



University
of Victoria

Graduate Studies

Notice of the Final Oral Examination
for the Degree of Doctor of Philosophy

of

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MSc (University of Washington, 2011)
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**“New Organic Chromophores for Metal Complexation: Investigations
into the Synthesis and Photophysics of Thioindigo Diimines,
AzaDIMEs, and their Metal Complexes”**

Department of Chemistry

Tuesday, April 17, 2018
1:00 P.M.
Elliott Building
Room 305

Supervisory Committee:

Dr. Robin Hicks, Department of Chemistry, University of Victoria (Supervisor)
Dr. Cornelia Bohne, Department of Chemistry, UVic (Member)
Dr. Tom Fyles, Department of Chemistry, Uvic (Member)
Dr. Geoff Steeves, Department of Physics and Astronomy, UVic (Outside Member)

External Examiner:

Dr. Michael Wolf, Department of Chemistry, University of British Columbia

Chair of Oral Examination:

Dr. Lisa Mitchell, Department of Anthropology, UVic

Abstract

The synthesis and comprehensive characterization of diamine and diimine derivatives of thioindigo are reported. X-ray crystal structures demonstrate a planar structure for the diimine derivatives and a twisted conformation for the diamines. The diamine compounds absorb in the UV (λ_{\max} 324 nm - 328 nm), and exhibit moderate fluorescence ($\Phi_F = 0.25, 0.045$). A transient triplet state is observed in laser flash photolysis (LFP) experiments, with lifetimes an order of magnitude longer than those of the triplet state of thioindigo. The diimine compounds absorb at longer wavelengths than the diamines (λ_{\max} 495 nm - 510 nm), but are still slightly blue-shifted from thioindigo. The diimines have molar extinction coefficients 17 – 70% higher than thioindigo. The diimine compounds are not emissive, and LFP studies show transient species with microsecond lifetimes. The transient absorption spectra and quenching experiments of the diimines are consistent with *trans-cis* isomerisation about the central double bond.

Mono- and diruthenium hexafluoroacetylacetonate (hfac) complexes of thioindigo-*N,N'*-diphenyldiimine have been prepared. The monoruthenium complex was isolated as a racemic mixture and the diruthenium complexes were isolated as the *meso* ($\Delta\Lambda$) and *rac* ($\Delta\Delta$ and $\Lambda\Lambda$) diastereomers. Extensive structural characterization of the compounds revealed intrinsic diastereomeric differences in the X-ray crystal structures, cyclic voltammograms, and NMR spectra. Variable temperature NMR experiments demonstrated that the *rac* diastereomer undergoes conformational exchange with a rate constant of 8700 sec⁻¹ at 298 K, a behavior that is not observed in the *meso* diastereomer. Ground state optical properties of the complexes were examined, showing that all the complexes possess metal-to-ligand charge transfer (MLCT) absorption bands in the near-infrared (λ_{\max} 689 nm – 783 nm). The compounds do not display photoluminescence in room temperature solution-phase experiments or in experiments at 77K. Ultrafast transient absorption spectroscopy measurements revealed excited states with picosecond lifetimes. Unexpectedly, the transient absorption measurements revealed differences in the transient spectra and disparate time constants for the excited state decay of the diastereomers, which is linked to the conformational changes observed in the NMR experiments.

Investigations into the synthesis of azaDIMEs and azaDicarbazolyls are described.