

CHAPTER 1

Introduction

1.1 Background

Porphyryns are naturally occurring tetrapyrrolic macrocycles that are ubiquitous in nature and often referred to as pigments of life.¹ This is because life depends on many biological processes that are performed or catalyzed by proteins containing porphyrin or its derivatives. For instance chlorophyll containing a reduced Mg(II)-porphyrin, plays a vital role in photosynthesis, which converts light to chemical energy, producing oxygen. This oxygen is transported, stored, and reduced in various ways by heme containing proteins, viz. hemoglobin, myoglobin, hemerythrin etc. in many organisms including mammals. In addition, porphyrins function as an excellent metal-complexing ligand. Therefore, porphyrins remain of fundamental interest to researchers and arguably the most widely studied macrocycle among all ring system present.² Consequently

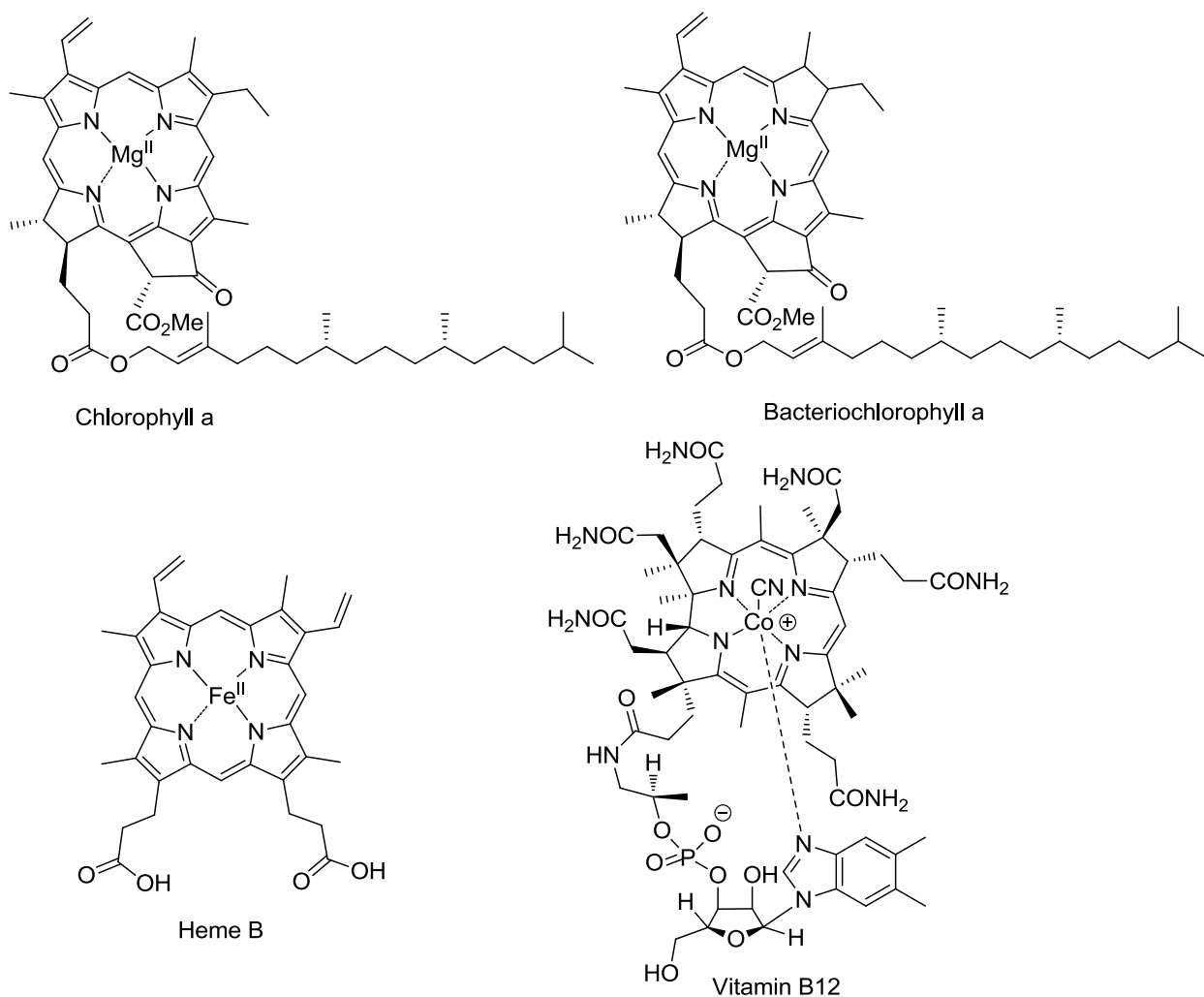


Figure 1.1 Some of the naturally occurring porphyrinoids of biological importance.

