependent UV-vis data (Figure 4.4). Also shown for comparison is the measured molar absorptivity of [Fe(tpy)$_2$]$^{2+}$ in room-temperature acetonitrile.

Discussing first the low-spin basis spectrum, we note that the shape bears a remarkable similarity to that of the low-spin parent [Fe(tpy)$_2$]$^{2+}$, although it is blue-shifted by ~50 nm. Care must be taken assessing this shift using electrochemical data given that both oxidation and reduction events in [Fe(dftpy)$_2$]$^{2+}$ are positively shifted by similar amounts (0.32 V and 0.35 V, respectively) relative to corresponding potentials measured for the parent [Fe(tpy)$_2$]$^{2+}$ (Table 4.3). This leads to comparable values of $\Delta E_{1/2}$, a quantity that is generally considered to be a useful proportional indicator of MLCT energy.$^{22}$ However, as we have noted previously for [Fe(dctpy)$_2$]$^{2+}$, the quantity $\Delta E_{1/2}$ is expected to underestimate the MLCT values when there is significant high-spin character in the sample as is the case for [Fe(dftpy)$_2$]$^{2+}$ at room temperature.
(97 %) because of a suppression of the 3+/2+ couple due to the orbital origins of the oxidation event: nominally $e_g^*$ in high-spin systems rather than $t_{2g}$ expected for low-spin complexes. With this in mind, we can understand the blue shift of the MLCT in low-spin populations of $[\text{Fe(dfpy)}_2]^{2+}$ versus $[\text{Fe(tpy)}_2]^{2+}$ as being driven by the orbital origins of the electronic transition. In addition to having $\pi$-donor character, the fluorine substituents are $\sigma$-withdrawing. This reduces electron density at the metal center and in turn makes the formal oxidation of the metal center that accompanies MLCT more positive.

The high-spin basis spectrum for $[\text{Fe(dfpy)}_2]^{2+}$ is shown in Figure 4.7 along with molar absorptivities measured for the larger members of the halogen series $[\text{Fe(dctpy)}_2]^{2+}$ and $[\text{Fe(dbtpy)}_2]^{2+}$. These data highlight a trend of increasing absorptivity for the broad shoulder (~500 nm) on going from a bromine substituent to a chlorine and finally to fluorine. We can rationalize this in terms of how halogen size impacts metal ligand distances across the series (in particular Fe-N_{terminal}), which then affects $^5\text{MLCT} \leftarrow ^5\text{GS}$ intensity through orbital overlap (see Tables 4.1 and 4.2). The broadness of the shoulder precludes determination of $^5\text{MLCT}$ energies and whether there is any systematic variation. However, the similarity of band shapes does suggest that $^5\text{MLCT}$ energy shifts within the series must be subtle.
Figure 4.7. Measured molar absorptivities of [Fe(dctpy)]$_2^{2+}$ and [Fe(dbtpy)]$_2^{2+}$ in room-temperature acetonitrile and the calculated molar absorptivities of the high-spin state of [Fe(dftpy)]$_2^{2+}$ from global fitting of temperature dependent spectra in acetonitrile.

4.7. Structural Data for [Fe(dftpy)]$_2$(BF$_4$)$_2$

As a final exploration of SCO in [Fe(dftpy)]$_2^{2+}$, we have directly explored structural changes that accompany temperature variation using X-ray diffraction. Two data sets were collected for a single crystal at two different temperatures: 120 K and 300 K. The higher temperature data set was collected first, followed by slow cooling (60 K/hour) to 120 K for collection of the second data set. In previous experimental attempts that reversed this order (first data collection at low temperature followed by raising the temperature) we observed crystal fracturing upon warming. Accompanying the temperature change was a significant color change from light red to a deep purple, consistent with the solution-phase temperature-dependent absorption spectra seen in Figure 4.4. In addition to the color change, we observed a change in the geometric parameters of the unit cell. As can be seen in Chapter 2, while the space group
remains as $P2_1/c$ at both temperatures, there is a volume decrease from 3425.9(5) to 3212.2(5) Å$^3$ upon cooling the crystal driven by a contraction from 10.9455(9) to 10.1127(9) Å along one axis.

**Table 4.2.** Temperature-Dependent Structural Data for [Fe(dftpy)$_2$](BF$_4$)$_2$

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Fe-N$_{central}$ (Å)</th>
<th>Fe-N$_{terminal}$ (Å)</th>
<th>$\angle$ N-N-N (°)</th>
<th>$\Theta$ (°)</th>
<th>X-pyridyl (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>1.904(2)</td>
<td>2.027(1)</td>
<td>103.86(8)</td>
<td>1.1(1)</td>
<td>2.680(2)</td>
</tr>
<tr>
<td>300</td>
<td>2.116(1)</td>
<td>2.206(1)</td>
<td>108.80(7)</td>
<td>3.89(9)</td>
<td>2.848(2)</td>
</tr>
</tbody>
</table>

Superimposed ball and stick plots for [Fe(dftpy)$_2$]$^{2+}$ at both temperatures are shown in Figure 4.8 to highlight structural differences. While the viewpoint focuses on a single dftpy ligand and its metal coordination environment, comparable changes are evident for the second ligand. Immediately noticeable are the elongation of the three Fe–N bonds and the increase in the N-N-N angle as the temperature is changed from 120 K to 300 K. These are, of course, hallmarks of a low-spin to high-spin transition. Examining the structures quantitatively (Table 4.2), we see that upon conversion to the high-spin structure, Fe-N$_{central}$ increases by 0.212(2) Å while Fe-N$_{terminal}$ increases by 0.179(1) Å, consistent with a weakening of the ligand field and population of metal-ligand antibonding orbitals. This weakening of the metal-ligand bonds allows the N-N-N angle to relax into a more obtuse conformation by 4.94(5)°. The combination of these two motions allows the fluorine atoms to shift 0.168(1) Å farther from the central pyridine on the other ligand, yet in both configurations, this distance is smaller than the sum of the Bondi radii of the two species (3.17 Å for C and F).
Figure 4.8. Overlaid crystal structures of the Fe-containing complex in [Fe(dftpy)₂][BF₄]₂ collected at 300 K and 120 K (semi-transparent). Both structures are plotted as ball-and-stick models due to the thermal ellipsoid differences at the two temperatures. C = gray, F = purple, Fe = orange, N = blue, H = white.

4.8. Cyclic Voltammetry

Potentials for the first oxidation and reduction events for the three halogenated complexes and the parent, [Fe(tpy)₂]²⁺, are collected in Table 4.3. All of the halogenated complexes were found to be harder to oxidize, but easier to reduce. The addition of highly electronegative groups to the ligands should generally lower the orbital energies on the ligand including the LUMO. However, beyond simply adding an electronegative substituent, the halogenated complexes are now high-spin where there are significant geometric distortions. Since the ligand-based LUMO can mix with the metal t₂g set allowing for π-backbonding, we would predict a reduction in backbonding to ease ligand reduction. We expect the extent of backbonding to be determined largely by the Fe-N bond distances and the extent of deviation from truly octahedral coordination. The potentials generally track with the Fe-Nterminal bond distances and N-N-N angles, which we can use as geometric indicators for the amount of octahedral distortion and
diminished π-backbonding (Tables 4.1 and 4.2). While, the Fe-N_{central} bond distances do not track as well, they can be misleading when looked at in isolation due to the extensive contortions that these complexes undergo to limit steric interactions and a holistic view is required.

### Table 4.3. Cyclic Voltammetry Data for Halogenated Complexes in MeCN versus SCE

<table>
<thead>
<tr>
<th>complex</th>
<th>( E_{1/2}^{3+/2+} ) (V)</th>
<th>( E_{1/2}^{2+/1+} ) (V)</th>
<th>( \Delta E_{1/2} ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe(tpy)}_2]^{2+})</td>
<td>1.10</td>
<td>-1.26</td>
<td>2.36</td>
</tr>
<tr>
<td>([\text{Fe(dftpyp)}_2]^{3+})</td>
<td>1.42</td>
<td>-0.91</td>
<td>2.33</td>
</tr>
<tr>
<td>([\text{Fe(dctpy)}_2]^{2+})</td>
<td>1.60</td>
<td>-0.83</td>
<td>2.43</td>
</tr>
<tr>
<td>([\text{Fe(dbtpy)}_2]^{2+})</td>
<td>1.62</td>
<td>-0.81</td>
<td>2.43</td>
</tr>
</tbody>
</table>

\( E_{1/2} \) potentials measured versus \( \text{Fe}^{3+} / \text{Fe}^{2+} \) with 0.38 V added to obtain values vs. SCE. \(^{23}\) Cyclic voltammetry conditions: 0.1 M tetrabutylammonium hexafluorophosphate electrolyte; Pt disc working electrode; Pt wire counter electrode; Ag/AgNO\(_3\) reference electrode with 0.01 M AgNO\(_3\); 100 mV/s scan rate; error = ± 0.02 V. \(^{2} \Delta E_{1/2} = E(3+/2+) - E(2+/1+).\)

On the oxidative side, we see that changes in the Fe\(^{3+/2+}\) couple follow a similar trend to those of the reduction potentials in that they become more positive with larger halogens. This is also largely influenced by the geometric changes in these complexes. However, as opposed to π-backbonding, we expect σ-bonding to have a greater effect on the metal center. In this case the geometric alterations increase Fe-N distances, leading to less sigma donation from the ligand into the metal center. With less negative charge being donated into the metal center, it is expected to be more difficult to oxidize as observed in the cyclic voltammetry results.

### 4.9. Excited-State Dynamics

Having established an understanding of ground-state electronic properties within this series of Fe(II) complexes using UV-Vis spectroscopy, magnetic susceptibility measurements, and single crystal x-ray diffraction, we turn to time-resolved absorption spectroscopies to characterize excited-state dynamics including ground-state recovery. Our starting point is the complex with the largest halogen in the series, \([\text{Fe(dbtpy)}_2]^{2+}\) with a purely quintet ground state.
similar to [Fe(dctpy)$_2$]$^{2+}$, which was discussed in detail in Chapter 3. TA spectra resolved on a picosecond time scale are shown in Figure 4.9 following excitation with laser pulses centered at 400 nm and with a duration of ~ 150 fs. This excitation wavelength accesses a broad tail in the absorption spectrum (Figure 4.2) that is expected to be associated with $^5$MLCT $\leftarrow$ $^5$GS excitation. As may be seen in Figure 4.9, there are two main features: a bright, sharply-peaked UV absorption (in the vicinity of 370 nm) and a weaker, significantly broader visible absorption. There is evidence for subtle spectral shifting in the UV feature at early times (< 4 ps; vide infra), but the dominant character of the data is decay of both UV and visible features to baseline on a 10s of picoseconds time scale.
Figure 4.9. TA spectroscopy of [Fe(dbtpy)]$^{2+}$ in room temperature acetonitrile following 400 nm excitation. Top: full 2D surface plot of data. Bottom: selected spectra (pump scatter is not shown; data are interpolated between 392 nm and 405 nm).

We emphasize that all spectral and temporal features bear a close resemblance to what has been previously reported for the chlorinated analogue [Fe(dctp)$_2$]$^{2+}$ in Chapter 3. Computational and spectroelectrochemical experiments on [Fe(dctp)$_2$]$^{2+}$, we concluded that the UV and visible TA features have redox origins and can be attributed to the formally reduced ligand and oxidized metal center of a high-spin $^{5,7}$MLCT state. The thermalization of this state is the origin of the early-time spectral shifting and the decay of this state on a longer time scale
heralds recovery of the high-spin ground state with no evidence for population of an intermediate. Given the high degree of similarity between the data collected and shown for [Fe(dbtpy)₂]^{2+} (Figure 4.9) and the data previously presented for [Fe(dctpy)₂]^{2+}, we are confident in drawing the same mechanistic conclusion. Details about the kinetic analysis will be presented below, after introducing TA results for [Fe(dftpy)₂]^{2+}.

TA spectral data for [Fe(dftpy)₂]^{2+} collected with similar experimental conditions are shown in Figure 4.10 and exhibit markedly different behavior than what is seen for [Fe(dbtpy)₂]^{2+} or [Fe(dctpy)₂]^{2+}. Most notable is a long-lived bleach feature centered at 504 nm that is invariant over the 50 ps timescale of the experiment and whose shape closely matches calculated low-spin spectrum of [Fe(dftpy)₂]^{2+} (Figure 4.6). These observations are consistent with TA studies of low spin Fe(II) polypyridyl systems where evolution from the ¹MLCT to ⁵MC is ultrafast. At the same time, however, there are UV and visible features flanking the bleach, whose kinetic behavior and shape bear strong resemblance to features attributed to the ⁵,⁷MLCT in [Fe(dbtpy)₂]^{2+} and [Fe(dctpy)₂]^{2+} within similar spectral regions. Given our findings (vide supra) that room temperature samples of [Fe(dftpy)₂]^{2+} consist of a 3:97 admixture of low- and high-spin states, it appears clear that 400 nm pulses excite both states. In another Fe(II) spin crossover system [Fe(2-Me-phen)₃]^{2+}, Gallé et al. selectively excited the low- or high-spin MLCT state using a blue or near-UV pump, respectively. They proposed a bifurcating kinetic model following excitation into the ⁵MLCT that results in sub-picosecond formation of low energy ¹A and ⁵T states, with the transient population of the singlet persisting for several nanoseconds. We are able to rule out such a mechanism in high-spin excitation of [Fe(dftpy)₂]^{2+} due to our observation of the near-UV feature that matches what is seen in [Fe(dctpy)₂]^{2+} and [Fe(dbtpy)₂]^{2+}, which is indicative of an MLCT state. Further, there is no
evidence of early decay of the $^1$MLCT $\rightarrow ^1A$ bleach as would be expected if $^5$MLCT excitation was followed by transient population of the singlet state. Despite this result, low-temperature TA measurements would be needed to assess the potential for reverse-LIESST$^3$ using this molecule.

Figure 4.10. TA spectroscopy of [Fe(dftpy)$_2$]$^{2+}$ in acetonitrile at room temperature following 400 nm excitation. Top: full 2D surface plot of data. Bottom: selected spectra (pump scatter is not shown; data are interpolated between 397 nm and 403 nm).

Attempting a similar selective excitation experiment of our own, we shifted the pump wavelength in our TA spectrometer to 515 nm. At this wavelength, the molar extinction of the low spin state in [Fe(dftpy)$_2$]$^{2+}$ is 35 times larger than that of the high-spin state at room
temperature. Four transient spectra are shown in Figure 4.11 collected at times ranging from 6 ps – 730 ps. Again the same bleach feature mentioned above is seen peaked at 504 nm, but it is now the dominant feature and any component due to excitation in the high-spin manifold is within the noise in less than 6 ps. In addition to the bleach of the $^1$MLCT $\leftarrow$ $^1$A absorption, there is a small excited state absorption in the near-UV. We attribute this to increased LLCT in this spectral region due to the transient increase in the $^5$MC population.

![Figure 4.11](image)

**Figure 4.11.** TA spectra of [Fe(dftpy)$_2$]$^{2+}$ in room-temperature acetonitrile following 515 nm excitation.

To determine the lifetime of the bleach feature, we utilized a nanosecond transient absorption experiment. At room temperature, the lifetime is 22 ns, which represents a substantial elongation compared to the reported value of 5.35 ns for [Fe(tpy)$_2$]$^{2+}$ under comparable conditions.$^{28}$ The increased lifetime is likely the result of two contributing factors. First, interligand steric interactions exacerbated by the halogen substituents in [Fe(dftpy)$_2$]$^{2+}$ may be expected to increase the reorganization energy in going from a geometry relevant for the $^5$MC to
one relevant for the $^1A$, resulting in a larger barrier. Second, the $^5MC/^1A$ inter-conversion driving force is reduced (the origin of the near room temperature spin crossover behavior) and this would lead to an increased activation barrier even under circumstances where the reorganization energy is comparable. A full temperature-dependent data set and Arrhenius analysis for $[\text{Fe(dctpy)}_2]^{2+}$ is given elsewhere.$^{29}$

Finally, we address the kinetic behavior of the full halogen series and ask whether trends emerge as the ligand substituent is varied. Within the series, the two largest species $[\text{Fe(dctpy)}_2]^{2+}$ and $[\text{Fe(dbtppy)}_2]^{2+}$ are again the simplest to analyze. As was discussed in our previous work, the transient spectral data for $[\text{Fe(dctpy)}_2]^{2+}$ (362 nm – 610 nm) for $\Delta t = 1$ ps and beyond may be cleanly reproduced using a global kinetic model inclusive of two exponential components with time constants $\tau_1 = 3.6$ ps and $\tau_2 = 16.0$ ps. The same is true for $[\text{Fe(dbtppy)}_2]^{2+}$ leading to a determination of $\tau_1 = 3.7$ ps and $\tau_2 = 17.4$ ps. The transient spectral data for $[\text{Fe(dftpy)}_2]^{2+}$ may be similarly modeled with the caveat that the 400 nm laser excitation also accesses some of the singlet ground state population in this spin crossover system. This simply means that the kinetic expression necessary to globally model the data is inclusive of a third exponential component whose decay is fixed to the 22 ns that were measured for the compound at room temperature using the 515 nm excitation. With this in place, $\tau_1$ and $\tau_2$ are measured for $[\text{Fe(dftpy)}_2]^{2+}$ at 3.2 ps and 14.0 ps, respectively. All the measured time constants are shown in Table 4.4 with values and reported error based on three independent sets of data collected for each species in the halogen series.
Table 4.4. Global Fit Lifetimes Collected in Room-Temperature Acetonitrile

<table>
<thead>
<tr>
<th>complex</th>
<th>$\tau_1$ / ps (2$\sigma$)$^a$</th>
<th>$\tau_2$ / ps (2$\sigma$)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(dftpy)$_2$]$^{2+}$</td>
<td>3.2 (1.0)</td>
<td>14.0 (1.5)</td>
</tr>
<tr>
<td>[Fe(dctpy)$_2$]$^{2+}$</td>
<td>3.6 (0.6)</td>
<td>16.0 (1.0)</td>
</tr>
<tr>
<td>[Fe(dbtpy)$_2$]$^{2+}$</td>
<td>3.7 (1.0)</td>
<td>17.4 (2.0)</td>
</tr>
</tbody>
</table>

$^a$Average tau values and standard deviations calculated from the independent data sets based on a global fit of the full spectral range beginning 1 ps after excitation.

