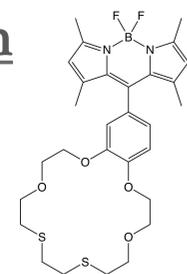
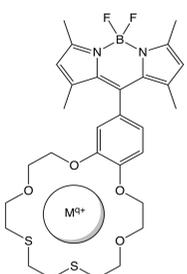


# The Effect of Fluorophore Rotation on the Excited State Energies of BODIPY-Appended Thiocrown Ether

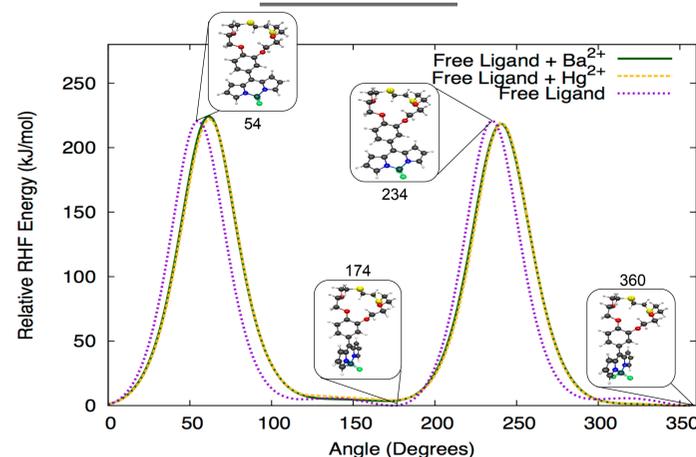
 Alyssa da Costa, Meagan Oakley, Mariusz Klobukowski  
 Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2

## Introduction

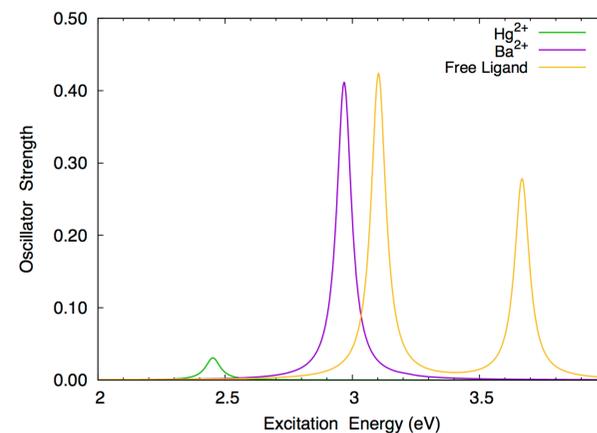
- The detection of toxic heavy metals in various environments is essential.<sup>1</sup>
- This can be done using a chemosensor containing a fluorophore and an ionophore that binds to heavy metals<sup>2</sup>
- BODIPY-appended thiocrown ether (Figures 1 and 2), discovered by Kim and coworkers<sup>3</sup> is one such chemosensor, which selectively binds to mercury (II).
- By examining the excitation energies based on the rotation of the fluorophore, more efficient chemosensors can be designed.
- If a specific rotation provides a greater difference in wavelength absorption in the presence of heavy metals versus the free ligand, heavy metals become easier to detect.
- This project explores the idea of rotation by computing the theoretical excitation energy of the chemosensor in both the ground state and excited states.