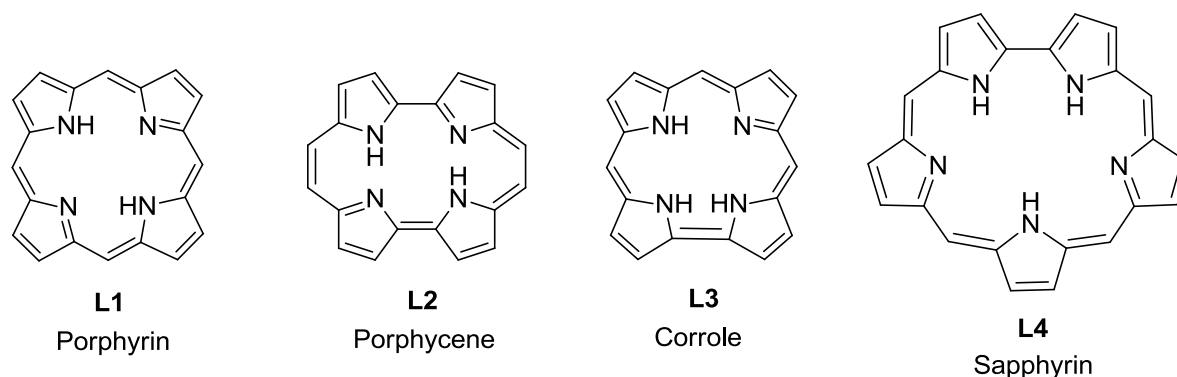


Figure 1.2 Examples of isomeric, contracted and expanded porphyrins.

the rich chemistry of porphyrin stimulates interest among the researcher to study non-porphyrin polypyrrolic macrocycles.³ As a result a new area of research emerged where principal objective is to generate synthetic systems that bear structural resemblance to naturally occurring porphyrins while being chemically quite different. Thus three major direction of research evolved involving synthesis of expanded, contracted and isomeric porphyrinoids (Figure 1.2).

1.2 Contracted and isomeric porphyrins

Among the contracted isomers of porphyrin the corrole **L3** is the most notable one.⁴ Corrole can be considered as an intermediate between porphyrin and corrin, the chromophoric constituent of vitamin B₁₂. First synthesis of corrole was achieved by A. W. Johnson in 1964.^{4a} Free-base corrole, like porphyrin is an 18π aromatic macrocycle. Unlike porphyrin, corroles are strong acids and forms stable anions with aqueous alkali. Corrole also acts as a trianionic ligand and stabilizes metal ions in high oxidation state.^{2a,3b} However, chemistry of corrole remains underdeveloped compared to porphyrin owing to formidable synthetic challenges. In 1999, research group of Zeev Gross reported a facile synthetic route towards stable *meso*-triaryl corrole.⁵ This triggered interest in corrole, which was reflected in large number of scientific reports appeared thereafter describing synthesis of new corroles and their versatile applications including catalysis, dye sensitized solar cell, sensors and medicinal applications.⁶ The most widely studied isomer of porphyrin is the porphycene **L2** reported by Vogel in 1986.⁷ A detail description about this macrocycle is presented in chapter 3 of this thesis.