As previously discussed, the faster time component ($\tau_1$) in these molecules reflects thermalization within the $5,7$MLCT while the slower component ($\tau_2$) reflects the state’s lifetime prior to decay to the high-spin ground state. These conclusions are supported using $\tau_1$ and $\tau_2$ basis spectra generated from the respective global fits, focusing on features in the near-UV. the $\tau_2$ spectrum for each molecule in the series points to the excited state absorption of the thermalized $5,7$MLCT state corresponding to $\pi^* \leftarrow \pi^*$ of the ligand-based radical anion as is seen in other $d^6$ terpyridyl and bipyridyl MLCT complexes.\textsuperscript{30-32}

The $\tau_1$ basis spectrum for each species resembles the derivative of the sharp UV-fetature in the respective $\tau_2$ spectrum. This has the effect of blue-shifting and narrowing the band in the first few ps following excitation. Similar observations were made for the early evolution of [Fe(CN)$_4$(bpy)]$^{2-}$ and [Os(bpy)$_3$]$^{2+}$ and attributed to vibrational redistribution and cooling.\textsuperscript{30,33}

There is some evidence in Table 4.3 for a systematic trend in cooling within our halogen series, where the largest member [Fe(dbtpy)$_2$]$^{2+}$ is slowest and where the smallest member [Fe(dftpy)$_2$]$^{2+}$ is fastest. This halogen-series cooling trend could be explained if final dissipation of vibrational energy occurs along low-frequency modes such as metal-ligand bond stretching coordinates and/or ligand distortions and where the weakest metal-ligand bond of the series (in [Fe(dbtpy)$_2$]$^{2+}$) and/or the lowest-frequency distortion (in dftp) is more poorly coupled to the
solvent bath. However, the series effect is small and a more detailed analysis would be needed to characterize the effect.

Finally, we can use the derivative shape of the $\tau_1$ basis spectra within the halogen series (in particular their zero-valued-crossing) to determine the wavelength at which it is possible to isolate $\tau_2$ dynamics corresponding to $5,7$MLCT loss and high-spin ground state recovery. In Figure 4.12 we plot on a log scale the normalized $\Delta A$ decay for each molecule isolated from the corresponding 2D data sets at 369 nm for $[Fe(dbtpy)_2]^{2+}$, at 366 nm for $[Fe(dcpty)_2]^{2+}$, and at 356 nm for $[Fe(dftpy)_2]^{2+}$.

![Figure 4.12.](image)

**Figure 4.12.** Single-exponential fit at the peak wavelength of the thermalized TA spectrum: $[Fe(dftpy)_2]^{2+}$ (blue) at 356 nm, $[Fe(dcpty)_2]^{2+}$ (green) at 366 nm, and $[Fe(dbtpy)_2]^{2+}$ (red) at 369 nm. In the $[Fe(dftpy)_2]^{2+}$ data, the positive feature due to the $\tau_3$ component has been subtracted.

Clearly from the fits, the isolation of $\tau_2$ dynamics is reasonable. Most importantly, the data indicate a trend across the halogen series where the $5,7$MLCT lifetime increases with halogen size. Given the picosecond lifetimes of these species, we do not expect a direct transition between $5,7$MLCT and $5MC$. These states should be nested (both have configurations with
population of two metal-ligand antibonding orbitals) and firmly in the Marcus inverted regime given the ~ 2.5 eV driving force. Thus, it appears unlikely that potential variations in reaction free energy as the halogen changes is the origin of the $\tau_2$ trend. An interpretation we favor is that the observation supports the original design strategy where larger halogen substituents are impacting surface crossings between states during non-radiative decay. We anticipate that the $^3$MLCT (with no occupancy of metal-ligand antibonding orbitals) is not of importance given its significant conformational difference. On the other hand, if the decay pathway from the $^{5,7}$MLCT to the $^5$MC within which it is nested is facilitated by transient population of a triplet with a configuration that now has one metal-ligand antibonding electron, such as the $^3$MC, it would be reasonable to encounter slower non-radiative decay in cases where there is a more significant energy penalty upon decreasing Fe–N bond distances, as would be the case for larger halogen atoms due to steric repulsion. Further, we strongly suspect that the energy of the $^3$MC relative to the $^{5,7}$MLCT is impacted by the size of the halogen substituent. This idea is informed by the observation of SCO in the smaller $[\text{Fe(dftpy)}_2]^{2+}$ and not in the larger species. As the halogen substituent increases in size, those states with more metal-ligand bonding character – such as $^1$A that we observe through SCO but also $^3$MC where there is only a single electron in an antibonding ligand field orbital – are destabilized according to interligand steric interactions relative to states bearing configurations with two electrons in antibonding ligand field orbitals ($^5$MC and $^{5,7}$MLCT). One would then encounter slower non-radiative decay in the limit that this increases the barrier for crossing between $^{5,7}$MLCT and $^3$MC. Both the reorganization energy and the state energy shift ideas are presented as a cartoon in Figure 4.13.
**Figure 4.13.** Cartoon of potential energy surfaces and orbital occupancy diagrams for states used to describe the dynamics in the series of Fe(II) dihaloteryridine complexes. The reorganization energy argument is captured by the increase in curvature (grey dashed lines) as steric hindrance is increased, while the \(^3\)MC energy argument is captured by the increase in the energy of the potential energy curve (red dashed lines) as steric hindrance is increased. The grey circle indicates the significant surface crossing (the rate-limiting step) in determining non-radiative decay of the MLCT state.

Of note, it would not be unreasonable for both processes to contribute to changes in decay rates by impacting a rate-limiting crossing between \(^{5,7}\)MLCT and \(^3\)MC (see the barrier increase highlighted within the circle of Figure 4.13). Alternatively, it would not be impossible for the two effects to oppose each other, and this will ultimately depend on the true (as opposed to hypothetical) placement of the relevant states in an energetic and conformational landscape. In this context, theory is needed to gain further insight. As a final point, it should be emphasized that while steric effects do appear to impact relaxation rate constants, the overall effect in this halogen series is subtle and appears to have come close to reaching its limit. There is a 24% increase in lifetime from [Fe(dftpy)_2]^{2+} to [Fe(dbtpy)_2]^{2+} (Table 4.4) but for the last two members, from [Fe(dctpy)_2]^{2+} to [Fe(dbtpy)_2]^{2+}, the increase is only 9%. Overall, this suggests that new strategies are needed beyond halogen steric effects in order to realize significant additional gains in high-spin MLCT lifetime.
4.10. Conclusions

X-ray diffraction, magnetic measurements, electrochemistry, and static and time-resolved optical spectroscopies were used to characterize molecules and explore systematic variations within a series of Fe(II) bis-6,6''-dihaloterpyridine complexes: \([\text{Fe(dbtpy)}_2]^{2+}\), \([\text{Fe(dctpy)}_2]^{2+}\), and \([\text{Fe(dftpy)}_2]^{2+}\), that incorporate bromine, chlorine, and fluorine substituents, respectively. For the larger members of the series, \([\text{Fe(dbtpy)}_2]^{2+}\) and \([\text{Fe(dctpy)}_2]^{2+}\), structural and magnetic susceptibility data provided strong evidence for a high-spin quintet ground state. Optical absorption measurements indicate that the lowest energy feature is a broad visible shoulder that has been assigned to \(5\text{MLCT} \leftarrow 5\text{GS}\). Although both molecules appear to be high spin with very similar absorption features and band energies, a modest increase in molar extinction is observed from \([\text{Fe(dbtpy)}_2]^{2+}\) to \([\text{Fe(dctpy)}_2]^{2+}\), consistent with an enhancement in metal-ligand electronic interaction as the halogen atom size is decreased from Br to Cl.

When the halogen size decreases further in \([\text{Fe(dftpy)}_2]^{2+}\), complexity emerges in the structural, optical, and magnetic data that manifests in significant temperature dependence. Notably, a spin crossover equilibrium is uncovered where the singlet state, \(1\text{A}\), is enthalpically favored and where the quintet state, \(5\text{MC}\), is populated due to entropic contributions to the free energy. At room temperature, a sample of \([\text{Fe(dftpy)}_2]^{2+}\) is 97:3 of quintet to singlet. Variations in optical features within this spin equilibrium are useful for disentangling excited state dynamics attributable to excitation origins in two different ground state populations. For example, using a redder pump wavelength (520 nm) the singlet manifold may be selectively addressed \((1\text{MLCT} \leftarrow 1\text{A})\), ultimately leading to transient excess in the \(5\text{MC}\) population. In reestablishing the \(1\text{A}/5\text{MC}\) spin equilibrium, the time constant for \(5\text{MC} \rightarrow 1\text{A}\) is measured to be 22 ns at room temperature, a value that is four times longer than what is observed for the parent
molecule \([\text{Fe(tpy)}_2]^{2+}\). Turning to bluer excitation (400 nm), the quintet manifold in \([\text{Fe(dftpy)}_2]^{2+}\) may be selectively addressed \((^{5}\text{MLCT} \leftarrow ^{5}\text{MC})\), an experiment that is useful because it enables measurement of the \(^{5,7}\text{MLCT}\) lifetime needed for comparison. Across the halogen series as a whole, we observe an increase in high-spin MLCT lifetime from 14.0 ps \(([\text{Fe(dftpy)}_2]^{2+})\) to 16.0 ps \(([\text{Fe(dctpy)}_2]^{2+})\) to 17.4 ps \(([\text{Fe(dbtpy)}_2]^{2+})\). On one hand these values are significant in magnitude, indicative of some of the longest lived MLCT states known in Fe(II) complexes. At the time of initial publication, the 17.4 ps measured for \([\text{Fe(dbtpy)}_2]^{2+}\) was exceeded only by the 18 ps\(^{34}\) and 26 ps\(^{35}\) \(^3\text{MLCT}\) lifetimes that were measured in high ligand-field N-heterocyclic carbene Fe(II) complexes and the 20 ps MLCT lifetime measured for \([\text{Fe(CN)}_4(\text{bpy})]^{2-}\).\(^{30}\)

Still, these lifetimes are short enough to argue against direct nonradiative decay to the ground state. Both states have configurations with two electrons in metal-ligand antibonding orbitals with the expected consequence of being nested and unable to interconvert on sub-nanosecond timescales given the relaxation driving force. These lifetimes then suggest that the decay pathway involves participation by additional states. Triplets with a single electron in a metal-ligand antibonding orbital, such as the \(^3\text{MC}\), are likely candidates. Certainly the relative energy of participating states could play a role in our observation of lifetime control in the halogen series. Judging from comparative absorption spectroscopy there is little reason to believe that the \(^{5,7}\text{MLCT}\) energy is significantly perturbed relative to the \(^5\text{MC}\) as substitution varies from F to Cl to Br. On the other hand, the \(^3\text{MC}\), with shorter metal-ligand bond lengths, is expected to be sensitive to the structural and steric differences explored in the halogen series. If the rate-limiting barrier to interconversion from \(^{5,7}\text{MLCT}\) to \(^3\text{MC}\) increases with the size of the halogen substituent, the lifetime variation would track our observations of increasing from 14.0 ps to 17.4
ps on going from [Fe(dftpy)$_2$]$^{2+}$ to [Fe(dbtpy)$_2$]$^{2+}$. A complementary mechanism involves variations in reorganization energy. The larger the halogen atom, the more difficult it is energetically for the $^{5,7}$MLCT to adopt geometries needed for conversion to the $^3$MC in its pathway to the ground state $^5$MC. These ideas are at this stage based on observations tied to structural modifications and will require additional support, presumably through theory and subsequent measurements of temperature dependent lifetimes.

A final conclusion to be made is that improvements to Fe(II) $^{5,7}$MLCT lifetimes, with halogen substitution at 6 and 6’’ positions of terpyridine, appear to be approaching a limit with bromine. At this stage a change in design strategy is needed. New strategies should seek to change the energetic relationship between states involved in nonradiative decay and they should seek to reduce the coupling between MLCT and metal-centered states using electronic perturbations. Efforts along these lines are presented in the following chapters.

4.11. References


Chapter 5

Highly-Strained Iron(II) Terpyridines Containing Electron-Donating and –Withdrawing Substituents

5.1. Introduction and Motivation

Having previously explored how tuning steric strain via halogen choice can alter the ground- and excited-state properties of high-spin iron(II) polypyridyl chromophores, we decided to look at employing electron-donating and –withdrawing substituents. We were initially inspired to pursue this approach by the groups of Gros\(^1,2\) as well as Wärnmark and Sundström\(^3\) who showed that a carboxylic acid substituent could substantially extend the lifetime of the MLCT excited state in low-spin iron(II) complexes containing N-heterocyclic carbene (NHC) ligands. Using this approach on two different chromophores, these groups were able to prolong the \(^3\)MLCT lifetime by 60-100\%.\(^1-3\)

Computational modeling of these systems showed that the dramatic lifetime extension was due to lowering of the energy of the \(^3\)MLCT relative to the \(^3\)MC state through which relaxation occurs.\(^3,4\) This state-specific energy reduction is possible because of the molecular orbitals involved in the two transitions. The carboxylic acid group can accept electron density from the \(\pi\) system of the ligand, effectively stabilizing the ligand-based LUMO. A lower energy LUMO will reduce the overall energy of the MLCT transition if the substituent has a weaker effect on the metal-based HOMO. This is generally the case for electron-withdrawing substituents on the ligand, but not necessarily true for electron-donating substituents (\textit{vide infra}).\(^5-9\) Furthermore, these 4’-substitutions should similarly be largely agnostic towards the energy of any other MC states. The left-hand side of Figure 5.1 shows a potential energy surface...
diagram of how these changes in the excited-state energies would increase the barrier to relaxation. If the energy of the $^{1,3}\text{MLCT}$ potential energy surfaces are reduced and the $^{3}\text{MC}$ is unaffected, the energy difference between the $^{1,3}\text{MLCT}$ energy minimum and the $^{3}\text{MC}$ crossing point would increase. In this new scenario, a higher activation energy would be required to reach the crossing point and relax to the ground state.

![Potential energy surfaces showing how decreasing the energy of the $^{1,3}\text{MLCT}$ or $^{5,7}\text{MLCT}$ states could raise the barrier to relaxation into the $^{3}\text{MC}$ state in a hypothetical low-spin (left) and high-spin (right) iron(II) complex.](image)

**Figure 5.1.** Potential energy surfaces showing how decreasing the energy of the $^{1,3}\text{MLCT}$ or $^{5,7}\text{MLCT}$ states could raise the barrier to relaxation into the $^{3}\text{MC}$ state in a hypothetical low-spin (left) and high-spin (right) iron(II) complex.

Recalling the potential energy surface picture that was presented in Chapter 4 for the high-spin iron(II) complexes, we would likewise expect that reducing the energy of the $^{5,7}\text{MLCT}$ states would increase the barrier to relaxation into the $^{3}\text{MC}$ state, which likely serves as the dominant relaxation pathway (Figure 5.1). To investigate this idea, a series of ligands and their iron(II) bis-homoleptic complexes were synthesized (Figure 5.2).
Figure 5.2. Structures of 4'-substituted ligands and the related Fe(II) complexes.

