
SUMMARY

Porphyrins are tetrapyrrolic macrocycles characterized by a 16-atom inner core with an 18π -electron conjugated pathway, adhering to Hückel's aromaticity rules. Modifying the inner core by either reducing or adding an atom results in contracted or expanded porphyrinoids. Replacing one or more pyrrole units with polycyclic aromatic structures, such as arene or pyridine, yields carba- or pyriporphyrinoids. These modified porphyrinoids are primarily utilized to investigate weak metal-arene interactions and the stabilization of organometallic complexes. This thesis, titled "Synthesis, Spectral, Structural Analyses, Coordination and Binding Studies of Triaryl-Embedded Expanded Porphyrin and Calixphyrin Analogues," is organized into five chapters. The first chapter provides a detailed literature review on carba- and pyri- porphyrins, focusing on structural modifications achieved by substituting pyrrole units with heterocyclic or arene moieties and varying the number of *meso*-carbons. These structural changes give rise to porphyrinoids with unique coordination properties, especially with metal ions. While expanded porphyrins with *para*- or *meta*- connectivity are well explored, polycyclic aromatic hydrocarbons in porphyrins remain underexplored. The second chapter reports on the synthesis, characterization, and coordination chemistry of the protonated form of 2,6-di-*m*-phenylpyridine embedded isosmaragdyrin and its organo-Pd(II) complex. These new compounds show promising potential in stabilizing metal complexes, with their structures confirmed by single-crystal X-ray diffraction. The third chapter discusses the synthesis and spectral properties of two new macrocycles, non-fused hexaphyrin and N-fused hexaphyrin, containing the 2,6-di-*m*-phenylpyridine unit. Hexaphyrins have garnered interest due to their conformational flexibility and unique electronic properties. The chapter outlines how the incorporation of 2,6-di-*m*-phenylpyridine into the macrocyclic structure alters the behavior and properties of these macrocycles. Both macrocycles are characterized using a variety of spectroscopic techniques, and their molecular structures are discussed. The fourth

chapter focuses on calixphyrins, a hybrid of porphyrins and calixpyrroles. These molecules are highly versatile, with potential applications in anion binding, cation coordination, and other areas. The chapter introduces a new (*o-p-o*)-terphenyl embedded calix[2]pyrin(2.2.1.1.1) and its copper(II) complex. The structure of this novel macrocycle is confirmed by single-crystal X-ray analysis, and its metal-ion stabilization capabilities are explored. The chapter provides a deep dive into the molecular structure, showing how the macrocycle achieves both rigidity and flexibility. In the final chapter, a contorted terphenyl-macrocycle hybrid is synthesized, which incorporates higher arene rings into the calix[2]pyrin core. The chapter emphasizes the structural flexibility of this new macrocycle due to sp^3 hybridization in the *meso*-carbons. It also explores its ability to bind fluoride ions, forming a stable complex. The potential for this compound in anion binding and supramolecular assembly is highlighted.