1.3 Expanded porphyrins

According to definition put forwarded by Sessler in his review paper, an expanded porphyrin is

defined as a macrocyclic compound containing pyrrole, thiophene, furan or other heterocyclic subunit connected directly or through one or more spacer unit in such a way that internal ring pathway contains at least 17 atoms.⁸ The history of expanded porphyrin begins with serendipitous discovery of sapphyrin (**L4**) during the synthesis of vitamin B₁₂ by Woodward and coworkers. He briefly mentioned about the formation of a blue color compound during the synthesis of vitamin B₁₂ at the aromaticity conference in Sheffield, UK, 1966 and subsequently characterized as sapphyrin and published the synthetic detailed in 1983 only.⁹ However, the first authentic work describing synthesis of sapphyrin was published much before by Johnson's group

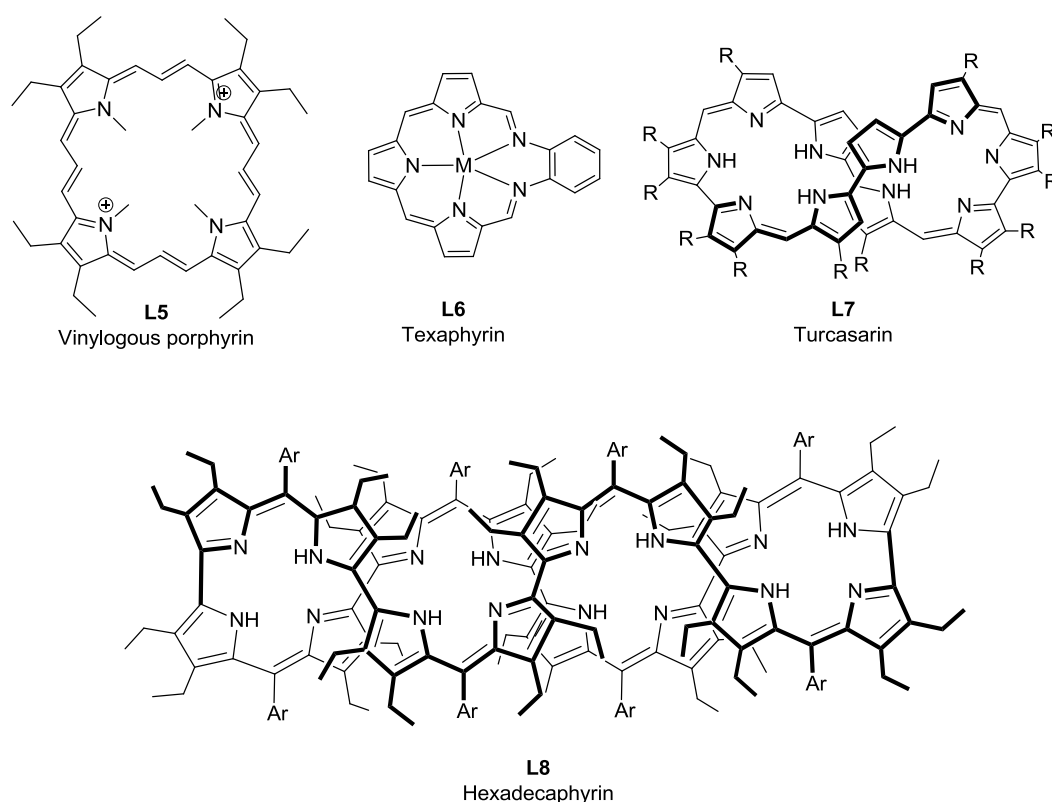


Figure 1.3 Some of the important expanded porphyrins of historical importance.

in 1972.^{9b} In 1990 Sessler and coworkers published a report regarding the improved synthesis of sapphyrin and its unexpected anion binding behavior in the deprotonated state.¹⁰ Further details about this macrocycle is presented in chapter 5 of this thesis.

In the early stage studies of extended π -conjugated system such as vinylogous porphyrins (also known as platyrins), expanded aromatic tetrapyrrolic macrocycles lead to anticipation that

enlargement of the π -conjugation would give rise to unusual physical and chemical properties to the expanded porphyrin. For instance N,N',N'',N'''-tetramethyl[26]porphyrin-(3.3.3.3) **L5** and its tetraoxa derivative shows record molar extinction coefficient ($\lambda_{\text{max}} = 528 \text{ nm}$, $\epsilon = 1.16 \times 10^6 \text{ M}^{-1} \text{ cm}^{-1}$).¹¹