The ligands studied in this chapter are 4'-methylcarboxylate-6,6”-dichloroterpyridine (mc-dctpy), 4’-phenyl-6,6”-dichloroterpyridine (Ph-dctpy), and 4’-amino-6,6”-dichloroterpyridine (NH2-dctpy). If utilizing an electron-withdrawing group to lower the 5,7 MLCT energy proves to be beneficial in the high-spin systems as well, [Fe(mc-dctpy)2]2+ would be expected to have the longest lifetime in this series of complexes and a lifetime greater than the 16 ps previously observed in [Fe(dctpy)2]2+. On the other hand, [Fe(NH2-dctpy)2]2+ would likely have the shortest lifetime due to the opposite effect: the introduction of a π electron-donating substituent and subsequent raising of the 5,7 MLCT state energy. Such a 4’-amino substitution in low-spin [Fe(tpy)2]2+ has previously been shown to raise the energy of the MLCT transition.8,9 Intriguingly, this is different than the observed trends for low-spin Ru(II) terpyridines.5 Ostensibly, the electron-donating substituent has such a strong effect on destabilizing the metal-based HOMO that the overall MLCT transition energy is reduced in spite of an increase in the LUMO energy.

Finally, [Fe(Ph-dctpy)2]2+ may have a longer-lived excited state due to an increase in the delocalization of the electron in the ligand-based LUMO of the 5,7 MLCT state, while having the added benefit of increasing the absorptivity of the MLCT. Such absorptivity increases have been seen previously in both low-spin Ru(II)10 and Fe(II).11,12 However, without strong electron-
withdrawing or -donating effects, the MLCT energy should be largely unchanged relative to [Fe(tpy)_2]^{2+}. The predicted MLCT lifetime increase has been observed in low-spin Ru(II) analogues using tolyl substituents, however, there was also a decrease in the MLCT state energy, making it difficult to attribute the lifetime increase to a single cause.¹⁰

A variety of tools will be used to investigate the effects of 4′-substitution on the ground and excited states of high-spin iron(II) terpyridyl complexes. UV-vis absorption spectroscopy, cyclic voltammetry, and x-ray crystallography will provide an understanding of the energetic and geometric effects caused by the substituents. Transient absorption (TA) spectroscopy will provide information on the excited-state dynamics of these systems to test the hypotheses put forth in the introduction. Finally, a simple computational model will be used to deepen our understanding of the observed photodynamics and to suggest further improvements to the system.

### 5.2 Synthesis of 4′-Substituted Ligands and Complexes

In order to synthesize the desired 4′-substituted ligands a Suzuki coupling approach was used. Suzuki coupling is known to be tolerant of a wide variety of functional groups including both amines¹³,¹⁴ and esters¹³,¹⁵ in the production of terpyridine derivatives.¹⁶ Furthermore, this approach would require the preparation of only the central coupling partners, while the terminal arenes would be formed from the commercially available 6-chloropyridine-2-boronic acid pinacol ester (Figure 5.3).
Figure 5.3. Retrosynthesis of 4'-substituted ligands.

We chose to synthesize a methyl-ester-substituted terpyridine instead of a carboxylic acid-substituted terpyridine because the starting material, 2,6-dibromopyridyl-4-methlycarboxylate, was available commercially, and similar esterified complexes have previously been found to exhibit improved solubility in organic solvents relative to their acid analogues.\textsuperscript{10} The central pyridyl coupling partners for Ph-dctpy and NH\textsubscript{2}-dctpy were synthesized according to the procedure in Figures 5.4 and 5.5 by a divergent pathway, which has been published previously.\textsuperscript{17,18} Following the synthesis of 4-amino-2,6-dibromopyridine, this molecule can be transformed into 4-phenyl-2,6-dibromopyridine in a single step.

Figure 5.4. Synthesis of 4-amino-2,6-dibromopyridine using the procedure of van Ammers et al.\textsuperscript{17} This product serves as the central Suzuki coupling partner in the synthesis of NH\textsubscript{2}-dctpy.

Figure 5.5. Synthesis of 4-phenyl-2,6-dibromopyridine following the procedure of Yuan et al.\textsuperscript{18} This product will serve as the central Suzuki coupling partner in the synthesis of Ph-dctpy. Only the final product was isolated.
This set of reactions will be explained in some detail to elucidate the reasoning behind this approach and its potential for the synthesis of other substituted terpyridines. In the first step, 2,6-dibromopyridine is transformed into the pyridyl-N-oxide using hydrogen peroxide in order to facilitate the para-addition of the nitro group. The resonance structures shown in Figure 5.6 show how the pyridyl N-oxide is amenable to electrophilic substitution at the 4 position.

\[ \text{Br} \quad \text{N}^+ \quad \text{Br} \quad \text{Br} \quad \text{N}^- \quad \text{Br} \]

**Figure 5.6.** Resonance structures of 2,6-dibromopyridine N-oxide.

Following this first step, the addition of the nitro group proceeds easily via a standard electrophilic aromatic substitution. Sulfuric acid and nitric acid are combined to produce the nitronium ion which acts as the electrophile and is readily attacked by the pyridyl ring and selectively added at the 4 position. $^1$H NMR showed no evidence of addition to the 3 or 5 positions. 4-amino-2,6-dibromopyridine is then produced by reduction of the nitro group to an amine using iron(0) and acetic acid, concurrently reducing the N-oxide bond. We were able to purify this compound by extractions of the organic layer with water, weak base, and brine due to the near quantitative yield of these reactions and the low incidence of side products. 4-amino-2,6-dibromopyridine can be used as is to synthesize NH$_2$-dctpy or it can be converted into 4-phenyl-2,6-dibromopyridine using a modified Sandmeyer reaction. The scheme for this reaction is shown in Figure 5.5.

The initial step in this reaction is a diazotization using a nitrite source in acidic conditions. This step is likely followed by the loss of dinitrogen to leave the aromatic carbocation, which rapidly reacts with the solvent, benzene, to form a C-C bond. The Wheland intermediate is re-aromatized by the loss of a proton. While it is well-documented that aryl
radicals are generated in other Sandmeyer-type reactions,\textsuperscript{20,21} there is also evidence for a cationic intermediate in some circumstances.\textsuperscript{22} The electron-withdrawing ability of the N-heteroatom, bromo, and diazonium groups likely encourages the nucleophilic attack by benzene followed by the loss of N\textsubscript{2}.

We considered using toluene instead of benzene for this reaction to later functionalize the benzylic carbon, but a variety of regioisomers were formed. Presumably the toluene did not attack selectively and the methyl group was located at the ortho or para positions, although the para-tolyl product was desired. These isomers were difficult to separate with flash chromatography. Further attempts to functionalize the isomeric mixture were not performed, though these would likely improve the chromatographic separation.

Overall, this synthetic strategy enabled us to produce functionalized dibromopyridines via a divergent synthesis starting with inexpensive, commercially available 2,6-dibromopyridine. Once the substituted dibromopyridines were made, Suzuki-coupling reactions were used to produce all three terpyridyl ligands from each of the three functionalized dibromopyridines (Figure 5.7). Due to low reaction yields in the synthesis of mc-dctpy using a similar procedure as that used in the synthesis of dctpy, toluene was used as the solvent instead of 1,4-dioxane. This change led to higher yields, possibly due to the higher boiling point and better solubility of all reactants (Chapter 2).

![Figure 5.7. General synthetic scheme for 4’-substituted terpyridyl ligands.](image-url)
After purification via column chromatography, the ligands can be combined with \( \text{Fe(BF}_4\text{)}_2 \) in refluxing acetonitrile to form the bis-homoleptic complex in a method similar to that previously described for other iron(II) complexes (See Chapters 2 and 3). Like other high-spin iron(II) complexes investigated in Ch. 3 and 4, paramagnetic broadening of the \(^1H\) NMR peaks made assignment of the \(^1H\) NMR spectra challenging. Proof of purity and identity of these complexes was provided with CHN elemental analysis and mass spectrometry (Chapter 2).

5.3 Electronic Absorption and Magnetic Susceptibility of 4’-Substituted Complexes

Upon initially synthesizing \([\text{Fe(mc-dctpy)}_2]^{2+}\), \([\text{Fe(NH}_2\text{-dctpy)}_2]^{2+}\), and \([\text{Fe(Ph-dctpy)}_2]^{2+}\), all three appeared to be orange or yellow, strongly indicative of high-spin iron(II) polypyridines as opposed to their low-spin analogues, which are generally purple in color. This is expected due to the steric effects of the 6 and 6” substituents based on our previous results and those of Constable et al.\(^{23}\) The high-spin ground state of all three complexes was confirmed through magnetic susceptibility measurements using the Evans NMR technique (Table 5.1).\(^{24}\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\chi_M T) (cm(^3) K mol(^{-1}))</th>
<th>(\mu_{\text{eff}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe(dctpy)}_2]^{2+})</td>
<td>3.5</td>
<td>5.3</td>
</tr>
<tr>
<td>([\text{Fe(mc-dctpy)}_2]^{2+})</td>
<td>4.0</td>
<td>5.7</td>
</tr>
<tr>
<td>([\text{Fe(Ph-dctpy)}_2]^{2+})</td>
<td>3.9</td>
<td>5.6</td>
</tr>
<tr>
<td>([\text{Fe(NH}_2\text{-dctpy)}_2]^{2+})</td>
<td>3.2</td>
<td>5.0</td>
</tr>
</tbody>
</table>

From the table, it can be observed that \(\mu_{\text{eff}}\) is between 5.0-5.7 for all four complexes. This is consistent with an iron(II) quintet state containing four unpaired electrons.\(^{25}\) The spin-only moment for such a quintet state is 4.9 as given by Equation 5.1, where \(n\) is the number of unpaired electrons.

\[
\mu_{\text{eff}} = \sqrt{n(n + 2)} \quad \text{Equation 5.1}
\]
The values of 5.6 and 5.7 suggest that there are substantial orbital angular momentum contributions in [Fe(mc-dctpy)$_2$]$^{2+}$ and [Fe(Ph-dctpy)$_2$]$^{2+}$ complexes, which are largely quenched in [Fe(NH$_2$-dctpy)$_2$]$^{2+}$. This is potentially due to reduced degeneracy of the t$_{2g}$ orbitals (in a pseudooctahedral field approximation) in [Fe(NH$_2$-dctpy)$_2$]$^{2+}$. The amino group acts as an electron donor to the central pyridyl ring and substantially increases the σ donation from that nitrogen. This is supported by the X-ray crystallographic data (vide infra) which show that the Fe-N$_{central}$ bond is significantly shorter for [Fe(NH$_2$-dctpy)$_2$]$^{2+}$ than in the other complexes. This greater donation into the metal center from the central pyridyl ring could destabilize the $d_{xz}$ and $d_{yz}$ orbitals, leaving $d_{xy}$ as the lowest energy orbital (where the z-axis passes through the metal center and bisects both terpyridyl ligands). In this scenario, the loss of degeneracy would result in the orbital angular momentum contributions being substantially quenched.$^{25}$

Although all three complexes are high-spin, there are significant visual differences between the complexes with [Fe(NH$_2$-dctpy)$_2$]$^{2+}$ appearing more yellow when dissolved in acetonitrile and [Fe(mc-dctpy)$_2$]$^{2+}$ appearing more red in solution. These differences can be seen quantitatively in the electronic spectra presented in Figure 5.10.
Figure 5.8. UV-vis absorption spectra of the $[\text{Fe(mc-dctpy)}_2]^2^+$, $[\text{Fe(Ph-dctpy)}_2]^2^+$, and $[\text{Fe(NH}_2\text{-dctpy)}_2]^2^+$ complexes taken in room-temperature acetonitrile.

The nature of the electronic transitions in the parent complex, $[\text{Fe(dctpy)}_2]^2^+$, were identified via spectroelectrochemistry and computational work (See Chapter 3) and they will only be discussed here as they relate to the effects of the substituents. The transition at ~290 nm in all complexes is a ligand-based $\pi^* \leftarrow \pi$ transition and is similar to that observed in the free ligands (Figures 5.8 and 5.9). It is considerably more absorptive in the 4'-phenyl substituted complex due to the extension of the $\pi$ system, which likely increases the length of the transition dipole moment. This phenomenon has been observed with phenyl-substitution in both Ru(II) terpyridyl$^{10}$ and low-spin Fe(II) terpyridyl$^{11,12}$ complexes. Two peaks at ~350 nm are observed for $[\text{Fe(mc-dctpy)}_2]^2^+$ as opposed to the single peak observed for the three other complexes. This split is also evident in the free ligand spectra, and it seems as though it may be due to the red-shifting of a peak that appears only as a shoulder in $[\text{Fe(dctpy)}_2]^2^+$ and completely disappears in $[\text{Fe(NH}_2\text{-dctpy)}_2]^2^+$ (as it has been blue-shifted). We surmise that this is the $\pi^* \leftarrow \pi$ transition most affected by the LUMO lowering properties of the substituents.
Figure 5.9. UV-vis absorption spectra of mc-dctpy, NH$_2$-dctpy, and Ph-dctpy in room-temperature acetonitrile normalized to the peak at ~290 nm.

The $^5$MLCT $\rightarrow$ $^5$GS transition is observed in these complexes as a long tail beyond 400 nm and is shown more clearly in the spectra presented in Figure 5.10. [Fe(Ph-dctpy)$_2$]$^{2+}$ seems to have the strongest absorption, which again is expected due to the extension of the $\pi$ system and lengthening of the transition dipole. However, we are cautious to read too much into these molar absorptivities since they are all being affected by the tail of the much larger ligand-based transitions discussed above.
Figure 5.10. UV-Visible absorption of [Fe(mc-dctpy)$_2$]$^{2+}$, [Fe(Ph-dctpy)$_2$]$^{2+}$, and [Fe(NH$_2$-dctpy)$_2$]$^{2+}$ in room temperature acetonitrile focusing on 400-600 nm.

The energy of this transition is expected to be highly dependent on the electron-withdrawing or –donating nature of the 4’-substituent. Electron-withdrawing substituents (carboxylates) are expected to make reduction of the ligand easier, effectively reducing the energy of populating the ligand-based LUMO. An amine is expected to do the opposite, due to its electron-donating nature, shifting the MLCT to higher energy. The $^5$MLCT energy in these two extremes differs by ~50 nm, validating our rationale for making these substitutions. The magnitude of these shifts in the absorption wavelength are similar to those observed for low-spin Fe(II) complexes.$^8$,$^9$
5.4. Electrochemistry of 4'-Substituted Complexes

The energetic differences observed in UV-vis spectroscopy are corroborated by cyclic voltammetry (CV) with the results shown in Table 5.2. The addition of the methyl carboxylate group shifts the 2+/1+ reduction couple for the Fe(II) complex by +290 mV relative to the unsubstituted complex. This is a demonstration of the increased facility of reducing the methylcarboxylate-substituted ligand as would occur in the $^5\text{MLCT}$ excited state of the complex, which can be considered as $\text{M}^{3+}(\text{L}^-)\text{L}$. On the other hand, the 3+/2+ couple was found to be 50 mV more positive in $[\text{Fe}(\text{mc-dctpy})_2]^{2+}$ than in $[\text{Fe}(\text{dctpy})_2]^{2+}$. It’s possible that this change in oxidation potential is due to reduced electron donation into the metal center. The carboxylate substituted complex likely has weaker metal-ligand bonding due to the electron-withdrawing nature of the carboxylate group, which reduces the ligand’s sigma-bonding ability. The reduced sigma-bonding ability was evidenced anecdotally by its increased sensitivity to water in synthesis and storage, and manifests geometrically as longer Fe-N bond lengths (vide infra). Taken together, the changes in the 3+/2+ and 2+/1+ couples result in an overall reduction in $\Delta E_{1/2}$ by 240 mV. For comparison, the observed difference in the energy of the $^5\text{MLCT} \leftarrow ^5\text{GS}$ transition $[\text{Fe}(\text{mc-dctpy})_2]^{2+}$ than in $[\text{Fe}(\text{dctpy})_2]^{2+}$ is ~200 meV.

