Chiral Transition Metal Molecular Switches: Synthesis and Analysis of 1,1'-Binaphthyl-2,2'-Bis(Dipyrrin)s

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ABSTRACT
This summer I synthesized and characterized chiral 1,1'-binaphthyl-2,2'-bis(dipyrrin)s for use as ligands. Upon complexation of these ligands with Cu(II) and Zn(II), these molecules displayed excitation coupled circular dichroism (ECCD) with exceptionally high molar ellipticities. Further studies into controlled reduction and oxidation of these complexes are ongoing and it is anticipated that these complexes might be useful as molecular switches.

1. INTRODUCTION
• Chiral molecular switches are chiral molecules which can switch between two different oxidation states.
• Molecular switches have generated a lot of interest because of their potential in optical switches, light modulators, and data storage.
• Transition metal complexes are particularly good molecular switches because they can easily switch between two oxidation states when an external electronic potential is applied.
• When these metal complexes change oxidation states, the ligand conformation also changes which can affect the chiroptical properties of the molecule.
• These changes can potentially be monitored by circular dichroism (CD).
• It has been previously reported by the Thompson Group that (R)-binol-2,2'-bis(dipyrrinato) Zn(I) helicates display ECCD with exceptionally high molar ellipticities.
• As well, 1,1'-binaphthyl groups with dipyrrinato substituents have been reported displaying ECCD and being electrochemically active.
• Therefore a ligand derived from 1,1'-binaphthyl and dipyrrinato groups at the 2 and 2'-positions with a redox sensitive transition metal could be a successful candidate for a molecular switch.

REFERENCES

2. SYNTHETIC ROUTE

3. ANALYSIS
a) $^1$H and $^{13}$C NMR Assignments
$^1$H and $^{13}$C NMR zinc complexation-induced shifts ($\Delta \delta$) for phenyl and CF$_{3}$ phenyl Zn(II) complexes.

b) Circular Dichroism (CD)
CD spectroscopy for Zn(II) CF$_{3}$ phenyl and Cu(II) CF$_{3}$ phenyl exhibited similar positive Cotton effects displaying excitation coupled circular dichroism (ECCD) with exceptionally high molar ellipticities.

4. CONCLUSIONS
• Chiral 1,1'-binaphthyl-2,2'-bis(dipyrrin) ligands and their complexes were synthesized and characterized.
• Both ligands studied showed similar chemical shifts and complexation-induced shifts. This indicates very similar conformation(s).
• The Zn(II) and Cu(II) complexes displayed ECCD with exceptionally high molar ellipticities.

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