Another noteworthy example in the area of expanded porphyrin is the synthesis of texaphyrins **L6**, a hybrid schiff-base aromatic macrocycle by Sessler and coworkers.¹² Texaphyrin displays diverse metalation chemistry, unlike sapphyrin and other expanded porphyrin. In fact water-soluble Gd(III)-complex of texaphyrin referred to as motexaphin gadolinium (MGd) is a promising anticancer reagent that allows clear MRI contrast.¹²

A very important addition to expanded porphyrin by Sessler group is the serendipitous discovery of turcasarin **L7** during the synthesis of pentapyrrolic macrocycle, the first expanded porphyrin to display figure eight structure both in solid and solution states. Turcasarin is a decapyrrolic 40 π -nonaromatic system that exists in two interconvertible limiting helical conformations.¹³ In 1995 in another report, again through serendipity, Vogel and coworkers synthesized the first octapyrrolic expanded porphyrin, [32]octaphyrin(1.0.1.0.1.0.1.0), during the synthesis of corrole and was found to adopt a chiral figure-eight conformation both in solution and in the solid states.¹⁴ These reports began to attract interest of researchers towards figure eight motifs. Subsequently, it was noticed in general larger expanded porphyrins often adopt figure-eight conformations probably as a consequence of conformational flexibility and effective intramolecular hydrogen-bonding interactions.

Setsune and coworkers succeeded in synthesizing expanded porphyrins with up to 24 pyrrole rings using sterically hindered benzaldehyde derivatives with bipyrrrole and subsequently, using bis(azafulvene) as a building block, to carry out the condensation under neutral condition. Among them 16 pyrrole ring containing [64]hexadecaphyrin(1.0.1.0.1.0.1.0.1.0.1.0.1.0.1.0.1.0) **L8** have been characterized by X-ray diffraction analysis, which still remains the largest structurally characterized expanded porphyrin.¹⁵

Interestingly, figure-eight conformations are found to be basically chiral, however they interconvert rapidly between two enantiomeric forms owing to their structural flexibility. In 1999, Vogel and coworkers succeeded in separation of β -alkyl octaphyrins **L9** and bis-Pd^{II}

complex of **L10** to their corresponding enantiomers.¹⁶ Recently, Setsune and coworkers used octaphyrin(1.0.1.0.1.0.1.0) as an effective sensor for the direct determination of absolute configuration of a variety of chiral carboxylic acids at mM concentrations based on CD exciton chirality method.¹⁷

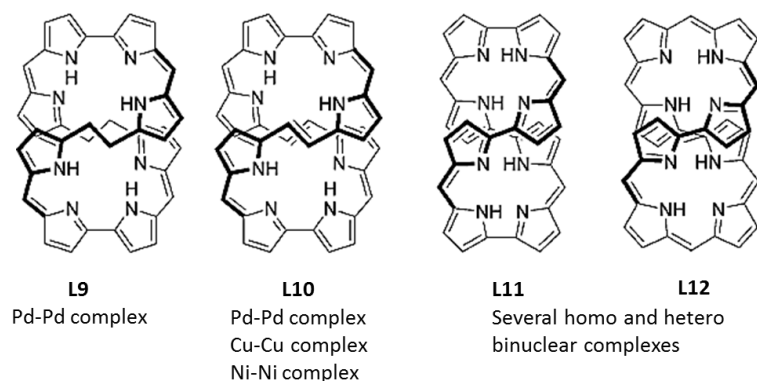


Figure 1.4 Figure eight octaphyrins (β -alkyl substitutions are omitted for clarity).