Table 5.2. Cyclic Voltammetry Data Collected in Acetonitrile versus SCE

<table>
<thead>
<tr>
<th>complex</th>
<th>$E_{1/2}$ (V)$^a$</th>
<th>$\Delta E_{1/2}$ (V)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe(tpy)}_2]^{2+}$</td>
<td>1.10</td>
<td>2.36</td>
</tr>
<tr>
<td>$[\text{Fe(dctpy)}_2]^{2+}$</td>
<td>1.60</td>
<td>2.43</td>
</tr>
<tr>
<td>$[\text{Fe(mc-dctpy)}_2]^{2+}$</td>
<td>1.65</td>
<td>2.19</td>
</tr>
<tr>
<td>$[\text{Fe(Ph-dctpy)}_2]^{2+}$</td>
<td>1.49</td>
<td>2.30</td>
</tr>
<tr>
<td>$[\text{Fe(NH}_2\text{-dctpy)}_2]^{2+}$</td>
<td>1.19</td>
<td>2.39</td>
</tr>
</tbody>
</table>

$^a$ $E_{1/2}$ potentials measured versus Fe/Fc with 0.38 V added to obtain values versus SCE. $^b$ $\Delta E_{1/2} = E(3+/2+) - E(2+/1+)$. Cyclic voltammetry conditions: 0.1 M tetrabutylammonium hexafluorophosphate electrolyte; Pt disc working electrode; Pt wire counter electrode; Ag/AgNO$_3$ reference electrode with 0.01 M AgNO$_3$; 100 mV/s scan rate; error = ± 0.02 V.
In $[\text{Fe(NH}_2\text{-dctpy})_2]^{2+}$ we see many of the opposite effects of those observed in $[\text{Fe(mcdctpy})_2]^{2+}$. The electron donation of the amine substituent should increase the electron density on the ligand and raise the amount of energy required for reduction. This effect is observed in the $2+/1+$ couple which occurs at -1.20 V, 660 mV more negative than when there is an electron-withdrawing substituent. The difficulty of this reduction is the primary reason for the blue-shifting of the $^5\text{MLCT} \leftarrow ^5\text{GS}$ transition for $[\text{Fe(NH}_2\text{-dctpy})_2]^{2+}$. However, the extent of this blue-shifting is limited by the relative ease of oxidizing $[\text{Fe(NH}_2\text{-dctpy})_2]^{2+}$. We have previously attributed the $3+/2+$ to a relatively localized oxidation of the Fe(II) center. However, the increased electron density on the ligand due to the amine may raise the energy of the ligand based occupied orbitals resulting in a HOMO that has significant electron density on the ligand. This more delocalized MO along with the ability of the amine to act as an electron donor likely act in concert to significantly lower the oxidation potential. It is interesting to note that although the MLCT transition energy is higher for $[\text{Fe(NH}_2\text{-dctpy})_2]^{2+}$, the $\Delta E_{1/2}$ is slightly lower. This is likely due to a difference in the orbital parentage of the electron in each situation. In CV, the oxidized electron likely comes the $e_g^*$ set whereas, in a MLCT transition, we expect the origin of the transferred charge to be $t_{2g}$ in nature, thus leading to an underestimate of the HOMO energy by CV.

A phenyl substituent is not expected to have significant effects on the energy of the ligand-based LUMO, since the potential for increased conjugation is limited by the lack of planarity due to steric constraints (see Section 5.4). Still, a ~100 mV decrease in the oxidation potential was observed for $[\text{Fe(Ph-dctpy})_2]^{2+}$ relative to $[\text{Fe(dctpy})_2]^{2+}$. It is possible that the phenyl ring increases the extent of sigma bonding into the Fe(II) center, thereby facilitating oxidation although a rationale for this is not obvious. We also considered the possibility that the
phenyl group at the 4’-position may prevent ligand distortions toward larger N-N-N angles and thereby enforce shorter Fe-N\textsubscript{terminal} bond lengths. However, such geometric changes are not evident in the solid state as shown by X-ray crystallography (\textit{vide infra}). It seems that this decrease in the oxidation potential has a minor effect on the MLCT transition energy (Figure 5.10) and may arise from some of the same reasons as outlined above for the discrepancy in oxidation potential and HOMO energy for [Fe(NH\textsubscript{2}-dctpy)\textsubscript{2}]\textsuperscript{2+}. Our overall conclusion is that the CV and electronic absorption experiments support the controlled altering of the \textsuperscript{5}MLCT state energy via synthetic modification.

5.5. X-Ray Crystallography of 4’-Substituted Complexes

X-ray crystal structures were obtained for all three complexes and selected geometric parameters are presented in Table 5.3. As seen in the parent complex, [Fe(dctpy)\textsubscript{2}]\textsuperscript{2+}, there is a significant lengthening of the Fe-N bond lengths relative to the low-spin iron(II) complex, [Fe(tpy)\textsubscript{2}]\textsuperscript{2+}. Interestingly, while the Fe-N\textsubscript{terminal} are quite similar across all the high-spin species, there is a greater change in the Fe-N\textsubscript{central} bond distance with the 4’-phenyl and 4’-carboxylate substituted complexes being the longest and the 4’-amine substituted complex being the shortest (Figure 5.11). Perhaps this is not surprising given that the substituents are all located on the central pyridine ring in the \textit{para} position relative to the bonding nitrogen. The electron-donating amine seems to be increasing the electron density of the central pyridine and increasing the sigma donor character to the Fe(II) center. The electron-withdrawing group in [Fe(mc-dctpy)\textsubscript{2}]\textsuperscript{2+} seems to have the opposite effect, increasing the Fe-N bond distance to 2.102 Å.
Figure 5.11. Crystal structures and average Fe-N<sub>central</sub> and Fe-N<sub>terminal</sub> bond lengths for [Fe(NH<sub>2</sub>-dctpy)<sub>2</sub>]<sup>2+</sup>, [Fe(dctpy)<sub>2</sub>]<sup>2+</sup>, and [Fe(mc-dctpy)<sub>2</sub>]<sup>2+</sup>.

Table 5.3. X-Ray Structural Data for 4'-Substituted Complexes – Selected Parameters

<table>
<thead>
<tr>
<th>complex</th>
<th>Fe-N&lt;sub&gt;central&lt;/sub&gt; (Å)</th>
<th>Fe-N&lt;sub&gt;terminal&lt;/sub&gt; (Å)</th>
<th>∠ N-N-N (°)</th>
<th>Θ (°)</th>
<th>X-pyridyl (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(tpy)&lt;sub&gt;2&lt;/sub&gt;]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>1.890(4)</td>
<td>1.988(3)</td>
<td>102.8(2)</td>
<td>1.5(3)</td>
<td>N/A</td>
</tr>
<tr>
<td>[Fe(dctpy)&lt;sub&gt;2&lt;/sub&gt;]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>2.080(2)</td>
<td>2.272(1)</td>
<td>111.4(1)</td>
<td>4.1(1)</td>
<td>3.074(1)</td>
</tr>
<tr>
<td>[Fe(mc-dctpy)&lt;sub&gt;2&lt;/sub&gt;]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>2.102(1)</td>
<td>2.268(1)</td>
<td>110.8(1)</td>
<td>6.3(1)</td>
<td>2.996(1)</td>
</tr>
<tr>
<td>[Fe(Ph-dctpy)&lt;sub&gt;2&lt;/sub&gt;]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>2.103(1)</td>
<td>2.273(1)</td>
<td>111.5(1)</td>
<td>5.3(1)</td>
<td>3.068(1)</td>
</tr>
<tr>
<td>[Fe(NH&lt;sub&gt;2&lt;/sub&gt;-dctpy)&lt;sub&gt;2&lt;/sub&gt;]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>2.062(3)</td>
<td>2.262(3)</td>
<td>111.7(2)</td>
<td>0.9(1)</td>
<td>3.063(2)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Structural data from reference. Data taken at 295 K for [Fe(tpy)<sub>2</sub>]<sup>2+</sup>; 120 K for [Fe(dctpy)<sub>2</sub>]<sup>2+</sup>; 100 K for [Fe(mc-dctpy)<sub>2</sub>]<sup>2+</sup>, [Fe(Ph-dctpy)<sub>2</sub>]<sup>2+</sup>, and [Fe(NH<sub>2</sub>-dctpy)<sub>2</sub>]<sup>2+</sup>. See Chapter 2 for additional details.

The phenyl group also has a longer Fe-N bond length that is not adequately explained by appealing to electron donating/withdrawing arguments. It is possible that this difference is due to crystal packing effects that are not seen in any of the other complexes. The additional phenyl ring appears to interact with the terpyridyl ligand on an adjacent molecule via a π stacking interaction (Figure 5.12). If so, this interaction would likely not be observed in the solution phase in which we perform most of our experiments. It is unknown whether an intramolecular reason for these longer bond lengths exists.
**Figure 5.12.** Thermal ellipsoid plot of [Fe(Ph-dctpy)$_2$]$^{2+}$ with $\pi-\pi$ interactions shown in red. C = gray, N = blue, Cl = green, Fe = orange. Hydrogen atoms have been omitted for clarity.

### 5.6. Excited-State Dynamics of 4’-Substituted Complexes

Having determined how these 4’-substituents effect the ground state and the energy of the $^5$MLCT transition in each of the three complexes, transient absorption (TA) spectroscopy was used to investigate the excited-state dynamics. Our original hypothesis for making these complexes was that by lowering the energy of the $^5$MLCT state, we would increase the barrier to relaxation, resulting in a longer MLCT excited-state lifetimes. Based on the previously discussed electronic absorption spectroscopy and cyclic voltammetry, we would expect a shorter lifetime for [Fe(NH$_2$-dctpy)$_2$]$^{2+}$ and a longer lifetime for [Fe(mc-dctpy)$_2$]$^{2+}$ relative to the parent, [Fe(dctpy)$_2$]$^{2+}$.

In [Fe(Ph-dctpy)$_2$]$^{2+}$ the $^5$MLCT is similar in energy relative to [Fe(dctpy)$_2$]$^{2+}$ which suggests that the barrier height for deactivation through a metal-centered state will remain unchanged. However, the additional phenyl ring may allow for greater electron delocalization.
across the ligand which could decrease coupling with the metal center. Contrary to this, the
crystal structure (Fig. 5.12) showed a lack of planarity between the phenyl substituent and the
central terpyridyl ring, which may diminish the extent to which these two aromatic systems can
interact with each other. However, published reports on related molecules have argued for
rotation of a phenyl substituent and increased planarity in the excited state.\textsuperscript{10,29,30}

Transient absorption spectra following 400 nm excitation of all three complexes show
similar spectral features and dynamic processes. The spectra for \([\text{Fe}(\text{mc-dctpy})_2]^{2+}\) are shown in
Figure 5.13 as a representative example. The general features are similar to those observed for
\([\text{Fe}(\text{dctpy})_2]^{2+}\): a sharp peak below 400 nm and broad visible absorption. Using a method
described previously, the full data set was fit using two basis spectra.\textsuperscript{26,31} These two spectra are
indicative of a shifting of the peaks due to vibrational cooling (\(\tau_1\)) and a decay of the excited
state to the ground state (\(\tau_2\)) with no intermediate states observed. Again, we see a faster
component for the thermalization within the \(^{5,7}\text{MLCT}\) state and a slower component for the
decay of the excited state. The excited-state spectra for \([\text{Fe}(\text{Ph-dctpy})_2]^{2+}\) and \([\text{Fe}(\text{NH}_2-\text{dctpy})_2]^{2+}\)
have similar qualitative features and show similar dynamic processes.
Figure 5.13. Transient absorption spectra of [Fe(mc-dctpy)$_2$]$^{2+}$ in room-temperature acetonitrile at the given time delay following 400 nm excitation. The TA signal value is plotted in OD.

A lifetime of $17.8 \pm 1.2$ ps was measured for $5,7$MLCT state decay in [Fe(Ph-dctpy)$_2$]$^{2+}$. This lifetime is slightly longer than the previously obtained $16.0 \pm 1.0$ ps for [Fe(dctpy)$_2$]$^{2+}$. The similar excited state energies for the two species agree with the minor difference in $5,7$MLCT lifetimes, since there should be nearly identical barriers to relaxation into metal-centered states. However, it may be that the coupling to the $3^{MC}$ state is altered, possibly due to some delocalization of charge onto the phenyl substituent in the excited state.

Moving on to [Fe(mc-dctpy)$_2$]$^{2+}$ and [Fe(NH$_2$-dctpy)$_2$]$^{2+}$ where the energy of the MLCT states has been altered, we again report that the excited-state spectra contain similar qualitative features. These spectra are also able to be fit by the same two processes as described above. In doing so excited-state lifetimes of $11.5 \pm 1.3$ ps for [Fe(NH$_2$-dctpy)$_2$]$^{2+}$ and $14.0 \pm 1.1$ ps for [Fe(mc-dctpy)$_2$]$^{2+}$ are measured. The significantly reduced lifetime for the $5,7$MLCT in [Fe(NH$_2$-dctpy)$_2$]$^{2+}$ coincides with our ideas about altering the potential energy surfaces. By raising the energy of the MLCT states relative to the metal-centered states, the energetic barrier has been lowered and even faster deactivation through the $3^{MC}$ state is allowed.
Contrary to expectations, \([\text{Fe}(\text{mc-dctpy})_2]^{2+}\) also shows a shortened MLCT lifetime relative to \([\text{Fe}(\text{dctpy})_2]^{2+}\). This is unexpected, since the cyclic voltammetry and electronic absorption results described above provide strong evidence that the methylcarboxylate substituent is effective at reducing the energy of the \(5,7\) MLCT energy. Furthermore, the results for \([\text{Fe}(\text{NH}_2\text{-dctpy})_2]^{2+}\) support our understanding of the relative ordering of states and our rationale for how the energy of the \(5,7\) MLCT will alter the MLCT lifetime. In spite of this, the excited state lifetime for \([\text{Fe}(\text{mc-dctpy})_2]^{2+}\) is shorter than in the parent \([\text{Fe}(\text{dctpy})_2]^{2+}\).

**Table 5.4.** Time Constants for the Thermalization (\(\tau_1\)) and MLCT Excited-State Relaxation (\(\tau_2\)) of 4'-Substituted Complexes

<table>
<thead>
<tr>
<th>complex</th>
<th>(\tau_1) (ps)(^a)</th>
<th>(\tau_2) (ps)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe}(\text{dctpy})_2]^{2+})</td>
<td>3.6 ± 0.3</td>
<td>16.0 ± 1.0</td>
</tr>
<tr>
<td>([\text{Fe}(\text{mc-dctpy})_2]^{2+})</td>
<td>2.9 ± 0.2</td>
<td>14.0 ± 1.1</td>
</tr>
<tr>
<td>([\text{Fe}(\text{Ph-dctpy})_2]^{2+})</td>
<td>4.0 ± 0.2</td>
<td>17.8 ± 1.2</td>
</tr>
<tr>
<td>([\text{Fe}(\text{NH}_2\text{-dctpy})_2]^{2+})</td>
<td>2.8 ± 1.5</td>
<td>11.5 ± 1.3</td>
</tr>
</tbody>
</table>

\(^a\)All values obtained from three independent data sets obtained in room-temperature acetonitrile.

5.7. A Computational Model for Understanding the Dynamics

In order to understand why electron-withdrawing group substituents were unsuccessful at extending the MLCT lifetime, we decided to model the system computationally using density functional theory (DFT) to see if any insights could be gleaned regarding the charge distribution in the excited state. A model of the reduced ligand was employed to serve as a proxy for the full MLCT excited state to reduce computational cost and complexity. A brief description of the model is described here, but additional experimental details will be published separately.\(^{32}\) As the model system, we chose to use \([\text{Zn}(\text{ligand}^-)(\text{MeCN})_3]^{1+}\). Zinc(II) contains a diamagnetic, full \(3d\) subshell and reduction is assumed to be difficult enough that the reduced complex will feature the additional electron density almost exclusively on the terpyridyl ligand. The three acetonitrile ligands are used to maintain the pseudo-octahedral geometry we observe in the iron(II) species.
and because they have a high energy LUMO, which will force the additional electron density onto the terpyridyl ligand. Finally, without a paramagnetic metal center, the additional charge can be visualized in a spin density plot since all other electrons should be paired. Stated again: the spin density plots will be used as a representation of charge density on the ligand in the MLCT state. Figure 5.14 shows a spin density plot of the representative complex [Zn(dctpy)(MeCN)$_3$]$^{1+}$. The model complex maintains the proper dctpy confirmation and > 98% of the spin density resides on the dctpy ligand. This was found to be the case for all the complexes modeled in this manner, namely nearly 100% of the spin density on the ligand and maintenance of a pseudo-octahedral geometry.

![Spin density plot](image)

**Figure 5.14.** Spin density plot for [Zn(dctpy)(MeCN)$_3$]$^{1+}$. 98% of the spin density is located on the dctpy ligand.

Using this computational model we can consider the changes induced by the substituted ligands relative to the parent. Table 5.5 shows the spin density on various parts of the terpyridyl ligand: the 4’-substituent, the central pyridine ($C_5H_2N$), and the terminal pyridines ($C_5H_3NCl$). Note that the sum of these values add up to ~100% in all complexes, indicating that the additional charge resides almost exclusively on the terpyridyl ligand. In [Zn(dctpy)(MeCN)$_3$]$^{1+}$ 48% of the spin density is on the central pyridine with 50% on the two terminal pyridines,
equivalent to what is observed for the ligand without the 6 and 6” Cl substituents. This is evidence that even though the added Cl atoms reduce the overall LUMO energy as observed in the cyclic voltammetry results above, they have a minimal effect on the spatial charge distribution. The change upon moving to [Zn(4’-Ph-dctpy)(MeCN)₃]⁺ is small with only 3% of the spin density residing on the added phenyl group. This is another argument against the delocalization we were hoping to achieve through this synthetic alteration. Without significant delocalization onto the phenyl group in the ligand radical anion, there is no reason to expect a dramatic lengthening of the ⁵MLCT lifetime, consistent with the TA spectroscopy results.

![Figure 5.15](image_url)

**Figure 5.15.** Selected structures showing DFT spin density results for [Zn(MeCN)₃(L)]⁺ where L = dctpy, 4’-COOH-dctpy, NH₂-dctpy.

