

Spectroscopic Characterization of Electronic and Magnetic Relaxation Phenomena in Molecular Systems

Thesis by

Ryan Dillon Ribson

In Partial Fulfillment of the Requirements

for the Degree of Doctor of Philosophy

CALIFORNIA INSTITUTE OF TECHNOLOGY

Division of Chemistry and Chemical Engineering

Pasadena, CA

2022

(Defended April 8, 2022)

© 2022

Ryan Dillon Ribson
ORCID: 0000-0002-3755-5777

Sou pequenininho...

... mas eu vou chegar

- O Areia

Acknowledgments

It's a long road, and no one walks it alone. I've had the immense pleasure to work with and be inspired by so many people during my time at Caltech, and it's hard to put into words the impact that has had on my life and my career. First, I will thank my adviser, Prof. Ryan Hadt, who has given me the ability to explore diverse research interests and has supported me through and through. I would not be graduating if it weren't for you. I also owe so much to Prof. Theo Agapie, who was an immense mentor to me in my time here at Caltech. He pushed me to be critical and hardworking and to reach beyond my comfort zones to learn and think deeply. I would also like to thank Profs. Jonas Peters and Julie Kornfield, members of my committee, for their continued advice and support.

I'd like to thank some of the outstanding graduate students, postdoctoral scholars, and undergraduates I've overlapped with in the Agapie group, including Dr. Guy Edouard, Dr. Kyle Horak, Dr. Justin Henthorn, Dr. Davide Leonetti, Prof. Joshua Buss, Dr. Marcus Low, Dr. Jessica Sampson, Dr. Heui Beom Lee, Dr. Chris Reed, Dr. Nate Hirscher, Dr. Charlie Arnett, Dr. Gyeongshin Choi, Prof. Graham De Ruiter, Prof. Zhiji Han, Dr. Alejo Lifschitz, Dr. Siti Riduan, Dr. Arnaud Thevanon, Prof. Gwen Bailey, Prof. Manar Shoshani, Angela Shia, Anna Scott, Meaghan Bruening, Sam Xiong, Gavin Heim, Linh Le, and Mike He. I'd also like to thank those whom I've overlapped with in the Hadt lab, including Dr. Alec Follmer, Dr. Gautam Strocio, Dr. Daniel Bim, Dr. Brendon McNicholas, Ruben Mirzoyan, Jaron Tong, David Cagan, Kaitlin Luedecke, Nathanael Kazmierczak, Chris Totoiu, Wren Steifel, Kate Benson, Nate Lopez, and Grace Chen.

Dr. Gyeongshin Choi was my first mentor in graduate school and taught me the ins and outs of Schlenk line chemistry. Dr. Jay Winkler, Dr. Brian Sanders, and Dr. Oliver Shafaat all helped me to do experiments in BILRC and helped me in some of my first experiences running laser experiments. Hopefully, these were the first of many more to come. Dr. Mike Takase and Larry Henling provided incredible support in the crystallography center. Dr. David Vander Velde helped me run and troubleshoot numerous NMR experiments. Dr. Paul Oyala has been an incredible collaborator, running the EPR center here, and an incredible trivia partner.

Dr. Meaghan Deegan, Dr. Nina Gu, Dr. Matthew Chalkley, Dr. Javier Fajardo Jr., and Dr. David Schuman, thank you all for being friends and giving advice. It was incredible to start in a cohort with such amazing people.

Guy, I couldn't be the Batman, but I will always remember the chats, the jokes, and the advice that you gave me early on that has helped carry me through to the end. Chris, my first neighbor in Pasadena, I miss the hikes and adventures. You had my back at times when I was feeling so far down on myself, and I can't tell you how grateful I am for that.

Katie, thank you for margaritas, but most importantly thank you for your inquisitive and passionate spirit in the lab. We need more people in science like you, and I'm so excited to see what you do. Gautam, it felt like we were brothers in the Hadt lab. You were my first collaborator, and submitting that first paper together was a feeling I'll never forget. I miss getting the chance to grab beers, but I'm sure we'll have the opportunity again soon.

Manar, I can't tell you how much you've helped me. You were always there to talk, and your patience, kindness, and creativity I am still learning from today. You welcome people with

open arms and help to create the kind of community in science and beyond that's worth striving for. Can't wait to get to visit you in Texas.

Alec, wings and rings baby. You've always been willing to dig deep with me on the science, include me in your ideas and questions, and seek my advice, even if I didn't think I was capable myself. You are genuine, welcoming, and will stand up for what you think is right, and I've learned so much from just being around you. You've been a teacher and a brother to me through all this.

