SUMMARY

Porphyrin is a cyclic, planar, and conjugated molecule, where four pyrrole units are linked by four *meso*-carbon atoms and follows Hückel aromatic character. The contracted porphyrins have less than 16 atoms in the core and can be achieved by removing of *meso* or pyrrole units, whereas the expanded porphyrin analogue have minimum 17 atoms in the core and well known for their confirmational plasticity, aromaticity switching, and multi-metal ion insertion in the core. One or more carbocyclic / arene units replace one or more pyrrolic units in the porphyrin skeleton, resulting in a new family of porphyrins known as carbaporphyrins, which are mostly used to research weak metal-arene interactions and organometallic complex stabilization. This thesis is primarily concerned with the synthesis of 1,2-, 1,3-stilbene units and 4′,5′-diphenyl-1,1′:2′,1″-terphenyl moieties placed in contracted and expanded porphyrins. This thesis, organisation including five chapters and entitle "*E*-stilbene imprinted Cyclic diphyrin, Porphyrin, Benzioctaphyrin, and Homocarbaporphyrin dimer: Synthesis, Coordination Chemistry and Aromaticity". The first chapter mainly based on the comprehensive literature survey of porphyrinoids. Chapter second introduced new class of contracted porphyrin and deals with synthesis of *E*-stilbene imprinted cyclic diphyrin and B^{III} ion coordinated fluorescent complex. The three-fold aromatic switching behavior of *ortho*-benzannulated tetraphyrins described in chapter 3. In the freebase form macrocycle adopt near planar confirmation and exhibits $4n\pi$ global paratropic electronic delocalization with antiaromaticity. However, the protonated form manifests a weak diatropic ring current and thus adopts moderate $4n\pi$ Möbius aromatic characteristics. The Rh(I) insertion in the macrocyclic core forms a bis-Rh(I) complex with foldameric nonplanar architecture and η^2-coordination through *meso*-linkages, triggering panchromatic absorption. The chapter 4 outlines Twists and Loops: Exploring Lemniscular

Vinylogous Benzioctaphyrin(2.0.1.0.2.0.1.0), where the macrocycle adopts a lemniscate topology and conformational desymmetrization upon protonation experiment. The chapter 5 demonstrates the development of homocarbaporphyrin dimer by merging two monomeric units of the homocarbaporphyrin through *ortho*-benzannulation at the C2-bridge of each monomer, thereby establishing a fused, double-looped macrocyclic architecture that embodies a Siamese twin structure with nonaromatic nature. Upon protonation and B^{III} insertion in the macrocyclic core, the local π-delocalization within the phenylene units continues to dominate over global conjugation, thereby precluding the onset of macrocyclic aromaticity in bis-B^{III} complex and protonated form.