**Figure 1.** Structure of BODIPY-appended thiocrown ether

**Figure 2.** Structure of BODIPY-appended thiocrown ether complexed with a heavy metal ion

## Energy Profile of BODIPY Rotation



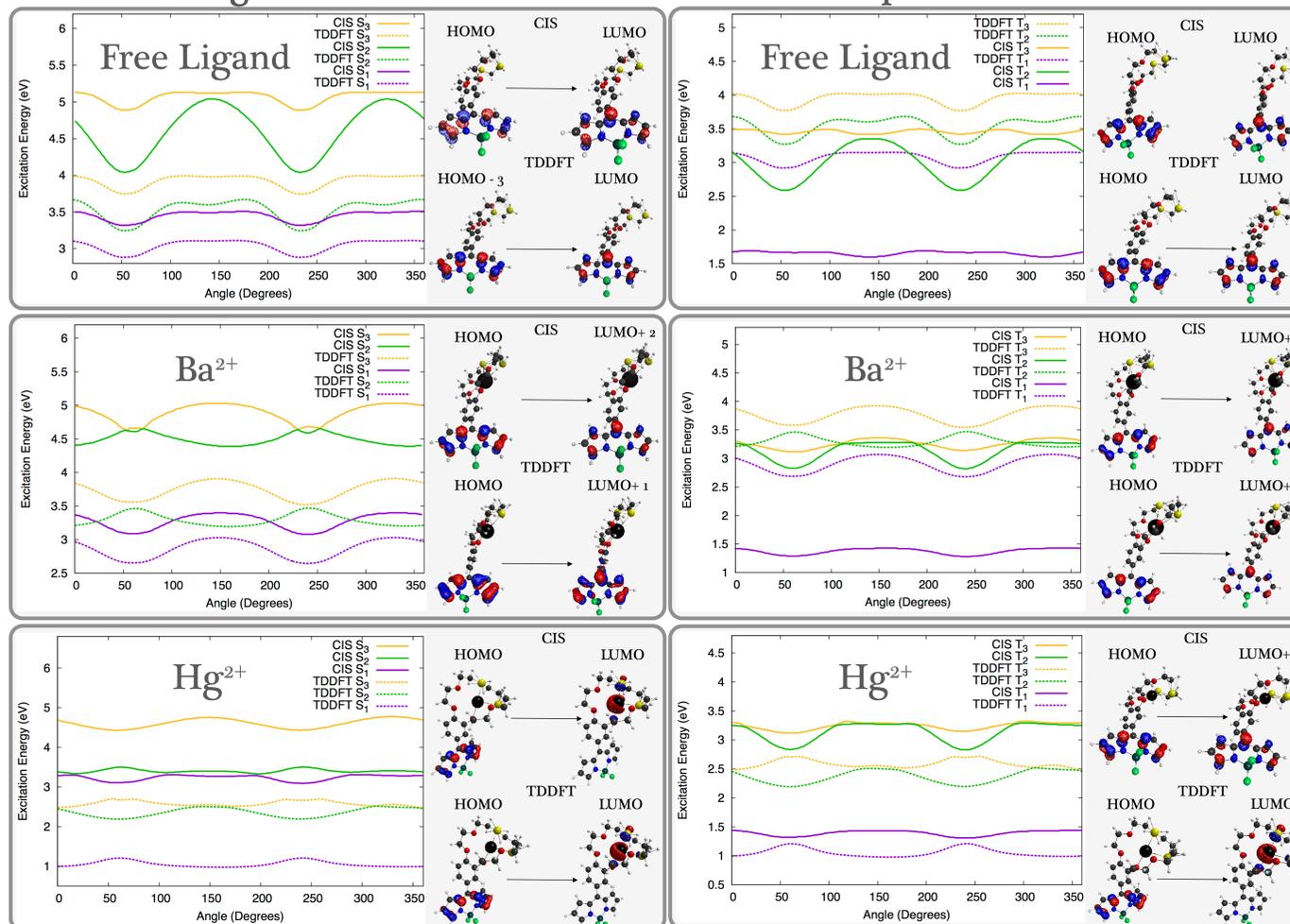
## Electronic Spectra

 TD-CAMB<sub>3</sub>LYP/MCP


## Excitation Energy Profile of Rotation

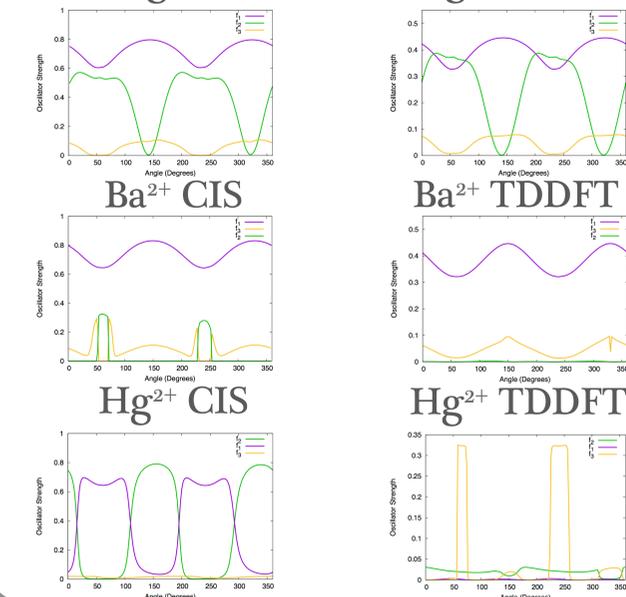
Singlet Excited State

Triplet Excited State



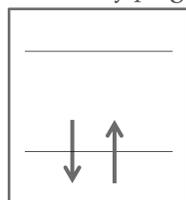
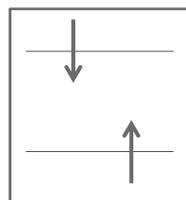
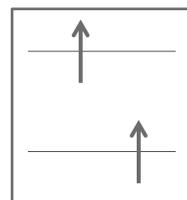
## Oscillator Strength

Free Ligand CIS Free Ligand TDDFT



## Computational Details

- The fluorophore portion of the chemosensor, boradiazaindecene (BODIPY), is rotated in relation to the ionophore portion.
- The energy of the chemosensor is calculated every two degrees using the Restricted Hartree Fock (RHF) method.
- The lowest three singlet and triplet excited state energies (Figures 3-5) were calculated with both interaction method with singles (CIS) and time-dependent density functional theory (TDDFT) with density functional CAM-B<sub>3</sub>LYP as BODIPY rotates.
- We used a pseudopotential basis set called model core potential (MCP), which does not model the core electrons explicitly, and instead uses potentials.
- We use MCP because it increases efficiency while still remaining accurate.
- All calculations were performed using the quantum chemistry program GAMESS.<sup>4</sup>


**Figure 3.** Ground state

**Figure 4.** Singlet excited state

**Figure 5.** Triplet excited state

## Conclusions

- The singlet and triplet excitation energies differ as BODIPY is rotated.