Jamie, you are the best roommate imaginable. Thank you for all the advice, help, and friendship you have given to me (and all the fried chicken, too). You're going to have to love Parsnip double for me when I'm gone. To Vera, Muito Tempo, and the rest of the Capoeira Batuque Pasadena crew, you took in a wounded wolf cub years ago, and I cannot repay the joy, kindness, and community you all welcomed me with. Thank you.

Finally, I'd like to thank my family. Mom and Dad, you have always been behind me, even if I sometimes made you worry. Cory and Danie, you always kept me connected and tethered. And Haley and Mochi, visiting home was always such a bright spot out of the year made even brighter by the two of you. I would have achieved nothing if it were not for all of you. I love you.

Thesis Abstract

The thesis herein describes the application of time-resolved spectroscopic techniques to the understanding of a variety of electronic and magnetic relaxation phenomena in molecular systems. Chapter I presents the techniques and theory behind transient absorption spectroscopy and electron paramagnetic resonance spectroscopy, which are two tools that are used throughout the thesis. Chapter II recounts the study of singlet fission in a series of bipentacene dipyrrolyl pyrrolides, including HDPP-Pent, $\text{Li}_2(\text{DPP-Pent})_2$, and KDPP-Pent. Using transient absorption and kinetic modeling, we found that deprotonation and metal coordination induced a change in the rate of singlet fission (~ 7 fold increase going from HDPP-Pent to $\text{Li}_2(\text{DPP-Pent})_2$) and ultimate triplet yield. Chapter III details the study of the temperature-dependent magnetic relaxation studies of $S = 1/2$ spin systems copper (II) phthalocyanine (CuPc) and vanadyl phthalocyanine (VOPc). Although the spin-lattice relaxation time (T_1) of CuPc is greater than that of VOPc at low temperatures (< 30 K), the CuPc T_1 's decline more substantially with temperature than those of VOPc, which we attribute to the increased spin-orbit coupling constant of Cu over V. Ultimately, the phase memory times (T_2) are T_1 -limited in CuPc by 150 K, whereas room temperature coherence is observed in VOPc. In Chapter IV, 2,9-dialkyl substituted 1,10-phenanthroline complexes of Cu(I) are studied computationally to assign entatic energies to the steric contributions attributed to the ligand that dictate the electrochemical and photophysical properties of the complexes. We performed experimental validation of reduction potential, low-temperature emission bandwidth and excited state relaxation energies, and $^3\text{MLCT}$ lifetimes to support the computational work. In Chapter V, we present ongoing work toward the characterization of triplet and triplet pair states generated via singlet fission in HDPP-Pent, $\text{Li}_2(\text{DPP-Pent})_2$, and KDPP-Pent

by time-resolved electron paramagnetic resonance spectroscopy in collaboration with Drs. Jens Niklas and Oleg Poluektov. Finally, in Chapter VI, we present data collected toward the photophysical characterization of a series of Ni(II) 2,2'-bipyridine aryl halide complexes synthesized by David Cagan, which are relevant for photochemical transformations. We provide supporting materials for Chapters II, III, and V in Appendices A, B, and C, respectively.

Published Content and Contributions

Ribson, R. D.; Choi, G.; Hadt, R. G.; Agapie, T. “Controlling Singlet Fission with Coordination Chemistry-Induced Assembly of Dipyridyl Pyrrole Bipentacenes.” *ACS Cent. Sci.* **2020**, *6*, 2088 – 2096. <https://doi.org/10.1021/acscentsci.0c01044>

R.D.R. synthesized the dipyridyl pyrrole bipentacene ligand framework HDPP-Pent following a route developed by G.C., synthesized the Li and K complexes of the ligand, carried out all steady-state and time-resolved spectroscopies, performed all data analysis presented in the paper, and wrote the manuscript.

Follmer, A. H.; Ribson, R. D.†; Oyala, P. H.; Chen, G. Y.; Hadt, R. G. “Understanding Covalent versus Spin–Orbit Coupling Contributions to Temperature-Dependent Electron Spin Relaxation in Cupric and Vanadyl Phthalocyanines.” *J. Phys. Chem. A.* **2020**, *124*, 9252 – 9260. <https://doi.org/10.1021/acs.jpca.0c07860>

R.D.R. contributed equally to the manuscript with A.H.F., preparing the diamagnetically diluted polycrystalline samples of the $S = \frac{1}{2}$ systems, characterizing with powder XRD, performing CW and pulsed EPR experiments, performing data analysis, and participating in writing the manuscript.