<table>
<thead>
<tr>
<th>Ligand (L)</th>
<th>PyCentral</th>
<th>Two PyTerminal</th>
<th>4’-substituent</th>
</tr>
</thead>
<tbody>
<tr>
<td>dctpy</td>
<td>48%</td>
<td>50%</td>
<td>N/A</td>
</tr>
<tr>
<td>Ph-dctpy</td>
<td>47%</td>
<td>47%</td>
<td>3%</td>
</tr>
<tr>
<td>4’-COOH-dctpy</td>
<td>58%</td>
<td>34%</td>
<td>7%</td>
</tr>
<tr>
<td>NH₂-dctpy</td>
<td>39%</td>
<td>58%</td>
<td>2%</td>
</tr>
</tbody>
</table>

Moving to 4’-COOH-dctpy, 58% of the additional spin density is found on the central pyridine with 7% more on the carboxylic acid group. Furthermore, effectively all of the spin density comes at the expense of the terminal pyridines and the spin density of the central pyridine actually increases in spite of the carboxylic acid substituent. The NH₂-substituted species shows the opposite result with the electron-donating group pushing charge to the terminal pyridines.
Given that the lower energy $^5$MLCT state in [Fe(mc-dctpy)$_2$]$^{2+}$ does not lengthen the excited-state lifetime as would be expected from the potential energy surface model, there must be an alternate phenomenon at work. The computational results show that moving spin density to the central pyridine at the expense of the terminal pyridines is an unanticipated consequence of the synthetic substitution. Considering the crystallographic data presented in Table 5.3, the central pyridine has a much shorter Fe-N bond distance than the terminal pyridines in these complexes and suggests additional metal-ligand orbital overlap. Specifically for [Fe(mc-dctpy)$_2$]$^{2+}$, the average Fe-N$_{\text{central}}$ bond length is 2.102(1) Å while the average Fe-N$_{\text{terminal}}$ bond length is 2.268(1) Å, 8% longer. This difference may be enough to significantly alter the coupling between the ligand and the metal center. If having additional spin density on the central pyridine is detrimental to our goals, then pushing spin density to the terminal pyridines should reduce the coupling and extend the $^5$MLCT lifetime.

5.8. Conclusion and Future Directions

Herein, we’ve described the synthesis of a series of 4'-substituted, high-spin iron(II) terpyridyl complexes. We were able to successfully alter the MLCT excited-state energies of these complexes using both electron-withdrawing and electron-donating substituents as evidenced by electronic absorption spectroscopy and cyclic voltammetry. A shortened $^5$MLCT excited-state lifetime was observed for [Fe(NH$_2$-dctpy)$_2$]$^{2+}$ as expected assuming a reduced barrier to relaxation into a $^3$MC state. However the opposite phenomenon, lifetime extension, was not observed in [Fe(mc-dctpy)$_2$]$^{2+}$ despite evidence for a lower energy MLCT state. A computational approach was used to explore the localization of electron density on the reduced ligand using a zinc(II) model system. It is possible that any energetic effect due to lowering the
MLCT energy is offset by localizing the electron density onto the central pyridine of the ligand where the Fe-N bond distance is shortest and coupling to the metal-centered states is greatest.

Further research will be needed to understand the significance of this effect on iron(II) and related systems. In particular, synthesis of a 4- or 4”-methylcarboxylate substituted dctpy would lend support to these ideas as it would allow a direct comparison of the substituent location. A related complex containing ethylcarboxylate substituted terminal rings will be discussed in Chapter 6, motivated in part by the coupling ideas presented in this chapter.

5.9 References


Chapter 6

Diquinolinylpyridyl Ligands to Increase Visible Absorption and Control Excited-State Charge Localization in High-Spin Iron(II) Complexes

6.1. Introduction and Motivation

Having shown that it is possible to influence the MLCT excited-state lifetime by exploiting increased steric hindrance (Chapter 4) and 4’-substitution of electron-donating and – withdrawing groups (Chapter 5), we decided to investigate a new type of ligand that deviates from the standard high-spin terpyridyl backbone. In taking this step we had three aims: to maintain steric bulk around the metal center, enforcing a quintet geometry; to increase the absorptivity of the complex in the visible spectrum; and to increase the MLCT excited-state lifetime using push-pull substituent strategies to increase electron density on the rings adjacent to the terminal Fe-N bonds as opposed to the central Fe-N bonds. The ligands chosen for these goals were 2,6-(diquinolin-2-yl)pyridine (dqp) and the ethyl carboxylate substituted version (decqdp), pictured in Figure 6.1.

![Figure 6.1. Structure of dqp and decqdp ligands and the related iron(II) complexes.](image-url)
As can be seen from the figure, steric bulk around an iron(II) ion in a six-coordinate, pseudo-octahedral complex will be significant, similar to what was observed for the 6,6”-dihaloterpypiridyl complexes. Furthermore, it appears as though any movement of the terminal rings at these steric positions might be constrained since they are part of a larger fused-ring system.

To increase visible absorptivity it is necessary to either increase the molar absorptivity at a given wavelength, or to reduce the MLCT excitation energy such that it leads to a red-shifting of the absorption band and the complex absorbs across a broader visible wavelength range. This ligand design attempts to red-shift the MLCT band in the Fe(II) complex by lowering the ligand-based LUMO energy in two ways. First, replacing the terminal pyridyl rings with quinolinyl rings should increase delocalization of the π* orbital thereby decreasing its energy. Second, attaching two electron-withdrawing ester groups (decdqp) should significantly lower the energy of populating the ligand-based LUMO. The effects of the electron-withdrawing groups and increased delocalization of the quinolinyl π* orbital should also lead to a relative localization of the LUMO onto the terminal rings. Based on the computational results presented in Chapter 5, this change will reduce metal-ligand coupling by pulling electron density to the quinolinyl rings, where the Fe-N bonds are weakest and coupling to the metal center is likely reduced.

Previous studies on these ligands and complexes provide encouraging results. The synthesis of [Fe(dqp)₂]²⁺ was originally reported in 1969 by Harris et al.,¹ where the authors measured an effective magnetic moment of 5.25, confirming the dominance of the high-spin ground state.¹ [Fe(dqp)₂]²⁺ was revisited in the 1970s by Bonomo et al. who reported on the voltammetry² and the visible absorption properties³ of this complex. Intriguingly, Bonomo et al. reported an absorption band with λ_{max} = 530 nm,³ and although the nature of the transition wasn’t
assigned, it is likely the transition populating the quintet MLCT. 530 nm corresponds to a photon energy that is lower than any of the MLCT transitions in known iron(II) bis-dihaloterpyridyl complexes, confirming that using the dqp ligand can red-shift absorption in the visible spectrum. However, no further investigation of this complex and no studies of [Fe(decdqp)₂]^{2+} are reported in the literature. In particular, there are no reports on the time-resolved dynamics of these complexes.

The literature on ruthenium(II) analogues containing dqp and decdqp ligands is more developed. The synthesis and electrochemical characterization of [Ru(decdqp)₂]^{2+} has previously been reported in the literature.⁴ Electrochemical analysis of [Ru(decdqp)₂]^{2+} showed that it was able to undergo four sequential reductions over a range of only 0.66 V, thereby enabling the storage of up to four electrons.⁴ This indicates that there is at least some coupling between the quinolinyl moieties, although not so much that additional reductions after the first become significantly more difficult.

While the photophysics of [Ru(decdqp)₂]^{2+} has not been previously reported other than to report a lack of observed emission, [Ru(dqp)₂]^{2+} has been the subject of detailed photophysical studies. The MLCT excited-state lifetime of [Ru(dqp)₂]^{2+} has been reported to be shorter than that of [Ru(tpy)₂]^{2+} due to the accessibility of metal-centered states which promote non-radiative relaxation.⁴,⁵ This suggests a substantially weaker ligand-field than what is normally observed for octahedral Ru(II) complexes, likely due to interligand steric repulsion. This same effect in the related high-spin iron(II) complex may serve to stabilize quintet states relative to triplet and singlet states which are thought to serve as deactivation pathways in the quintet manifold.⁶ Interestingly, while dqp-derived ligands have not been successful in producing long-lived low-
spin chromophores involving Ru(II), they may find better use in high-spin iron(II) systems for the same reasons.

6.2. Synthesis of Diquinolinylpyridyl Ligands and Complexes

While the syntheses previously described for the various dihaloterpyridine ligands employed a palladium-catalyzed cross-coupling strategy, both dqp and decdqp were synthesized using condensation techniques. Such syntheses for the dqp framework are known\(^4\) and the starting materials can be readily obtained commercially. In both cases 2,6-diacetylpyridine was combined with two equivalents of either 2-aminobenzaldehyde (for dqp) or isatin (for decdqp) in a basic solution (Fig. 6.2). For the synthesis of dqp, the aminobenzaldehyde was produced in situ from 2-nitrobenzaldehyde via the Bechamp reduction. Condensation reactions were chosen for synthesizing these ligands because they proceed readily in aqueous solution and result in few side products, simplifying purification. The procedure for the synthesis of dqp is shown in Figure 6.2.

![Synthesis of dqp ligand](image)

**Figure 6.2.** Synthesis of dqp ligand. This procedure was adapted from a previously published synthesis.\(^1\)

While the condensation reaction to produce dqp led to few side products, the synthesis of decdqp by a similar procedure required chromatographic separation before the final product was obtained exclusively. The full multi-step procedure is shown in Figure 6.3 and all steps are
detailed in Chapter 2. Initial attempts to isolate the sodium salt from the hydrolyzed isatin via recrystallization resulted in low recovery of the desired product. Upon acidification, the bis-acid was found to interact strongly with (and streak on) a silica gel column. This prevented reasonable chromatographic separation at this stage. By carrying the crude material through the esterification step (Fig. 6.3), the final product was cleanly separated from any side products via flash chromatography.

![Chemical structure]

**Figure 6.3.** Three step procedure for the synthesis of decdqp ligand adapted from Marin et al. Only the final product was isolated.

The mechanism for the first reaction in Figure 6.3 (known as a Pfitzinger reaction) is shown in detail in Figure 6.4. In this mechanism, a hydroxide ion is used to cleave the amide bond. This is thought to occur in a single step with the transition state shown in Fig. 6.4. Although the carbonyl adjacent to the amide bond is likely more electrophilic, attack by the hydroxide at that position would be reversible and does not lead to cleavage of the isatin ring. Following amide bond cleavage, the resulting amine condenses with the acetyl pyridine to form an imine, releasing water in the process. This imine can tautomerize to form an enamine, which will allow intramolecular cyclization. Aromatization of the newly formed ring drives the
liberation of another equivalent of water and the formation of the final product. A similar mechanism is responsible for the condensation reaction to produce dqp, although the isatin is replaced with an aminobenzaldehyde.

![Chemical structure diagram](image)

**Figure 6.4.** Mechanism for the first of two Pfizinger reactions to form the 2,6-di(quinolin-2-yl)pyridinyl framework for the synthesis of decdq. Note that this reaction is run in 33\% NaOH\(_{aq}\), and the intramolecular proton transfer steps could also occur very rapidly with hydroxide and water molecules. Adapted from references.\(^7,8\)

The synthesis of iron(II) complexes from these ligands was straightforward and is given in detail in Chapter 2. Briefly, it mirrors the syntheses of other iron(II) complexes presented previously in which ligands and Fe(BF\(_4\))\(_2\) are combined in refluxing acetonitrile or 1,4-dioxane and the product is purified via recrystallization. Again, as in the other high-spin iron(II) complexes discussed in this manuscript, Fermi contact-shifting and peak broadening of the \(^1\)H NMR signals prevent simple interpretation of the chemical shifts and no splitting is observed.
Lacking this information, it was necessary to use mass spectrometry and combustion analysis to provide confirmation of identity and purity along with x-ray crystallography (available in Chapter 2). All of these analyses were performed on crystalline samples of materials, which were then dried under vacuum to remove residual solvent.

### 6.3. Magnetic and Structural Characterization of [Fe(dqp)_2]^{2+} and [Fe(decdqp)_2]^{2+}

As described previously by Harris et al.,[^1] [Fe(dqp)_2]^{2+} is high-spin at room temperature, likely due to the interligand steric strain, similar to what was observed in the iron(II) bis-dihaloterpapyridyl complexes. [Fe(decdqp)_2]^{2+} was confirmed to be high-spin as well by Evans’ NMR measurement. $\chi_{mol} T$ was found to be 3.6 cm³/mol for [Fe(decdqp)_2]^{2+} and 3.6 cm³/mol for [Fe(dqp)_2]^{2+}, which converts to an effective magnetic moment of 5.4 for both molecules assuming $g = 2$. This value is consistent with the assignment of a quintet ground state with a pseudo-octahedral geometry.[^9] We note here that our values are in general agreement, though slightly higher than the 5.2-5.3 determined by Harris et al. for [Fe(dqp)_2]^{2+} over a range of temperatures using a Gouy balance.[^1]

Crystallographic data is available for [Fe(decdqp)_2]^{2+}, but x-ray quality crystals were not obtained for [Fe(dqp)_2]^{2+} despite using a variety of solvent systems. The structure obtained for [Fe(decdqp)_2]^{2+} corroborates the assignment of a quintet ground state and provides additional information regarding the complex geometry. As is typical of a high-spin state, the Fe-N bonds are elongated relative to [Fe(tpy)_2]^{2+}, a low-spin complex, due to population of the antibonding $e_g$* orbitals (Table 6.1). Furthermore, the N-N-N angle in [Fe(decdqp)_2]^{2+} is wider than in [Fe(tpy)_2]^{2+}. The proximity of the two ligands is best visualized in Figure 6.5 where the
hydrogen atoms on the 8 position of the quinolinyl rings point towards the central pyridyl ring of the opposing ligand.

Table 6.1. Selected X-Ray Structural Parameters for [Fe(decdqp)₂][BF₄]₂

<table>
<thead>
<tr>
<th>complex</th>
<th>Fe-N&lt;sub&gt;central&lt;/sub&gt; (Å)</th>
<th>Fe-N&lt;sub&gt;terminal&lt;/sub&gt; (Å)</th>
<th>∠ N-N-N (°)</th>
<th>Θ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(ppy)₂]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>1.890(4)</td>
<td>1.988(3)</td>
<td>102.8(2)</td>
<td>1.5(3)</td>
</tr>
<tr>
<td>[Fe(dctpy)₂][BF₄]₂</td>
<td>2.080(2)</td>
<td>2.272(1)</td>
<td>111.4(1)</td>
<td>4.1(1)</td>
</tr>
<tr>
<td>[Fe(decdqp)₂][BF₄]₂</td>
<td>2.087(1)</td>
<td>2.302(1)</td>
<td>112.8(1)</td>
<td>5.7(1)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Structural data obtained at 295 K from reference. <sup>10</sup> Data for [Fe(dctpy)₂][BF₄]₂ and [Fe(decdqp)₂][BF₄]₂ obtained at 120 K.

The steric strain is partially alleviated by the ligand twisting about the inter-ring C-C bonds. In the right-hand image of Figure 6.5, it is possible to see the lack of co-planarity between the two quinolinyl moieties. The dihedral angle between the planes of each quinolinyl moiety in the horizontal ligand is 33.5(1)°, a significant distortion from what would normally be a more planar ligand. The other ligand is twisted less but is still distorted from planarity to 13.7(1)°. In general, these structural parameters show substantial strain and similar geometric deviations to those observed in other Fe(II) bis-6,6''-dihaloterpyidyl complexes. A holistic view of the geometric parameters in Table 6.1 indicates that [Fe(decdqp)₂]<sup>2+</sup> has an even greater degree of interligand steric strain than [Fe(dctpy)₂]<sup>2+</sup>. In conclusion, the magnetic susceptibility and crystallographic data provide compelling evidence that coordination of the decdqp and dqp ligands maintains steric bulk around the metal center to enforce a quintet geometry.
Figure 6.5. Ellipsoid plots of the crystal structure of the iron-containing complex in [Fe(decqdp)₂](BF₄)₂ at the 50% probability level from two distinct points of view. Gray = C, blue = N, white = H, red = O, and orange = Fe.

6.4. Lowering the Energy of the MLCT Transition in [Fe(dqp)₂]²⁺ and [Fe(decqdp)₂]²⁺

A second stated goal for designing this ligand set was to reduce the energy of the ⁵MLCT ← ⁵GS transition to red-shift the visible absorption of these chromophores relative to those discussed in Chapters 3-5. Figure 6.6 shows UV-vis spectra of [Fe(dqp)₂]²⁺ and [Fe(decqdp)₂]²⁺ compared to [Fe(dctpy)₂]²⁺. Evidence in Chapter 3 showed that the reddest feature (> 400 nm) is the ⁵MLCT ← ⁵GS and that intra- and interligand features dominate below 400 nm.⁶¹¹ Visible absorptivity, primarily due to the MLCT transition, is clearly greater for [Fe(dqp)₂]²⁺ and [Fe(decqdp)₂]²⁺ than for [Fe(dctpy)₂]²⁺. We suspect this is largely due to the significantly red-shifted MLCT transitions in the dqp-type Fe(II) complexes. [Fe(dqp)₂]²⁺ and [Fe(decqdp)₂]²⁺ may also have slightly more absorptive MLCT transitions, although direct comparison is difficult due to the overlap of ligand-based transitions with the MLCT transition in [Fe(dctpy)₂]²⁺. A red shift across the series of complexes is also seen in the ligand-based transitions. The red-shifting of both bands is likely due to the same effects: greater LUMO delocalization due to the
additional ring of the quinolinyl moiety and electron-withdrawing substituents lowering the LUMO energy.

