ABSTRACT OF THESIS

In the field of chemistry, the design and development of new helical structures has surfaced as an ever-demanding area of science with a scope of building some new molecules and understanding its properties and applications. Helicenes are part of an intriguing class of polycyclic aromatic compounds formed from ortho-fused benzene or other aromatic rings that adopt a helical topology to avoid overlapping of the terminal rings resulting in helically chiral structures. In this way, simple achiral compounds upon forming helix generate helical chirality. The entire focus of our study is on aromatic helices. Nitrogen-containing helicenes belong to the most popular class of enantioenriched helicenes. Carbazole fused heterohelicenes are called as pyrrolohelicenes. Pyrrole-incorporating PAHs are known for remarkable physical properties such as effective hole-transporting ability and bright emission. They have been used to constitute extended π-conjugated systems with a characteristic low oxidation potential.

The main objective of this research work is to synthesize novel helical molecules with fused carbazole rings namely pyrrolohelicenes, expand their structural diversity by selective functionalization of the molecules and to study their properties so that their applications in chiral recognition, asymmetric catalysis, and organic electronics can be explored. The contents of the thesis are mainly divided into two chapters: Chapter 2 unfolds the chemistry of **five-membered pyrrolohelicenes** and Chapter 3 is about the chemistry of **unsymmetrical hepta-helicenes.** Chapter 3 is subdivided into two portions. Chapter 3A deals with the seven-membered helicenes with **unsymmetrical helical scaffold** and Chapter 3B is the discussion about heptahelicenes with **unsymmetrical functionalization.**

C**hapter 2** is subdivided in two parts **Part-I** deals with the synthesis and study **of C-2 substituted pentahelicene** and its functionalization. The synthesis was carried out using oxidative photocyclization strategy. However, the final helicene was found to be labile for racemization so a more sterically crowded pentahelicene was required to be developed. As per literature reports, it was known that a C-1 substituted helicene is more sterically hindered. Hence in **Part-II**, our target was to synthesize **C-1 methyl substituted pentahelicene**. As expected, stereodynamically stable pentahelicene was synthesized. However, a major challenge was to separate the linear regiomer of photocyclization. This was possible by crystallization and repeated column chromatography. Both the angular and linear regiomers were fully characterized by ^{1}H-NMR spectroscopy. After success in this area, its

functionalization was carried out which rendered good quality crystals of the angular regiomer. In order to improve the yield of photocyclization, a blocking group (-CN) was introduced in the helical skeleton which drastically improved the yield of angular regiomer after photocyclization. The photophysical properties of the C-2 and C-1 substituted compounds were investigated and the structural parameters were studied by single crystal XRD analysis and computational data.

Chapter 3 is about the study of pyrrolo[7]helicene and it is also subdivided in two parts. **Chapter 3A** deals with the synthesis and study of **pyrrolo[7]helicene with unsymmetrical helical scaffold**. The synthesis of heptahelicene was carried out as an extension of the pentahelicene. Hence double photocyclization was involved in the entire scheme. The optical properties of the heptahelicene were studied by UV-Vis, fluorescence spectra and the electrochemical properties were studied by CV analysis. The structural parameters were established by single crystal XRD data and computational analysis. The heptahelicene was further functionalized by formylation reaction which rendered two isomers. Both the isomers were characterized by ^{1}H-NMR and SCXRD data. All the compounds were explored for optical properties and resolution was attempted for the formyl derived aza[7]helicenes.

Chapter 3B is about the study of **heptahelicenes with unsymmetrical functionalization.** Various mono and di substituted helicene were synthesized by one-pot Wittig Heck strategy followed by photocyclization. The olefins were also synthesized by separate Wittig and Heck reaction in a sequential method and the overall yield for one-pot and sequential method was compared. One of the derivatives was an ester substituted helicene which was further hydrolysed to render aza[7]helicene carboxylic acid. All the derivatives were well characterized by spectroscopic techniques and screened for optical properties. Molecular recognition study was carried out for the aza[7]helicene carboxylic acid.