Spectroscopic Characterization of Electronic and Magnetic Relaxation Phenomena in Molecular Systems

Thesis by

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Sou pequenininho…

… mas eu vou chegar

- O Areia

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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 dipyridyl pyrrolides, including HDPP-Pent, Li_2(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 Li_2(DPP-Pent)$_2$) and ultimate triplet yield. Chapter III details the study of the temperature-dependent magnetic relaxation studies of S = ½ 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}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, Li_2(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 = ½ 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.

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