Figure 6.6. UV-vis spectra of \([\text{Fe(dqp)}_2]^{2+}\) and \([\text{Fe(decdqp)}_2]^{2+}\) taken at room temperature in acetonitrile.

Electrochemistry results largely support the conclusions of the electronic absorption data. Cyclic voltammetry data for \([\text{Fe(dctpy)}_2]^{2+}\), \([\text{Fe(dqp)}_2]^{2+}\), and \([\text{Fe(decdqp)}_2]^{2+}\) are provided in Table 6.2. The oxidation of \([\text{Fe(decdqp)}_2]^{2+}\) was not observed in the acetonitrile solvent window. It is possible that it has been shifted to even higher potentials than in \([\text{Fe(dctpy)}_2]^{2+}\) due to poor \(\sigma\) donation and poor metal-ligand orbital overlap. In \([\text{Fe(dqp)}_2]^{2+}\), oxidation occurs at a lower potential than in \([\text{Fe(dctpy)}_2]^{2+}\), but it was found to be irreversible in the experiment. Increasing the scan speed up to 500 mV/s did not alter the irreversibility. This irreversibility could be due to ligand loss in conjunction with the 3+/2+ oxidation. Characterization of the solution following bulk electrolysis may allow for identification of the degradation product. We stress that irreversibility in cyclic voltammetry does not necessarily indicate instability of the MLCT state. In the MLCT state the proximity of the reduced ligand and oxidized metal center may serve to
limit any degradation and the timescale is significantly shorter for electronic excitation than the cyclic voltammetry experiment.

Table 6.2. Cyclic Voltammetry Data versus SCE for \([\text{Fe(dqp)}_2]^{2+}\) and \([\text{Fe(decdqp)}_2]^{2+}\)

<table>
<thead>
<tr>
<th>complex</th>
<th>(E_{1/2} \text{ (V)}^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe(dctpy)}_2]^{2+})</td>
<td>1.60 -0.83 -1.17</td>
</tr>
<tr>
<td>([\text{Fe(dqp)}_2]^{2+})</td>
<td>1.37(irr.) -0.67 -1.04</td>
</tr>
<tr>
<td>([\text{Fe(decdqp)}_2]^{2+})</td>
<td>─── -0.48 -0.74</td>
</tr>
</tbody>
</table>

\(^a\) Electrochemical potentials in room-temperature acetonitrile with 0.01 M TBAPF\(_6\) and a platinum disc working electrode. Further details about the experimental apparatus can be found in Chapter 2.

Figure 6.7. Oxidative electrochemistry of \([\text{Fe(dqp)}_2]^{2+}\) in MeCN with 0.01 M TBAPF\(_6\) and Fc/Fc\(^+\) internal standard versus a pseudoreference electrode (Ag wire, 0.01 M AgNO\(_3\) in MeCN). Note that the presumed 3+/2+ oxidation shows no return wave, indicating the potential degradation. Further details about the experimental apparatus can be found in Chapter 2.

On the other hand, the first and second reductions (2+/1+ and 1+/0) are reversible in all complexes. In high-spin Fe(II) complexes, the diquinolinylpyridyl ligands exhibit significantly lower reduction potentials relative to previously studied terpyridyl ligands. The lower reduction potentials in \([\text{Fe(dqp)}_2]^{2+}\) and \([\text{Fe(decdqp)}_2]^{2+}\) are better able to accept an electron into the ligand based LUMO where delocalization is greater than in \([\text{Fe(dctpy)}_2]^{2+}\). The lowest reduction potential is observed in \([\text{Fe(decdqp)}_2]^{2+}\) as the attached ethyl carboxylate groups act to withdraw electron density and stabilize the \(\pi^*\) orbital on the ligands. This corroborates the UV-vis data,
which showed the lowest energy MLCT transition for [Fe(decdqp)₂]²⁺. It is likely that the facile ligand reduction is primarily responsible for decreasing this transition energy. The measured 2nd reduction potentials in all three complexes show a similar trend as the 1st reduction potentials. Finally, the values provided here for [Fe(dqp)₂]²⁺ agree with the values determined previously by Bonomo et al. using an alternate experimental method.²

Three additional reductions beyond the neutral complex were observed in [Fe(dqp)₂]²⁺ by Bonomo et al. culminating in [Fe(dqp)₂]³⁻. The ability of this type of complex to store five charge equivalents was also observed by Marin et al. in [Ru(decdqp)₂]²⁺ where cyclic voltammetry measurements showed five reversible reduction waves, but an irreversible oxidation.⁴ Given these precedents, it is not surprising that multiple reduction peaks are also observed for [Fe(decdqp)₂]²⁺ (Fig. 6.8). Compared to its Ru(II) analogue, [Fe(decdqp)₂]²⁺ exhibits some peculiarities. Four reversible reduction waves were observed within the solvent window (acetonitrile with 0.1M TBAPF₆). However, between the second and third well-defined waves, there is a muted cathodic response combined with a sharp anodic peak in the reverse scan. It is possible that this is due to a slow adsorption/plating onto the electrode surface (cathodic current) followed by the analyte being rapidly stripped off in the reverse wave (anodic current). This effect is not seen at potentials below -1.2 V versus 0.01 M Ag/AgNO₃ (Fig. 6.8). Further electrochemical testing in other solvents or with a different working electrode could eliminate this behavior.
Figure 6.8. Cyclic voltammograms of [Fe(decdeq)₂]²⁺ in MeCN with 0.01 M TBAPF₆ versus a pseudoreference electrode (Ag wire, 0.01 M AgNO₃ in MeCN). Further details about the experimental apparatus can be found in Chapter 2.

6.5. Charge Localization in [Fe(dqp)₂]²⁺ and [Fe(decdeq)₂]²⁺

In Chapter 5, it was hypothesized that charge localization on segments of the ligand which are poorly coupled to the metal may be helpful in extending the lifetime. This is the impetus for attaching ethylcarboxylate groups to the quinolinyl moieties where the Fe-N bond distances are longer: 2.302(1) Å compared to 2.087(1) Å for the pyridyl Fe-N bonds (Table 6.1). Electrochemical and spectroscopic evidence showed that the quinolinyl moieties have lower energy π* orbitals than the pyridyl moiety presumably due to increased delocalization across
both rings. The energy of the quinolinyl $\pi^*$ orbital should be lowered even further by attaching resonance-withdrawing groups, which should result in increased electron density on these moieties in the $^5$MLCT state.

Using the singly-reduced zinc(II) complex computational model that was detailed in Chapter 5, the approximate charge distribution in the MLCT excited state can be modeled using spin density plots. The computational results confirm that additional spin density lies on the lower energy quinolinyl rings (Table 6.3 and Figure 6.9). While only 50% of the additional spin density lies on the terminal pyridines in dctpy there is 58% on the terminal quinolines in dqp, and 74% in decdqp. This is an indication that in the MLCT excited state, both the increased ring size and the ester groups contribute to drawing charge density away from the central pyridine where the Fe-N bond is shortest and coupling to the metal center is strongest. Note that this is different to the results for [Fe(mc-dctpy)$_2$]$^{2+}$ highlighted in Chapter 5 where substitution increased the electron density on the central pyridine in the reduced ligand and we measured diminished MLCT lifetimes despite favorable electronic effects.

![Figure 6.9. Selected structures showing DFT spin density results for [Zn(MeCN)$_3$(L)]$^+$ where L = dctpy, 4'-COOH-dctpy, and decdqp.](image-url)
Table 6.3. DFT Spin Density Results for [Zn(MeCN)₃(L)]⁺ for dqp, decdqp

<table>
<thead>
<tr>
<th>Ligand (L)</th>
<th>Central Pyridine</th>
<th>Terminal Rings</th>
</tr>
</thead>
<tbody>
<tr>
<td>dctpy</td>
<td>48%</td>
<td>50%</td>
</tr>
<tr>
<td>4’-COOH-dctpy</td>
<td>58%</td>
<td>34%</td>
</tr>
<tr>
<td>dqp</td>
<td>39%</td>
<td>58%</td>
</tr>
<tr>
<td>decdqp</td>
<td>25%</td>
<td>74%</td>
</tr>
</tbody>
</table>

We’ve now shown that [Fe(decdqp)₂]²⁺ should be an improved chromophore. While maintaining the high-spin ground state, the MLCT transition has been significantly red-shifted to increase visible light absorption and electron density in the excited state resides primarily on the terminal rings where longer Fe-N bonds may reduce coupling to the metal center. The lower energy and selective charge localization should result in longer MLCT lifetimes.

6.6. MLCT Lifetimes and Photophysical Picture for [Fe(dqp)₂]²⁺ and [Fe(decdqp)₂]²⁺

The TA spectra for the quinolinyl complexes show qualitative features similar to those observed in the other high-spin iron(II) complexes discussed throughout this manuscript. Again, there is a sharp absorption feature in the near UV and a broad, weaker excited-state absorption in the visible. The decay of these features can be modeled well with two components: a blue-shift of the sharp peak at early times and a slower decay of the spectrum to zero. These two components have been previously assigned as the thermalization of the excited state and relaxation to the ground state (⁵,⁷MLCT → ⁵GS), respectively.⁶,¹¹ A deeper comparison of the spectral differences for these quinolinyl-containing complexes will be published at a future time upon collection of additional TA data sets.¹² Table 6.4 shows the extracted time constants for the two processes in [Fe(dqp)₂]²⁺ and [Fe(decdqp)₂]²⁺.
Table 6.4. Time Constants for the Thermalization ($\tau_1$) and MLCT Excited-State Relaxation ($\tau_2$) of Fe(II) bis-(diquinolinylpyridyl) Complexes Measured in Room-Temperature Acetonitrile

<table>
<thead>
<tr>
<th>complex</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(dctpy)$_2$]$^{2+}$</td>
<td>3.6 ± 0.3</td>
<td>16.0 ± 0.5</td>
</tr>
<tr>
<td>[Fe(dqp)$_2$]$^{2+}$</td>
<td>3.2 $^a$</td>
<td>17.5 $^a$</td>
</tr>
<tr>
<td>[Fe(dedcqdp)$_2$]$^{2+}$</td>
<td>3.2 $^a$</td>
<td>20.1 $^a$</td>
</tr>
</tbody>
</table>

$^a$ These values are only based on a single experiment instead of three independent data sets and are subject to change in a future publication of these experiments.$^{12}$

We were excited to observe increased lifetimes in both Fe(II) diquinolinylpyridyl species and a new record Fe(II) $^{5,7}$MLCT lifetime of 20.1 ps for [Fe(dedcqdp)$_2$]$^{2+}$. This 20.1 ps MLCT excited-state lifetime is 25% longer than the $^{5,7}$MLCT lifetime observed for [Fe(dctpy)$_2$]$^{2+}$ and orders of magnitude greater than the 50-150 fs MLCT lifetime of [Fe(bpy)$_3$]$^{2+}.^{13,14}$ These improved lifetimes reflect a number of effects, and it is difficult to isolate the relative importance of each change. Reducing the relative energy of the $^5$MLCT is thought to be important as shown in strong-field ligand strategies.$^{15-17}$ However, research on [Fe(mc-dctpy)$_2$]$^{2+}$ showed that this does not necessarily work and charge localization may also play a role.

In [Fe(dqp)$_2$]$^{2+}$ and [Fe(dedcqdp)$_2$]$^{2+}$, not only has the $^5$MLCT state energy been reduced, the quinolinyl moiety and electron-withdrawing group substitution on the terminal rings also serve to localize excited-state electron density on the terminal rings where coupling to the metal center is reduced. Overall, the TA data suggest that the effects of both $^{5,7}$MLCT reduction and terminal ring charge localization in the excited state have been successful at extending the excited-state lifetimes when employed in tandem.

In this chapter we have shown how thoughtful manipulations can both improve the visible light absorption properties and extend the MLCT excited-state lifetimes of high-spin iron(II) chromophores. By altering the ligand framework to both lower the $^5$MLCT state energy and shift the electron density to a more weakly coupled part of the $\pi$-system, we achieved the longest Fe(II) $^{5,7}$MLCT lifetimes yet reported. [Fe(dedcqdp)$_2$]$^{2+}$ was found to have the longest
MLCT lifetime at 20.1 ps, a 25% increase from the original high-spin iron(II) complex we studied, [Fe(dctpy)]$^{2+}$. Additionally, this is an example of how molecular design can effect electron density localization in the excited state and influence excited-state dynamics. Also significant for its potential use as a photoredox chromophore, [Fe(decdqp)]$^{2+}$ absorbs across a broader portion of the visible spectrum and has the ability to undergo reversible reduction at very low potentials. These two properties may be important for improving both the possible and efficiency of high-spin Fe(II) chromophores.

6.7. Conclusions on the Overall State of High-Spin Iron(II) Chromophores

Throughout these four chapters (Ch. 3 – Ch. 6) we have explored a new paradigm for producing Fe(II) polypyridyl chromophores with significantly lengthened MLCT lifetimes relative to the prototypical [Fe(bpy)$_3$]$^{2+}$. In this section the possible deactivation pathways will be examined to understand how they might be avoided.

Following the initial excitation in all of the high-spin Fe(II) complexes studied, non-radiative decay back to the ground state is observed at a rate that is likely too rapid to be a direct pathway for states that we assume are nested (5MLCT and 5GS). This led us to invoke the triplet state ($t_{2g}^5 e_g^1$) in Chapter 4 which also agreed with our observations in changing the size of the steric substituent. Decreasing the energy of the 5,7MLCT relative to the 3MC in Chapters 5 and 6 resulted in only limited extension of the MLCT lifetime. An alternate approach would be to raise the energy of the triplet state instead. This has already done this to some extent in the development of high-spin chromophores since the singlet and triplet states must be above the quintet. Utilizing larger halogens seemed to raise the energy of these states further as shown in Chapter 4. However, the lifetime changes were small in moving from F to Cl to Br, and larger
groups are likely to present other problems. With enough steric hindrance, the metal-ligand bonds could be weakened so much that the complex is subject to solvolysis or the homoleptic complex could become four-coordinate to alleviate the steric strain as previously seen in a related Fe(II) complex.\(^\text{18}\) The other approach to raising the \(^3\text{MC}\) energy is to strengthen the ligand field and destabilize the \(e_g^*\) orbitals. However, this would have the effect of raising the \(^5\text{GS}\) to a greater extent it has two electrons in these antibonding orbitals, moving toward a low-spin complex. Therefore, modification of the \(^3\text{MC}\) energy is not the best approach to achieving significant lifetime extension.

In addition to the \(^5\text{GS}\) (\(^5\text{T}\)) and \(^3\text{MC}\) (\(^3\text{T}\)) states, it’s also possible that an excited quintet metal-centered state, \(^5\text{E}\), contributes to the excited-state dynamics. The \(^5\text{E}\) state could provide a non-radiative relaxation pathway since it likely lies in between the \(^5\text{GS}\) and the \(^5\text{MLCT}\). Orbital occupancy diagrams are presented below to illustrate differences in the MC states (Figure 6.10).

![Orbital Occupancy Diagrams](image)

**Figure 6.10.** Example orbital occupancy diagrams to facilitate discussion of the multielectron states.

Earlier work on \([\text{Fe(dqp)}_2]^{2+}\) noted the existence of a weak absorption band at 835 nm that was assigned as \(^5\text{E} \rightleftharpoons ^5\text{T} \) (assuming a pseudo-octahedral geometry).\(^1\) This energy would place the vertical \(^5\text{E}\) state at an intermediate energy between the ground state and the \(^5\text{MLCT}\) state (~540 nm, see Figure 6.6) where it could provide a non-radiative relaxation pathway. However, this will be highly dependent on the curvature of the potential energy surface and the equilibrium metal-ligand bond length. The equilibrium metal-ligand bond length is expected to
be longer for the $^5\text{E}$ state than the $^5\text{T}$ due to the greater occupation of antibonding $e_g^*$ orbitals (Figure 6.10), but it is unknown where a crossing point with the $^{5,7}\text{MLCT}$ surface may exist.