- Excitation energy also changes when a metal ion is complexed with the free ligand, as seen experimentally.
- When excited state energies are calculated using CIS, we have higher excitation energies than from TDDFT.
- We also see a difference in excited state energies with the free ligand compared to the metal complex; where S<sub>1</sub> of the metal complex becomes lower than S<sub>1</sub> of the free ligand.

## Acknowledgements

Special thanks to Dr. Klobukowski and his lab, along with Shakiba Azimi, a Chem 403 student whose work provided the foundation for this research. Also thanks to the Faculty of Science for sponsoring this project, and the WISEST team for the wonderful opportunity. This research was enabled in part by support provided by WestGrid (<http://www.westgrid.ca>) and ComputeCanada (<http://www.computeCanada.ca>).

## References

- Boens, N.; Dehaen, W.; Leen, V. Fluorescent indicators based on BODIPY. *Chem. Soc. Rev.* 2012, 41, 1130-1172.
- Jang, W. D.; Li, J.; Yim, D.; Yoon, J. Recent progress in the design and applications of fluorescence probes containing crown ethers. *Chem. Soc. Rev.* 2017, 46, 2437-2458.
- Kim, H. J.; Kim, S. H.; Kim, J. H.; K, K. W.; Kim, J. S.; Lee, E. H. BODIPY Appended Crown Ethers: Selective Fluorescence Changes for Hg<sup>2+</sup> Binding. *Bull. Korean Chem. Soc.* 2008, 29, 9, 1831-1834.
- "General Atomic and Molecular Electronic Structure System" M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery J. *Comput. Chem.*, 14, 1347-1363(1993).