Abstract

Studies on the Use of Label Assisted Laser Desorption/Ionization Mass Spectrometry for Analyte Detection and Garratt-Braverman Cyclization for the Synthesis of Heterocycles

This thesis is divided into two parts- Part A and Part B. Part A includes exploration of Label-assisted Laser Desorption/Ionization (LALDI) MS and it consists of three chapters. Chapter 1 contains a literature survey on the recent progress of LALDI technique. In chapters 2 and 3, LALDI technique has been applied for the selective and specific detection of small molecules having primary amine functionality and metal ions respectively, through a Time of Flight (TOF) mass spectrometric measurement. This technique required a probe which contained a polyaromatic moiety as well as a chelating group targeting the particular small molecules or metal ions. The presence of polyaromatic part helped the ligand-target molecule complex to absorb the laser light and then desorb from the surface. Subsequent ionization led to ions which show up in the TOF detector. By excluding the external matrix, the mass spectrum becomes lot cleaner being free of matrix related peaks and noises. Peaks corresponding to compounds/complexes formed between the analytes and the label are mostly seen in the spectrum. The probe molecules along with few relevant mass spectra are shown in **Figure 1**.

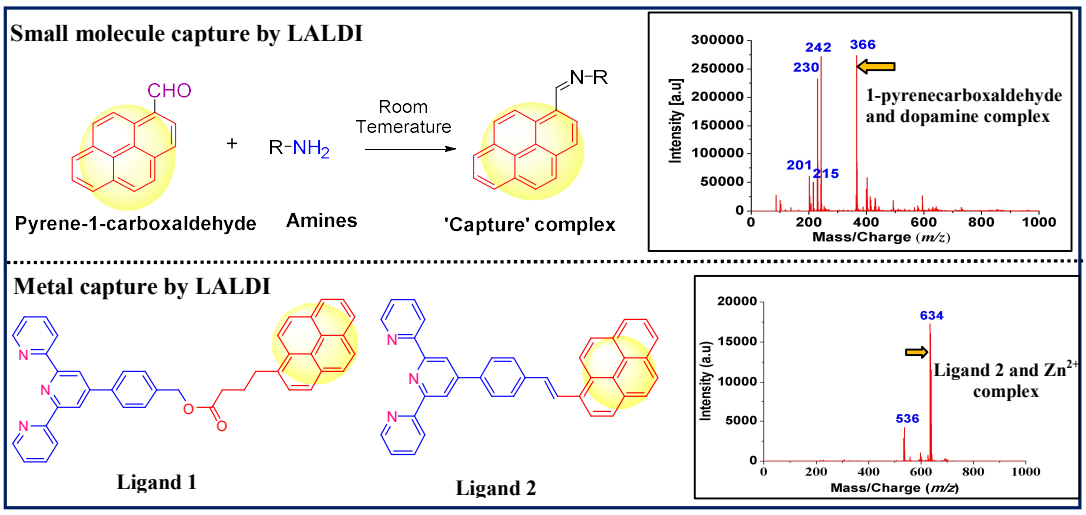
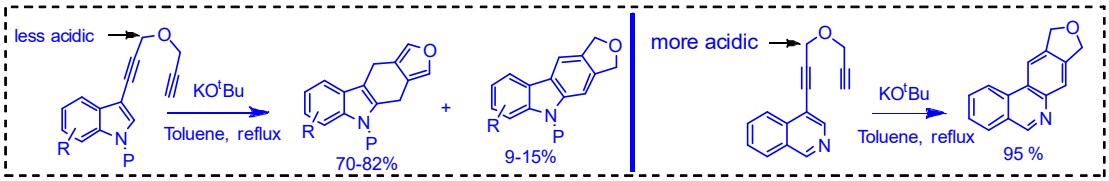


Figure 1: LALDI based detection of small molecules and metal ions

Part B contains studies on reactivities of indole and quinoline/isoquinoline *bis*-propargyl ether system under Garratt-Braverman (GB) cyclization condition (Chapter 4 and Chapter 5). In fourth chapter, a new strategy has been developed to achieve the reaction of *bis*-propargyl ether to follow a diradical pathway under GB cyclization condition. In the process, a methodology for synthesizing 3, 4-furan fused dihydrocarbazole derivatives has been established by tunning the progress of the reaction upto intermediate stage. Some of these dihydrocarbazole derivatives showed good antifungal activity. In chapter 5, a methodology for synthesizing furan fused phenanthridine derivative, the normal GB product, which showed good DNA binding property, has been demonstrated. An explanation for this differential behaviour of the two systems is also included.



Scheme 1: Studies on reactivities of *bis*-propargyl ether derivatives of heterocycles under GB cyclization condition

Keywords: LALDI, Garratt-Braverman cyclization, dihydrocarbazole, phenanthridine, antifungal, DNA binding