Notice of the Final Oral Examination for the Degree of Master of Science

of

TIANYI WANG

BSc Hons. (University of Victoria, 2018)

“Towards Bis-benzimidazole Near-Infrared Absorbing and Emitting Dyes”

Department of Chemistry

Friday, February 19, 2021
11:00 A.M.
Conducted Virtually

Supervisory Committee:
Dr. Robin Hicks, Department of Chemistry, University of Victoria (Supervisor)
Dr. Neil Burford, Department of Chemistry, UVic (Member)

External Examiner:
Dr. Jay Cullen, School of Earth and Ocean Sciences, UVic

Chair of Oral Examination:
Dr. Charles Curry, School of Earth and Ocean Sciences, UVic

Dr. Stephen Evans, Acting Dean, Faculty of Graduate Studies
Abstract

A conjugated bis-benzimidazole chromophore is predicted to show absorptions in the near-infrared (NIR) region of the electromagnetic spectrum. However, there are no reports to-date of any NIR absorbing and emitting dyes that based on a bis-benzimidazole structural backbone. This thesis reports recent advancements in the discovery and study of this new class of dyes.

Following literature procedures, the syntheses of bis(benzimidazolyl)methane compounds are successful. An unexpected product isolated during the attempted oxidation of a bis(benzimidazolyl)methane compound using p-chloranil showed intense absorption in the NIR ($\lambda_{\text{max}} = 712$ nm, $\varepsilon = 14600$ L · mol$^{-1}$ · cm$^{-1}$) solubilities in polar solvents like methanol and water, and electrochemical activities. X-ray crystallography, mass spectrometry, and NMR spectroscopy confirmed the connectivity and structure of the product to contain a combination of quinone and benzimidazole moieties, which later revealed to be the core chromophore by computational studies. This unprecedented combination of moieties gave a chromophore that is predicted to absorb in the far-red even without substitution.

Attempts to synthesize boron-based bis-imidazole dyes with N-methylation shed light on the feasibility of the design of such moiety. Considering the additional functionality that could be accessed through the methylation of the labile benzimidazole nitrogen atoms, N-methylated bis(benzimidazolyl)methane precursors were successfully synthesized and fully characterized. Attempts of the boron coordination showed promising signs, as the $^1$H, $^{11}$B, and $^{19}$F NMR spectra showed solid evidence of the successful isolation of the boron chelate. Computational studies of methyl, phenyl, and triazole-substituted boron chelate derivatives projected absorptions in the NIR region. Intense transitions are found to be based on frontier molecular orbitals and differ significantly among the derivatives, predicting substantial tunability of this type of dyes.