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Title Synthesis and Photophysical Properties of Functional Tetracoordinate Boron Containing Organic Compounds

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Abstract:

Over the past few decades, exploring pathways to access the triplet excited states of organic chromophores has been an appealing area of research. In this regard, tetracoordinate boron containing organic compounds have emerged as a fascinating class of luminescent molecules and photosensitizers. Overlap of the empty p-orbital of boron with π- conjugated core in tetracoordinate boron containing organic compounds leads to the delocalization of the electron cloud and planarization of the π -systems thereby resulting in interesting photophysical properties. Boron coordination also results in red shifted absorption and emission as compared to the corresponding chelating units. BODIPYs are renowned boron containing fluorescent dyes with strong and tuneable absorption in the visible region, high thermal and photo-stability and exceptional fluorescence quantum yields, and they have been turned into efficient triplet photosensitizers by appropriate design strategy with strong absorption in the visible to NIR region. A major drawback with BODIPYs is low reactions yields and the precise reaction conditions that are necessary for their synthesis. This issue could be overcome by chelating boron to simple organic ligands. Among them, N,Ochelated salicylideneimine-boron difluoride complexes, popularly known as boranils, are interesting as they can be easily synthesized in good yields via one pot synthesis using simple, commercially available starting materials like amines and aldehydes. This methodology enables the synthesis of a wide variety of molecules whose properties can be easily tuned across the entire range of electromagnetic spectrum with suitable derivatisation. While they are popularly known for their luminescence properties, their photosensitisation properties are largely unexplored to date. Considering these facts, this thesis dissertation is devoted to the design and synthesis of novel tetracoordinate boron-containing organic compounds with the objective of tuning their photophysical properties through systematic variations in their chemical structures. Chapter 1 discusses the importance of triplet states and photosensitized generation of singlet oxygen for applications in various fields. An extensive overview of BODIPYs as photosensitizers has been presented from the literature. Common strategies adopted to achieve populated triplet states with a special focus on halogenation and transition metal complex incorporation in BODIPYs are also discussed. We have also thrown some light on the structural features and the associated photophysical properties of a few boranil derivatives. Chapter 2 describes the synthesis and characterization of appropriately functionalized BODIPY and boranil derivatives. The compounds synthesized include various boron difluoride complexes ranging from heavy metal and transition metal complex incorporated BODIPYs A- C to N,O-chelated salicylideneimine boron difluoride complexes D-G to diiodosalicylideneimine-boron difluoride functionalized polyethyleneimine H.

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