Strocio, G. D.; Ribson, R. D.; Hadt, R. G. “Quantifying Entatic States in Photophysical Processes: Applications to Copper Photosensitizers.” *Inorg. Chem.* **2019**, *58*, 16800 – 16817. <https://doi.org/10.1021/acs.inorgchem.9b02976>

R.D.R. synthesized a series of Cu(I) bis-phenanthroline complexes and characterized them by cyclic voltammetry, low temperature luminescence, and steady-state and time-resolved optical absorption spectroscopy to support the theoretical findings of the paper. R.D.R. also helped prepare figures and edit the manuscript.

Table of Contents

Acknowledgments	iv
Preface	vii
Thesis Abstract	viii
Table of Contents	x
List of Figures	xiv
List of Equations	xx
List of Tables	xxii
Chapter I – Introductions	1
Introduction	2
Transient Absorption	3
Spin Hamiltonian	16
Electron Paramagnetic Resonance Spectroscopy	29
Chapter II – Singlet Fission in Coordination Complexes of Dipyrrolyl Pyrrole Bipentacenes	41
Introduction	42
Synthesis and NMR Characterization	45
Analysis of NMR Data	47
Steady-State Absorption and Emission	49
Time-Resolved Luminescence	51
Emission Analysis	51
Transient Absorption Spectroscopy – HDPP-Pent	52
Kinetic Modeling	54

Triplet Yield Estimation – HDPP-Pent	55
Analysis of Singlet Fission in HDPP-Pent	56
Li ₂ (DPP-Pent) ₂ and KDPP-Pent	56
Comparisons Within the DPP-Pent Series	59
Comparison to Previously Reported Bi- and Polypentacenes	61
Conclusion	63
Chapter III – Temperature Dependent Electron Spin Relaxation in Cupric and Vanadyl	
Phthalocyanines	69
Introduction	70
Results	74
Orientation Dependence of T ₁ and T _m in VOPc	75
Frequency Dependence of T ₁ and T _m in VOPc	76
Temperature Dependence of T ₁ and T _m in VOPc	78
Orientation Dependence of T ₁ and T _m in CuPc	80
Frequency Dependence of T ₁ and T _m in CuPc	82
Temperature Dependence of T ₁ and T _m in CuPc	84
Discussion	85
Conclusions	89
Chapter IV – Entatic Effects on the Photophysical Processes in Copper Photosensitizers	
	93
Introduction	94
Experimental Results	96
Synthesis of [Cu(mmp) ₂][PF ₆]	96
Cyclic Voltammetry	97
77 K Luminescence Experiments	98
Steady-State and Transient Absorption Spectroscopy	101
Computational Results	102
2,9-Alkyl Substituted Copper(I) Bis-phenanthrolines	102

Entatic Contributions and Cu(I/II) Reorganization Energies	110
Entatic Contributions and Cu(I/II) Metal-to-Ligand Charge Transfer Relaxation	114
Entatic Contributions and the Cu(I/II) Metal-to-Ligand Charge Transfer Energy Gap	116
Discussion	117
Conclusion	121
Chapter V – Time-Resolved Electron Paramagnetic Resonance Spectroscopy on HDPP-Pent, Li₂(DPP-Pent)₂, and KDPP-Pent	126
Introduction	127
Time-Resolved EPR Spectroscopy	128
Results	130
Li ₂ (DPP-Pent) ₂	130
HDPP-Pent	137
KDPP-Pent	141
Discussion and Summary	146
Chapter VI – Ultrafast Transient Absorption Spectroscopy on Ni 2,2'-bipyridine Aryl Halide Complexes	149
Introduction	150
Results	151
Ni(tBu-bpy)(o-tolyl)Cl	151
Ni(COOCH ₃ -bpy)(o-tolyl)Cl	155
Ni(tBu-bpy)(mesityl)Br	162
Discussion and Summary	164
Appendix A – Experimental Methods and Supplementary Figures for Chapter II: Singlet Fission in HDPP-Pent, Li₂(DPP-Pent)₂, and KDPP-Pent	167

Appendix B – Experimental Methods and Supplementary Figures for Chapter III: Magnetic Relaxation in CuPc and VOPc	238
Appendix C – Triplet Pair Spin Operators and Spin Hamiltonian	264
Curriculum Vitae	284