If the $^3\text{E}$ and the $^{5,7}\text{MLCT}$ do cross, we can conceive of two general potential energy surface scenarios for relaxation through the $^5\text{E}$ (Figure 6.11). Either the crossing is in the Marcus normal regime for deactivation through both the $^3\text{MC}$ and the $^5\text{E}$, or relaxation through the $^5\text{E}$ is in the Marcus inverted regime. In the first scenario, the $^{5,7}\text{MLCT}$ energy is still too high and further stabilizing the reduced ligand will lead to longer lifetimes. In the second scenario, since both surface crossings occur at shorter Fe-N bond lengths, it may be necessary to increase the curvature of the $^{5,7}\text{MLCT}$ surface by introducing greater steric hindrance which prevents any metal-ligand bond contraction. In this case, a detailed model of the potential energy surface along which the crossing occurs would be helpful in understanding which motions need to be impeded to prevent the crossing.

**Figure 6.11.** Potential energy surface cartoons displaying the two possible scenarios for the $^5\text{E}$ state depending on its exact energy and curvature. Left: crossing point occurs at longer Fe-N bond lengths; Right: Crossing occurs at shorter Fe-N bond lengths.
6.8. Potential Applications

Aside from looking to further improve the characteristics of the chromophore itself, a system approach may be preferable in which other components act to shuttle charge at rates competitive with the 16-20 ps excited-state relaxation observed for the high-spin Fe(II) complexes. One method for doing this would be to utilize the carboxylate groups on the decdqp ligand as attachment points to a metal-oxide semiconductor with a conduction band below the energy of the $^5\!d\!^7$ MLCT state. Electron injection into bulk semiconductors is known to be quite fast with Wärnmark et al. measuring the rate of electron injection from an iron(II) N-heterocyclic carbene (NHC) complex into a semiconductor at 3.1 ps. In addition, they found a substantial increase in the excited state lifetime from 18 to 37 ps upon immobilizing the dye on a semiconductor substrate. These numbers compare favorably with those measured for [Fe(dcdqp)$_2$]$^{2+}$, which also has carboxylate moieties to provide attachment points to a metal oxide semiconductor. Despite Wärnmark et al. achieving an injection yield of 92%, a significant portion of the injected electrons suffered from ultrafast electron-cation recombination, limiting the overall efficiency of semiconductor dye-sensitization (Figure 6.11). It is unknown whether this would also be an impediment to utilizing these high-spin complexes in such a system, though computational studies provide guidance on how to achieve high injection rates and limit recombination in iron(II) chromophores. If slower recombination rates are achievable, quenching of the oxidized chromophore from a solution species prior to recombination is possible and the injected electron could be used in reductive catalysis schemes.
Lastly, as opposed to injection into a semiconductor, it would also be possible to build a donor or acceptor into the molecule itself. This would similarly avoid the issue of diffusional timescales being longer than the MLCT excited-state lifetime by utilizing a charge separated state instead. Following excitation into the MLCT band with electron density preferentially on one ligand a molecular electron donor covalently bound to a second ligand could reduce the metal center. Indirect evidence suggests that such processes can occur on a picosecond timescale, rapid enough to compete with relaxation in these complexes. A prototypical system might be synthesized by attaching a known donor group such as a tetrathiafulvene to the 4'-position of a dctpy ligand, likely through some sort of bridging group. Such complexes have been synthesized previously in Ru(II) bipyridyl systems where the charge-separated state was found to exhibit a much longer lifetime than the 3MLCT state. A possible example of such a charge-separation complex utilizing a high-spin Fe(II) metal center is shown in Figure 6.13. While synthesizing heteroleptic Fe(II) complexes can be more difficult than synthesizing the related Ru(II) complexes due to the increased lability of many 3rd row transition metals, various examples of such complexes exist in the literature. In these examples, the use of chelating
ligands seems to increase the kinetic inertness of the Fe(II) complex. If this path is to be pursued, further research would be necessary before embarking on such a project to determine the desired thermodynamics for the different processes and the couplings between the different groups.

![Figure 6.13](image)

**Figure 6.13.** Hypothetical complex for creating charge-separated excited states where the decdqp ligand would become reduced and the Donor moiety would become positively charged.

### 6.9. References


Chapter 7

Mechanisms of Cr(III) Photoredox Catalysis


7.1. Introduction and Motivation

In the final chapter, we turn our attention to understanding how a chromium(III)-based photocatalyst works to catalyze radical cation Diels-Alder cycloadditions. Yoon et al. originally developed this application of photoredox catalysis using using [Ru(bpz)_3]^{2+} as the photocatalyst.\(^1\)\(^-\)\(^4\) They showed that with certain diene/dienophile pairs this reaction would not proceed thermally, but would go to completion in an hour at room temperature under visible light illumination (Fig. 7.1).\(^1\)

\[ \text{O} \quad \text{+} \quad \text{X} \quad \rightarrow \quad \text{no reaction} \]

\[ \text{O} \quad \text{+} \quad \text{X} \quad \rightarrow \quad \text{Cycloaddition product} \]

**Figure 7.1.** Thermally-driven versus visible light photocatalyzed Diels-Alder cycloadditions. Figure adapted from Yoon et al.\(^1\)

This is an exciting example of new reactivity which is possible photocatalytically, but cannot be accomplished thermally at temperatures up to 200 °C. The Yoon group went on to explore similar photocatalyzed radical cation Diels-Alder reactions showing the wide
applicability of this reaction scheme.\textsuperscript{3,4} While disagreement about the basic mechanism for this reaction persists with arguments for both photoinitiated\textsuperscript{2} and photocatalytic\textsuperscript{5} pathways, its potential usefulness in enabling thermally inactive [4+2] cycloadditions cannot be overlooked.

However, one drawback of this reaction is that it requires a platinum group metal catalyst, [Ru(bpz)\textsubscript{3}]\textsuperscript{2+}, which presents the same obstacles to scale-up and wide-spread use as discussed in Chapter 1. It would be preferable to use alternate photo-oxidants based on abundant first-row transition metals, which could promote the same reactivity. In order to be successful, the replacement catalyst should have: significant visible absorption; a long-lived excited state to allow sufficient time for diffusion and electron transfer; high electrochemical reversibility upon reduction so that it can accomplish a high number of turnovers; and an excited state reduction potential such that it can match [Ru(bpz)\textsubscript{3}]\textsuperscript{2+}(See Fig. 7.2). In seeking to replicate these parameters with a first-row transition metal complex, we looked toward prior work in our groups on Cr(III) complexes conducted by Tseng and McDaniel et al.\textsuperscript{6} In their investigation of a wide variety of Cr(III) complexes, they measured microsecond excited-state lifetimes, fully reversible reductions at low potentials ($E_{1/2} = -0.7$ to $-0.4$ vs. Fc\textsuperscript{+/−}), and visible light absorption. The excited state reduction potential (3+/2+) was calculated to be between $+1.0$ and $+1.4$ V vs. Fc\textsuperscript{+/−} depending on the tris-diimine framework used. A comparison of photocatalytic parameters for [Ru(bpz)\textsubscript{3}]\textsuperscript{2+} and a representative Cr(III) polypyridyl complex is presented in Figure 7.2. The similarities between the two complexes suggest that a Cr(III) polypyridyl complex would be an excellent candidate to replace [Ru(bpz)\textsubscript{3}]\textsuperscript{2+} in photocatalyzed Diels-Alder cycloadditions.
This hypothesis was initially tested by our collaborators, Stevenson et al.\textsuperscript{9}, when they showed that these photocatalyzed [4+2] cycloadditions proceeded in good yield (88\%) when using [Cr(Ph\textsubscript{2}phen)\textsubscript{3}]\textsuperscript{3+} as the photocatalyst (Fig. 7.3). However, the role of the photocatalyst in the reaction was poorly understood and there were some anomalies. In particular, it was counterintuitive that the presence of oxygen was necessary to obtain high yields (\textit{vide infra}). Interestingly, the Yoon group reported that the [Ru(bpz)\textsubscript{3}]\textsuperscript{2+} catalyzed reaction also suffered from decreased yields under a N\textsubscript{2} atmosphere, but did not report the reason behind this. In the hopes of providing general guidelines for the development of other first-row transition metal photocatalysts and employing this photocatalyst in other reaction schemes, we undertook a variety of mechanistic studies to better understand the role of [Cr(Ph\textsubscript{2}phen)\textsubscript{3}]\textsuperscript{3+} in these reactions.
Figure 7.3. Reaction scheme for the [Cr(Ph₂phen)₃]³⁺ photocatalyzed Diels-Alder cycloaddition of *trans*-anethole and isoprene.

7.2. General Cr(III) Photophysics

In order to investigate the photocatalytic mechanisms of Cr(III) polypyridines, it is first necessary to understand the photophysics of the molecule by itself. The absorption and emission spectra of [Cr(Ph₂phen)₃]³⁺ are shown in Figure 7.4.

![Absorption and Emission Spectra](image)

**Figure 7.4.** Visible absorption and emission spectra for [Cr(Ph₂phen)₃]³⁺ in room-temperature nitromethane. The emission spectrum has been corrected to account for detector sensitivity across the wavelength range monitored.

While there are ligand-based π* ← π and LMCT transitions below 400 nm,⁶,¹⁰ the major visible feature is a broad shoulder that extends slightly beyond 500 nm with a maximum molar absorptivity of ~2500 M⁻¹cm⁻¹. Given the substantial absorptivity, we can rule out any pure chromium-based d-d transitions in assigning the transition.¹¹ However, it has been suggested that
intensity borrowing from LMCT or ligand-based $\pi^* \leftarrow \pi$ transitions and/or spin-spin coupling could substantially increase the absorptivity of a mixed d-d excitation in Cr(III) polypyridines.\textsuperscript{12,13} A second possibility is that the high absorptivities are more consistent with a charge-transfer assignment (MLCT or LMCT). It has been argued for related complexes that LMCT is more likely due to the difficulty of further oxidizing the Cr(III) metal center as would occur in an MLCT state.\textsuperscript{6,10,14} Because of this, the LMCT bands are often assigned to the stronger transitions at bluer wavelengths with the MLCT transitions occurring at higher energies. Overall, assignment of the $\sim$450 nm transition as a coupled d-d and intraligand excitation ($^4$[MC/IL] $\leftarrow ^4$A) seems to be the most likely.\textsuperscript{10,12}

Following excitation of [Cr(Ph$_2$phen)$_3$]$^{3+}$ into the $^4$[MC/IL] band, there is an extremely rapid intersystem crossing into the $^2$E state ($\sim$100 fs in related Cr(III) systems) from which we can observe emission at a peak of $\sim$740 nm (Fig. 7.4 & 7.5).\textsuperscript{6,14–16} [Cr(Ph$_2$phen)$_3$]$^{3+}$ was previously measured to have an emission quantum yield ($\Phi_{em}$) of 0.030(5) and a $^2$E excited state lifetime of 425 $\mu$s in aqueous acidic solution.\textsuperscript{6} This long-lived, low-energy emission is extremely useful as a handle for monitoring the relevant photoexcited state (\textit{vide infra}). Perhaps most importantly for photooxidation, the $3^+*/2^+$ couple for [Cr(Ph$_2$phen)$_3$]$^{3+}$ in the $^2$E state is calculated to be 1.02 V vs. Fc$^+$/Fc, making it a powerful excited-state oxidant and roughly equivalent to [Ru(bpz)$_3$]$^{2+}$. Given this photophysical and electrochemical behavior, it is not surprising that [Cr(Ph$_2$phen)$_3$]$^{3+}$ can act as an efficient photoredox catalyst.
Figure 7.5. Modified Jablonski diagram for relevant transitions in general Cr(III) complexes.

7.3. Cr(III) Photoredox Behavior with Electron-Rich Substrates

Although [Cr(Ph₂phen)₃]³⁺ can photocatalyze a variety of [4+2] cycloadditions with electron-rich alkenes,⁹ the preliminary mechanistic studies have been focused on the representative reaction shown in Figure 7.3. In the initially proposed mechanism for [Cr(Ph₂phen)₃]³⁺ photocatalyzed [4+2] cycloadditions (Fig. 7.6), the Cr(III) photocatalyst was thought to serve two functions. First, the photocatalyst was proposed to oxidize trans-anethole from the long-lived excited state (²E). Second, the resulting reduced catalyst, [Cr(Ph₂phen)₃]²⁺, was proposed to serve as the reductant to form the final [4+2] product. Once the radical cation of the product has been formed, Yoon et al. also hypothesized that a radical chain mechanism could be active for the [Ru(bpz)₃]²⁺ photocatalysis mechanism.²
In order to investigate the photooxidation step of this catalytic cycle, we decided to employ time-resolved photoluminescence spectroscopy (TRPL). In this technique, we excite the sample with a brief laser pulse and monitor the emission intensity as a function of time at a right angle using a 750 nm bandpass filter to select for [Cr(Ph$_2$phen)$_3$]$^{3+}$ emission (See Ch. 2 for experimental details). By fitting the emission intensity over time to a single exponential function, we can extract an excited-state lifetime for the $^2$E state. Since we are selectively observing 750 nm emission, this technique is only sensitive to the Cr(III) molecules in the excited $^2$E state, and not to components or states that do not emit at 750 nm, allowing us to replicate in operando conditions. In order to use this technique to study the hypothesized electron transfer between [Cr(Ph$_2$phen)$_3$]$^{3+}$ and trans-anethole we employ a Stern-Volmer methodology.$^{17}$ In this technique, a known amount of the potential excited-state quencher is added sequentially to a sample of Cr(III) and, if quenching occurs, there is a decrease in the measured excited state lifetime with each addition due to the newly introduced decay pathway: electron or energy transfer from the excited state to the quencher. With this technique we can obtain a quenching rate constant ($k_q$) given by Equation 7.1.

Figure 7.6. Initially proposed mechanism for Cr(III) photocatalyzed [4+2] cycloadditions as described by Stevenson et al.$^9$
\[ \frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q] \]  

**Equation 7.1.**

Where \( \tau_0 \) is the excited-state lifetime in the absence of quencher and \([Q]\) is the concentration of the quencher. By plotting \( \tau_0/\tau \) versus \([Q]\), and fitting the data with a line, we can find \( k_q \) by dividing the slope by \( \tau_0 \).

With this technique in hand, we investigated the quenching of \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) by *trans*-anethole using TRPL and Stern-Volmer analysis. At increasing concentrations of *trans*-anethole, we see that the emissive lifetime of \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) decreases rather dramatically and that all of these curves can be fit well by single exponential decay function (Fig. 7.7). This suggests that our photoexcited catalyst is colliding with the quencher and an energy or electron transfer is occurring. When the TRPL data is replotted in a Stern-Volmer plot (Fig. 7.8), we obtain a linear relationship between \([Q]\) and \( \tau_0/\tau \) (Equation 7.1) allowing us to extract a quenching rate constant of \( 9.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \). We expect that this is within an order of magnitude of the diffusion limit, since previous studies have measured the diffusion-limited \( k_q \) at \( 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \) for oxygen in aqueous solution and *trans*-anethole’s larger size should lead to slower diffusion.\(^{17}\) This efficient quenching suggests that photoinduced electron transfer is a kinetically competent pathway for the overall reaction mechanism and could explain why the reaction proceeds rapidly and efficiently. However, this experiment does not differentiate between energy transfer and electron transfer; further justification is necessary.\(^{17}\)
Figure 7.7. Raw TRPL data showing emission of [Cr(Ph₂phen)_3]^{3+} in room-temperature nitromethane in air at various concentrations of trans-anethole. Single exponential fits of each data set are shown as black dashed lines.

Figure 7.8. Stern-Volmer plot for the quenching of [Cr(Ph₂phen)_3]^{3+} by trans-anethole in room-temperature nitromethane. The line of best fit is given by \( y = 12.49x + 1.65 \) (\( R^2 = 0.999 \)). \( k_q \) is 9.5 x 10^8 M^{-1}s^{-1}.
Additional evidence is consistent with electron transfer being the quenching mechanism. First, excited-state electron transfer is thermodynamically feasible for this catalyst and substrate at approximately +0.22 V. Conversely, it is unlikely that energy transfer to the triplet would be possible due to the low energy of the $^2E$ state (~1.6 eV). Second, a series of chromium(III) catalysts with similar $^2E$ energies were found to have dramatically different quenching rate constants when combined with various substrates that correlated with their different excited state oxidation potentials (vide infra). Third, we observe a buildup of the reduced form of the catalyst, [Cr(Ph$_2$phen)$_3$]$^{2+}$, when we eliminate the catalyst turnover pathway (Section 7.4). All three of these observations are consistent with an electron transfer quenching mechanism.

