



University
of Victoria

Graduate Studies

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

of

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BSc (University of Victoria, 2010)

**“Part I: The Synthesis and Characterization of Scorpionate Ligands for
Lanthanide Complexation for Potential PARACEST Applications**

**Part II: The Synthesis and the Characterization of New and Old Organic
Dyes”**

Department of Chemistry

Friday, April 10, 2015

1:30PM

Engineering/Computer Science Building
Room 130

Supervisory Committee:

Dr. Robin Hicks, Department of Chemistry, University of Victoria (Co-Supervisor)

Dr. David Jay Berg, Department of Chemistry, UVic (Co-Supervisor)

Dr. Cornelia Bohne, Department of Chemistry, UVic (Member)

Dr. Michel Lefebvre, Department of Physics & Astronomy, UVic (Outside Member)

External Examiner:

Dr. Tim Storr, Department of Chemistry, Simon Fraser University

Chair of Oral Examination:

Dr. Patti-Jean Naylor, School of Exercise Science, Physical & Health Education, UVic

Abstract

Reported in Chapter 2 of this thesis is the reliable and tolerant synthesis of a small library of pyrazole and triazole heterocycles. This synthesis was achieved in two steps in good yields from the reaction of acetophenone and benzamide derivatives with dimethyl formamide-dimethyl acetal followed by a cyclization with hydrazine. Also reported is the synthesis and characterization of their corresponding scorpionate ligands. Preliminary co-ordination chemistry was done with a variety of lanthanide metals and was studied by standard spectroscopic methods as well as variable temperature ^1H NMR, which revealed that Curie-Weiss behaviour was followed for these complexes in solution. An X-ray crystal structure of a nine co-ordinate ytterbium metal centre with eight nitrogen atom (four pyrazole, four pyridine) donors and one chloride atom was obtained, which may have been a product of decomposition during crystal growth. The bond lengths of this structure were compared with other lanthanide complexes of similar structural motifs. This comparison supported the theory of decomposition as the pyridine nitrogen atom-ytterbium bond lengths were longer than the average ytterbium-nitrogen atom bond length.

Reported in Chapter 4 of this thesis is the synthesis and partial characterization of a new organic dye named perinaphthindigo. Perinaphthindigo was synthesized with adapted Baeyer-Drewson reaction conditions for the synthesis of indigo which involved the treatment of 1,8-nitronaphthaldehyde with acetone under basic conditions, and was found to be an intense green colour in solution. Perinaphthindigo was produced in poor yields, so efforts were undertaken to improve the yields through an alternative two-step synthesis, first between 1,8-nitronaphthaldehyde and nitromethane in a Henry reaction followed by oxidative coupling. The synthesis of perinaphthindigo was adapted so as to structurally modify the final compound, either through incorporation of solubilizing *tert*-butyl groups or bromine atoms for future cross-coupling chemistry. The brominated derivatives of perinaphthindigo were also synthesized in low yields so cross-coupling conditions were scanned on model precursor compounds. The brominated perinaphthindigo compounds were found to have a bathochromically shifted absorbance maximum from the parent perinaphthindigo. This bathochromic shift was more pronounced in our compounds than in the comparison of indigo and 6,6'-dibromoindigo which indicates our compounds are more sensitive to perturbation by substitution.

Reported in Chapter 5 of this thesis is the study of the acid and base chemistry of Nindigo, a previously reported compound. The treatment of Nindigo with a series of strong acids led to an interesting "protoisomerization", or *trans* to *cis* isomerization of the central olefin, with ultimate structural determination through X-ray crystallographic methods. This isomerization was studied through absorbance stopped-flow methods which identified a probable pathway of the isomerization through a neutral, *cis* species. The investigation of neutral Nindigo was undertaken to attempt to identify two peaks which are red-shifted from the π -to- π transition at 586 nm. These two peaks appear at 657 nm and 741 nm and are present in all solvents. The preparative acid chemistry allowed us to assign the first red shifted peak at 657 nm to the cationic species. Aggregation studies showed concentration dependent behaviour of the ratio between the peaks at 586 nm and 657 nm with little effect on the species at 741 nm. In order to probe whether an autoionization process was occurring, variable temperature NMR and UV-Vis experiments were performed which did not provide a definitive answer to the species at 741 nm.