List of Figures

	Page
Chapter I –	
1.1: General schematic for transient absorption spectroscopy	4
1.2: Generalized Jablonski diagram denoting processes observed via transient absorption and example	7
1.3: Diagram of ultrafast transient absorption spectrometer	8
1.4: Plot of cross-phase modulation at various wavelengths observed in a THF blank	11
1.5: Vector representation of spin angular momentum	17
1.6: Vector representation of electron magnetic dipole moment	21
1.7: Zeeman splitting of the eigenstates of an $S = \frac{1}{2}$ spin system	30
1.8: Vector representation of the net magnetization of a spin system at equilibrium and the effect of a perpendicularly applied magnetic field in the rotating frame	32
1.9: Representations of T_1 and T_2 relaxation	35
1.10: Visualization of the Hahn echo pulse sequence	36
Chapter II –	

2.1: Scheme of singlet fission	42
2.2: Synthesis of HDPP-Pent and MDPP-Pent complexes	45
2.3: Structural data supporting dimeric $\text{Li}_2(\text{DPP-Pent})_2$ and monomeric KDPP-Pent assignments in solution	47
2.4: Steady-state absorption and emission spectra and time-resolved luminescence data of the DPP-Pent series	50
2.5: Visible femtosecond transient absorption spectra of HDPP-Pent	52
2.6: Visible femtosecond transient absorption spectra of $\text{Li}_2(\text{DPP-Pent})_2$ and KDPP-Pent	57
Chapter III –	
3.1: Bloch sphere representation of an arbitrary qubit superposition state	70
3.2: Spin densities and qualitative 3d-orbital energy diagrams for VOPc and CuPc and Zeeman splitting of the M_s sublevels of an $S = \frac{1}{2}$ system	74
3.3: Fits of the temperature dependence of $1/T_1$ vs temperature	77
3.4: X- and Q-band EDFS of CuPc/ZnPc and temperature dependent T_1 behavior of 1:1000 and 1:100 dilutions at X- and Q-band	82
3.5: Comparison of T_1 and T_M times vs. temperature at 329 and 1188 mT at X- and Q-band	83

3.6: Comparison between X-band T_I 's and T_M 's vs. temperature for VOPc and CuPc	86
Chapter IV –	
4.1: $^3\text{MLCT}$ excited state structural distortion in Cu(I) bis-phen complexes	95
4.2: Cyclic voltammograms of $[\text{Cu}(\text{phen})_2][\text{PF}_6]$, $[\text{Cu}(\text{dmp})_2][\text{PF}_6]$, and $[\text{Cu}(\text{mmp})_2][\text{PF}_6]$	98
4.3: 77 K Emission spectra and gaussian fittings for $[\text{Cu}(\text{dsbp})_2][\text{PF}_6]$, $[\text{Cu}(\text{dmp})_2][\text{PF}_6]$, and $[\text{Cu}(\text{mmp})_2][\text{PF}_6]$	100
4.4: Extinction coefficient determination for $[\text{Cu}(\text{mmp})_2][\text{PF}_6]$	101
4.5: Femtosecond transient absorption data of $[\text{Cu}(\text{mmp})_2][\text{PF}_6]$	102
4.6: Comparison between experimental and calculated E° 's for phen and 2,9-alkyl substituted Cu(I) complexes	104
4.7: Correlation between experimental E° 's and $\ln(\tau)$'s for bis-phen and 2,9-alkyl substituted Cu(I) complexes	107
4.8: Correlations between $\ln(\tau)$'s and ground state reorganization energies, excited state relaxation energies, and energy gaps for bis-phen and 2,9-alkyl substituted Cu(I) complexes	113
Chapter V –	

5.1: TREPR EDFS of $\text{Li}_2(\text{DPP-Pent})_2$ at 17 and 12 dB collected at 300 ns, 5 μs , and 70 μs	131
5.2: Simulated triplet pair TREPR spectrum of $\text{Li}_2(\text{DPP-Pent})_2$	132
5.3: Simulated triplet TREPR spectrum of $\text{Li}_2(\text{DPP-Pent})_2$	133
5.4: Kinetic traces and fitting for quintet features in the TREPR spectrum of $\text{Li}_2(\text{DPP-Pent})_2$	134
5.5: Kinetic traces and fitting for triplet features in the TREPR spectrum of $\text{Li}_2(\text{DPP-Pent})_2$	135
5.6: Rabi nutation experiments collected on $\text{Li}_2(\text{DPP-Pent})_2$	136
5.7: TREPR EDFS of HDPP-Pent at 17 and 12 dB collected at 5 μs , and 70 μs	138
5.8: Simulated triplet pair TREPR spectrum of HDPP-Pent	139
5.9: Kinetic traces and fitting for quintet features in the TREPR spectrum of HDPP-Pent	140
5.10: Rabi nutation experiments collected on HDPP-Pent	141
5.11: TREPR EDFS of KDPP-Pent at 20 and 14 dB collected at 5 and 100 μs	142
5.12: Simulated triplet pair TREPR spectrum of KDPP-Pent	143
5.13: Kinetic traces and fitting for quintet features in the TREPR spectrum of KDPP-Pent	144

