

Title: Development of novel photoactive cationic zirconocene complexes

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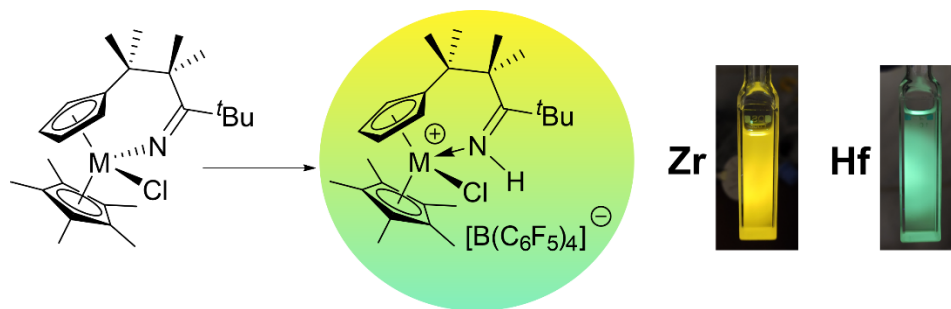
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Abstract: Environmental concerns have brought about an unprecedented demand for sustainable energy sources among which electromagnetic radiation, light, currently dominates. Development of novel light-harvesting compounds and materials is at the forefront of current science, as it is essential to further our technological progress.

This thesis contributes to the field by development of novel photoactive cationic group 4 metallocene complexes stabilized by pendant imine and pyridinyl donor groups, or *N,O*-donor aromatic ligands, as crystalline  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  salts. The complexes are prepared either by protonation of the intramolecularly bound imine moiety by  $\text{PhNMe}_2\text{H}[\text{B}(\text{C}_6\text{F}_5)_4]$  or by chloride ligand abstraction, by  $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4] \cdot 2.5\text{Et}_2\text{O}$  or *in situ* generated  $\text{Et}_3\text{Si}[\text{B}(\text{C}_6\text{F}_5)_4]$ . Prepared compounds were characterized by NMR spectroscopy. Solid state structures of the compounds were determined by X-ray diffraction analysis. The cationic complexes of Zr and Hf exhibited significantly enhanced luminescence which originates from triplet ligand-to-metal ( $^3\text{LMCT}$ ) excited states with lifetimes of up to 62  $\mu\text{s}$  and quantum yields of up to 58% in the solid state, at room temperature. DFT calculations were performed to explain the photophysical properties of the complexes. The complexes were investigated as potential photosensitizers of singlet oxygen (quantum yields of up to 77% in solution) and for applications in photoredox catalyzed reduction of arylhalogenides (reduction of bromopentafluorobenzene proceeded with complete conversion).



Keywords: metallocene complexes, group 4 elements, luminescence, DFT, singlet oxygen, photoredox catalysis, LMCT