To ensure that the findings for [Cr(Ph$_2$phen)$_3$]$^{3+}$ and trans-anethole were general, a wider scope of Cr(III) photocatalysts and substrates were investigated. Two catalysts, [Cr(bpy)$_3$]$^{3+}$ (bpy = 2,2’-bipyridine) and [Cr(dmcbpy)$_3$]$^{3+}$ (dmcbpy = 4,4’-dimethylcarboxylate-2,2’-bipyridine), were studied which have excited state reduction potentials of ($E_{1/2}^{3+/2+}$) vs. Fc$^+/Fc$ of 1.08 and 1.44 V, respectively. A series of molecules similar to trans-anethole were investigated as substrates and are pictured in Table 7.1 with their measured electrochemical potentials of oxidation, $E_{1/2}^{+/0}$ (Table 7.1). These substrates were chosen to provide a range of potentials spanning nearly one volt while being structurally similar so as to limit unanticipated steric or kinetic effects.
Table 7.1. Substrates for Quenching Studies and their Oxidation Potentials

<table>
<thead>
<tr>
<th>compound</th>
<th>$E_{1/2} M^{+/0}$ (V) vs. Fe$^{3+}$/Fe$^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Chemical Structure]</td>
<td>+1.00</td>
</tr>
<tr>
<td>![Chemical Structure]</td>
<td>+1.65</td>
</tr>
<tr>
<td>![Chemical Structure]</td>
<td>+0.80</td>
</tr>
<tr>
<td>![Chemical Structure]</td>
<td>+0.70</td>
</tr>
<tr>
<td>![Chemical Structure]</td>
<td>+1.26</td>
</tr>
</tbody>
</table>

All scans were performed using a platinum disc working electrode at 100 mV/s scan rates in nitromethane solutions containing 0.1 M TBAPF$_6$ and in the presence of oxygen. These potentials were determined by Robert F. Higgins at Colorado State University.\(^{18}\)

Linear Stern-Volmer plots were acquired for all substrates with each catalyst. The extracted $k_q$ values are plotted in Figure 7.9 for each photocatalyst versus the measured oxidation potential of the substrates. With all catalysts, the measured quenching rate constant increases with alkenes that are easier to oxidize. Furthermore for a given substrate, the quenching rate constants for the catalysts are ordered according to their excited state reduction potential: [Cr(dmcbpy)$_3$]$^{3+}$ (+1.44 V), [Cr(bpy)$_3$]$^{3+}$ (+1.08 V) and [Cr(Ph$_2$phen)$_3$]$^{3+}$ (+1.02 V).\(^{6}\) All photocatalysts seem to approach a limit of $\sim 4 \times 10^9 \text{M}^{-1}\text{s}^{-1}$, and it is expected that this is the diffusion-limited regime. The data is consistent with Rehm-Weller behavior\(^{19}\) where the
quenching rate constant is correlated with $\Delta G$ for the electron transfer process. This relationship indicates that an electron transfer mechanism is operative since all catalysts have very similar $^2E$ energies. Additionally, it suggests that in order to optimize the photocatalyzed reactions, judicious choice of photocatalyst is important since quenching rate constants can vary substantially for different Cr(III) catalysts.

![Figure 7.9. Measured quenching rate constants for three Cr(III) catalysts with five substrates plotted versus the oxidation potential of each substrate. The substrates and their oxidation potentials are provided in Table 7.1.](image)

**7.4. The Role of Oxygen**

The initial publication on [Cr(Ph2phen)$_3$]$^{3+}$ photocatalyzed [4+2] cycloadditions (see Fig. 7.3 and 7.6) noted that oxygen was necessary for reactivity but was did not provide a mechanistic reason why it was necessary.$^9$ On a related note, Yoon et al. found that excluding oxygen substantially reduced their yield from 98% to 46%.$^1$ This observation for the [Cr(Ph2phen)$_3$]$^{3+}$
catalyzed reaction is counterintuitive as it was already known\textsuperscript{20} that oxygen can quench the \(^2E\) state of other Cr(III) chromophores via an energy transfer pathway to form singlet oxygen according to the reaction:

\[ ^2[\text{CrL}_3]^{3+} + ^3\text{O}_2 \rightarrow ^4[\text{CrL}_3]^{3+} + ^1\text{O}_2 \]

We established that this pathway is operative for \([\text{Cr(Ph}_2\text{phen})_3]^{3+}\) in CH\(_3\)NO\(_2\) by measuring a decrease in the lifetime of the \(^2E\) state from 440 \(\mu\)s to 13 \(\mu\)s when samples were prepared in ambient oxygen as opposed to inside a N\(_2\)-filled glovebox. Therefore, the presence of oxygen opens up a deactivation pathway for the photocatalyst, which should significantly slow down the reaction. In the full reaction, the opposite effect was observed.

To test if the presence of oxygen affects the initial electron-transfer step, the quenching of \([\text{Cr(Ph}_2\text{phen})_3]^{3+}\) by \textit{trans}-anethole in both ambient and air-free conditions was investigated. In both of these experiments linear Stern-Volmer plots were observed, albeit with drastically different slopes (Fig. 7.10, top). However, by replotting the y-axis as \(1/\tau\) instead of \(\tau_0/\tau\) in order to account for the much shorter \(\tau_0\) in the presence of O\(_2\) (Fig. 7.10, bottom), we can see that the behavior as a function of quencher concentration is nearly identical. The determined value of \(k_q\) for \textit{trans}-anethole is the same regardless of whether oxygen is present: \(9.4 \times 10^8\) M\(^{-1}\)s\(^{-1}\) for the degassed sample and \(9.5 \times 10^8\) M\(^{-1}\)s\(^{-1}\) in ambient O\(_2\). These results are significant because they suggest that oxygen plays no role in the initial electron transfer between the Cr(III) chromophore and the alkene, but confirms that oxygen can quench the excited chromophore through an energy transfer pathway. Together, these observations still point to oxygen being detrimental to reactivity.
Figure 7.10. Oxygen dependence of the emission quenching of [Cr(Ph₂phen)₃]³⁺ by trans-anethole in room-temperature CH₃NO₂, showing Stern–Volmer behavior (τ₀/τ versus quencher concentration, top) and normalized to initial lifetime (1/τ versus quencher concentration, bottom). By plotting 1/τ, the quenching rate constant (kₚ) is equal to the slope: 9.4 × 10⁸ M⁻¹s⁻¹ degassed, 9.5 × 10⁸ M⁻¹s⁻¹ ambient O₂. The data are fit to a linear function using least-squares methodology.

In the continuing investigation of oxygen’s role in these reactions, it was noted that running the reaction in a nitrogen atmosphere resulted in a visible color change. In ambient conditions, the solution remained a vibrant yellow, but without oxygen, the reaction solution became a deeper brown with a brown precipitate forming over time (Fig. 7.11)
Figure 7.11. Photographs of the initial reaction mixture (left) and after 24 hours of irradiation in a nitrogen atmosphere (right).

We decided to further investigate this visible color change by monitoring the air-free reaction by UV-vis spectroscopy. The visible absorption increased throughout the length of the forty hour experiment, consistent with the qualitative observation of a darkening of the solution. The results of this experiment are plotted as a difference spectrum in Figure 7.12 (blue trace).

We can replicate the salient features of the spectrum as the formation of one equivalent of the reduced species, [Cr(Ph₂phen)₃]²⁺, for the loss of every five equivalents of [Cr(Ph₂phen)₃]³⁺. The brown solid that precipitates over the course of the experiment is likely to be a Cr(II) degradation product due to the enhanced lability of the that species relative to the Cr(III) complex. In contrast, in the presence of oxygen, there is only a subtle loss of [Cr(Ph₂phen)₃]³⁺ with no concurrent growth in features attributable to [Cr(Ph₂phen)₃]²⁺ nor any appearance of an insoluble brown solid. These spectra strongly suggest that oxygen serves to regenerate the catalyst. When oxygen is absent, the concentration of the reduced catalyst builds up, some of which falls out of solution as the brown precipitate. Based on the spectra (Fig. 7.12) we estimate that for every five reduced catalysts, four of them degrade or precipitate.
Figure 7.12. Electronic absorption difference spectrum after a 40 hour photoreaction in which oxygen was excluded (Experimental) and a simulated spectrum consisting of the growth of [Cr(Ph₂phen)₃]²⁺ and loss of [Cr(Ph₂phen)₃]³⁺ in a 1:5 ratio.

Although it was found that oxygen is critical for catalyst regeneration, ground state oxygen (³O₂) is not a sufficiently strong oxidant to reform [Cr(Ph₂phen)₃]³⁺ from its reduced state.¹⁸ An alternate mechanism has been proposed based on computational results which is shown in Figure 7.13.

![Figure 7.13. Computationally determined free energies for reactions relevant to the mechanism. Full experimental details are available elsewhere.](image_url)
In the computationally supported pathway, the reduced Cr catalyst is re-oxidized by $^1\text{O}_2$, which is always being produced via the energy transfer pathway described previously. In the oxidation step to reform $[\text{Cr(Ph}_2\text{phen)}_3]^{3+}$, superoxide ($\text{O}_2^-$) is also formed. $\text{O}_2^-$ is a strong enough reductant to reduce the radical cation product produced from the $[4+2]$ cycloaddition, completing the catalytic cycle. Combining the computational results with the experimental data leads to the proposed mechanism (Fig. 7.14).

**Figure 7.14.** Proposed mechanism for Cr(III) photocatalysis of $[4+2]$ cycloadditions.

In the proposed full mechanism, the Cr catalyst is photoexcited and undergoes ISC to the $^2\text{E}$ state from which it can either collide with $\text{O}_2$ or the alkene to undergo energy or electron transfer, respectively. Under constant illumination, a steady-state population of $^1\text{O}_2$ will build up. The reduced catalyst, $[\text{Cr(Ph}_2\text{phen)}_3]^{2+}$, produced from electron transfer can be oxidized by singlet oxygen to form $\text{O}_2^-$ while regenerating the ground state photocatalyst. Meanwhile, the radical cation alkene can perform a $[4+2]$ cycloaddition with a diene (formally a $[4+1]$ process due to the cation) which is then reduced to the final product by the previously produced superoxide. Although this mechanism is complex, simpler pathways that do not involve excited
state or reduced oxygen are not thermodynamically feasible. Finally, the radical propagation
pathway (shown in gray in Fig. 7.14), while thought to be the preferred pathway for
ruthenium(II) photocatalysts,\(^2\) is not thought to occur for this system due to computational and
actinometrical studies described elsewhere.\(^1^8\)

### 7.5. Chromium Photocatalysis with Electron-Poor Substrates

Interestingly, it was shown that \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) can also catalyze reactions with
electron-poor substrates for which a direct electron transfer step is not thermodynamically
feasible.\(^2^3\) 4-methoxychalcone (Fig. 7.15, \(E^{+/0} = 1.65\) V vs. Fc\(^+\)/Fc) was shown to undergo a
\([4+2]\) cycloaddition with isoprene (when by catalyzed \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) under illumination) even
though the photocatalyst is not thermodynamically competent as a photo-oxidant (\(E^{3+/2+} =
+1.02\) V vs. Fc\(^+\)/Fc). The thermodynamic parameters here suggest that an electron-transfer
mechanism is not viable for the electron-poor case. This is further confirmed by dynamic
quenching experiments of \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) by 4-methoxychalcone which measure \(k_q = 2 \times 10^6\)
M\(^{-1}\)s\(^{-1}\); nearly 500x smaller than the rate constant measured with \(\text{trans}\)-anethole (Fig. 7.16).

![Figure 7.15. Reaction scheme for the \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) photocatalyzed Diels-Alder cycloaddition of 4-methoxychalcone and isoprene.](image)

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163
Figure 7.16. Stern-Volmer plot for the quenching of \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) by 4-methoxylchalcone in room-temperature nitromethane. The line of best fit is given by \(y = 0.0315x + 0.982\) (\(R^2 = 0.998\)). \(k_q\) is \(2 \times 10^6\) M\(^{-1}\)s\(^{-1}\).

Despite this greatly reduced quenching rate constant, the reaction proceeds to completion in a similar amount of time — Stevenson et al. reported an 80% isolated yield after 16 hours irradiation\(^2\) versus 88% isolated yield after 27 hours for \(\text{trans-anethole}\).\(^9\) With the greatly reduced quenching rate constant, the overall reaction would be expected to be much slower since much of the photoexcited catalyst would be intercepted by oxygen prior to interaction with the substrate. This further suggests that the electron-poor reaction must proceed through an alternate mechanism. Furthermore, switching the catalyst to \([\text{Cr(dmcbpy)}_3]^{3+}\), a superior excited state oxidant, resulted in lower yields and slower reactivity despite a greatly enhanced quenching rate constant: \(k_q = 6.0 \times 10^8\) M\(^{-1}\)s\(^{-1}\) (Fig. 7.17). It seems as though \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) can instead utilize some alternate pathway to catalyze the reaction.
Figure 7.17. Stern-Volmer plot for the quenching of $[\text{Cr(dmcbpy)}_3]^{3+}$ by 4-methoxychalcone in room-temperature nitromethane. The line of best fit is given by $y = 42.495x + 1.296$ ($R^2 = 0.999$). $k_q$ is $6.0 \times 10^8 \text{M}^{-1}\text{s}^{-1}$.

Since the electron-transfer mechanism appears to be inoperative, alternate pathways were investigated. In particular, it was hypothesized that some ground state association is possible between 4-methoxychalcone and $[\text{Cr(Ph}_2\text{phen)}_3]^{3+}$ which could allow efficient energy or electron transfer, but would not be observed with TRPL. A possible association phenomenon was observed using NMR where the shifting of $[\text{Cr(Ph}_2\text{phen)}_3]^{3+}$ peaks was observed with titration of 4-methoxychalcone. If the two molecules are associated prior to irradiation, it is possible to have either electron- or energy-transfer that would not be observed in the TRPL experiments. Since TRPL is restricted to a specific emission wavelength, the technique is not able to detect any processes of an association complex in which the absorption or emission wavelength changes substantially. In order to investigate this possibility, we undertook static quenching experiments which monitor the emission spectrum as a function of quencher concentration. Gathering a broader emission spectrum allows for the observation of changes in the spectral shape that would be expected if different species were emitting (e.g. an association complex) and the observation
of a loss in integrated emission intensity due to non-emissive species (e.g. the association complex or quenching from another excited state). Figure 7.18 presents emission spectra from successive additions of 4-methoxychalcone to a solution of \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) in nitromethane.

**Figure 7.18.** Emission spectra from successive additions of 4-methoxychalcone to a solution of \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) in room-temperature nitromethane. Blue trace: \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) only; red, green, and black traces: increasing concentrations of 4-methoxychalcone. The concentration of \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) is constant in all experiments.

From the emission spectra we notice that the spectral shape is largely constant throughout the range of quencher concentrations and the emission intensity decreases as the \([4\text{-methoxychalcone}]\) increases. The spectral shape is indicative of \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) \(2\text{E}\) emission as seen in Figure 7.4. We see a slight increase in the emission between 650 and 695 nm which can be attributed to a small amount of emission directly from 4-methoxychalcone and can be replicated in pure samples of 4-methoxychalcone. Although the shape is constant, the emission intensity clearly decreases as the concentration of quencher increases. This is indicative of some quenching of the excited state by either a collisional or associative mechanism. When the quenching rate constant is calculated using this static emission data we find \(k_q = 2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}\),
in excellent agreement with the time-resolved experiment. Since both static and time-resolved experiments are in close agreement, there is no evidence for an associative quenching mechanism within the limits of these experiments. The observed quenching in both experiments can be attributed to a collisional mechanism.

Despite having neither associative quenching nor substantial collisional quenching, the \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) catalyzed 4-methoxychalcone cycloaddition reactions proceed at a reasonable rate (\textit{vide supra}). While the mechanism is not yet understood, we can hypothesize a potential pathway that is consistent with our current evidence. It’s possible that following the photoexcitation of \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\), formation of a state consisting of a doublet metal center and a triplet ligand is possible. An energy-transfer process could then allow for the creation of a triplet excited-state substrate, effectively photosensitization of the substrate. Computational studies suggest that the ligand and substrate triplet energies are similar and that low energy states exist for the complex in which the ligand has triplet character.\(^{24}\) This particular aspect of the work is ongoing and will be presented in an upcoming manuscript.\(^{24}\)

### 7.6. Conclusions

We’ve shown that this family of Cr(III) catalysts can be used to photocatalyze [4+2] cycloadditions using a variety of substrates. Substrate choice affects the mechanistic pathway and \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) in particular opens up unique reactivities. This is an example of utilizing a first-row transition metal catalyst to replace a platinum group metal analogue. While the reaction pathway for electron-poor substrates is poorly understood, further experimentation and modeling will likely provide new insights. It seems as though \([\text{Cr(Ph}_2\text{phen)}_3]^{3+}\) may be unique among both Ru(II) and Cr(III) catalysts in promoting reactions with electron-poor substrates.
We believe association unique to \([\text{Cr(Ph}_2\text{phen})_3]^{3+}\) may play a significant role in opening up alternate pathways with unique isomeric mixtures.\(^{24}\) It is unknown whether any sort of association interactions similar to those for \([\text{Cr(Ph}_2\text{phen})_3]^{3+}\) can be replicated in other catalyst designs, but if so, it may present a new design principle for future photoredox catalysts in addition to the standard consideration of thermodynamic potentials.

### 7.7. References


Bibliography