5.14: Kinetic traces for triplet features in the TREPR spectrum of KDPP-Pent	145
5.15: Rabi nutation experiments collected on KDPP-Pent	145
Chapter VI –	
6.1: Transient absorption time traces of Ni(tBu-bpy)(<i>o</i> -tolyl)Cl	151
6.2: Four component model EADS and fitted amplitudes of Ni(tBu-bpy)(<i>o</i> -tolyl)Cl fsTA dataset	153
6.3: Overlay of four component model fit with wavelength cuts of the Ni(tBu-bpy)(<i>o</i> -tolyl)Cl dataset	154
6.4: Steady-state absorption spectrum of Ni(COOCH ₃ -bpy)(<i>o</i> -tolyl)Cl with excitation wavelengths denoted	156
6.5: One component DADS, fitted amplitudes, and overlay of the fit with Ni(COOCH ₃ -bpy)(<i>o</i> -tolyl)Cl dataset	157
6.6: Two component DADS, fitted amplitudes, and overlay of the fit with Ni(COOCH ₃ -bpy)(<i>o</i> -tolyl)Cl dataset	158
6.7: Comparison of fitted rate and time constants for the variable excitation wavelength fsTA datasets on Ni(COOCH ₃ -bpy)(<i>o</i> -tolyl)Cl	160
6.8: Comparison of EADS for the variable excitation wavelength fsTA datasets On Ni(COOCH ₃ -bpy)(<i>o</i> -tolyl)Cl	160

6.9: Power dependence of Ni(COOCH ₃ -bpy)(<i>o</i> -tolyl)Cl ΔA signal	161
6.10: Overlay of time traces at 450 nm collected at variable power for Ni(COOCH ₃ -bpy)(<i>o</i> -tolyl)Cl	162
6.11: Three component model EADS and fitted amplitudes of Ni(tBu-bpy)(mesityl)Br fsTA dataset	163

List of Equations

	Page
Chapter I –	
1.1: Derivation of expression for ΔA for transient absorption	5
1.2: Beer-Lambert equation for transient absorption	13
1.3: Beer-Lambert equation summed over species i	13
1.4: Model equation for global kinetic analysis	15
1.5: Pauli spin matrices $\hat{S}_x, \hat{S}_y, \hat{S}_z$	17
1.6: \hat{S}^2 matrix spin operator	18
1.7: Spin operator commutation relations	18
1.8: Explicit calculation of $[\hat{S}_x, \hat{S}_y]$ commutator	19
1.9: General expression for many electron spin operators	19
1.10: Relationship between magnetic moment and spin angular momentum	20
1.11: Classical expression for the potential energy of a magnetic dipole in an external magnetic field	21
1.12: Zeeman Hamiltonian for an isotropic g value	22
1.13: Zeeman Hamiltonian for anisotropic electron-field interactions	23
1.14: g tensor in its principal frame and under an arbitrary rotation	23

1.15: Expression for the elements of the anisotropic g tensor	24
1.16: Hyperfine Hamiltonian	25
1.17: General expression for an electron-electron interaction Hamiltonian	27
1.18: J and D tensors	27
1.19: Isotropic exchange Hamiltonian	28
1.20: D tensor in its principal frame	28
1.21: Zero field splitting Hamiltonian	29
1.22: Expression for the nutation frequency of a given spin system	33
Chapter III –	
3.1: Expression for the elements of the anisotropic g tensor as derived from perturbation theory	86
Chapter V –	
5.1: Expression for the nutation frequency of a given spin system	129
5.2: Summary of triplet pair spin Hamiltonian terms	130

List of Tables

	Page
Chapter III –	
3.1: Fitting parameters of CuPc and VOPc	79
Chapter IV –	
4.1: Experimental and Calculated E° (V vs. NHE) for 2,9-alkyl substituted bis-phen complexes	105
4.2: Comparisons between excited state lifetimes and calculated ground state reorganization energies, excited state relaxation energies, and energy gaps for 2,9-alkyl substituted bis-phen complexes	111
4.3: Entatic state analyses of Cu(I) bis-phen complexes	119
Chapter VI –	
6.1: Comparison of the rate and time constants obtained from target fitting of the Ni(<i>t</i> Bu-bpy)(<i>o</i> -tolyl)Cl fsTA data	
6.2: Comparison of the two component sequential model fits of the various λ_{ex} experiments on Ni(COOCH ₃ -bpy)(<i>o</i> -tolyl)Cl	