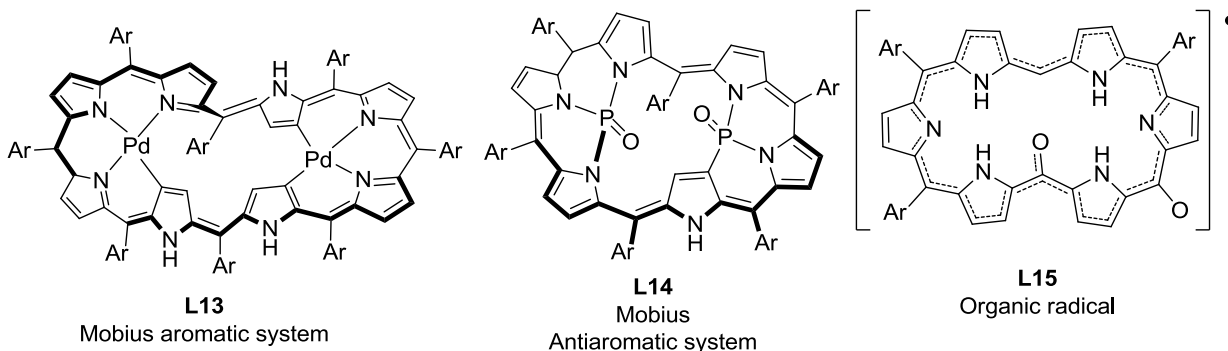


Figure 1.5 Recent examples of some of the important expanded porphyrins.

Another important role played by expanded porphyrin is to provide test bed for addressing various issues of aromaticity. Particularly in recent years, expanded porphyrins have been recognized as an effective platform to realize various stable Möbius aromatic and anti-aromatic systems which are very difficult to synthesize for other annulenes. Möbius aromaticity is the concept that predicts aromatic characters for $4n \pi$ cyclic conjugated systems based on a singly twisted Möbius topology.¹⁸ This concept, was introduced first by Heilbronner in 1964 and by Zimmerman in 1966.¹⁹ Heilbronner predicted on purely theoretical grounds that cyclic molecules with the topology of a Möbius band—a ring constructed by joining the ends of a rectangular strip

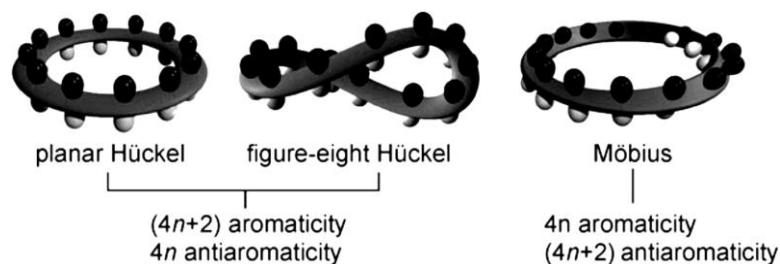


Figure 1.6 Schematic representations of topologies of π -conjugated systems.

after having given one end half a twist, should be aromatic if they contain $4n$, rather than $4n + 2$ π electrons. Thus the major difficulty to synthesize Möbius system is that it needs to merge two conflicting structural elements i.e. the fully conjugated cyclic electronic network and twisted topology of π systems, in a single molecule. Much later in 2003, Herges and coworkers reported a [16]annulene that has a twisted Möbius topology and moderate aromatic character.^{19d} In 2007, Latos-Grażyński and coworkers reported a dynamic Hückel–Möbius system, di-*p*-benzi[28]hexaphyrin that undergoes solvent and temperature-dependent conformational changes between Hückel and Möbius structures.²⁰ This stimulated interest to study expanded porphyrins in this context. Subsequently, Osuka group reported the first stable Möbius aromatic system, bis-palladium complex of [36]Octaphyrin(1.1.1.1.1.1.1.1) **L13**. Infact many of the metal complexes of hexaphyrin reported earlier by Osuka group could be realized in terms of Möbius aromaticity thereafter.²¹

Although there exists increasingly large number of Möbius aromatic molecules, existence of Möbius antiaromatic molecules are still rare. Again it was Latos-Grażyński and coworkers, who reported cationic Pd^{II} vacataporphyrin exhibiting a weak paratropic ring current, which was ascribed to an 18π antiaromatic species based on the calculated Möbius structure.²² However, first structurally characterized Möbius antiaromatic system was reported by Osuka and coworkers for a bisphosphorus [30]hexaphyrin **L14**.²³

Another noteworthy contribution from Osuka's group is the synthesis and characterization of stable organic radicals derived from expanded porphyrin. For instance oxygenated product of 5,20-*meso*-free hexaphyrin **L15** assigned as the first example of stable monoradical based on expanded porphyrin.²⁴ Delocalization of an unpaired electron through extended conjugation in expanded porphyrin probably causes unusual stability in these radicals.

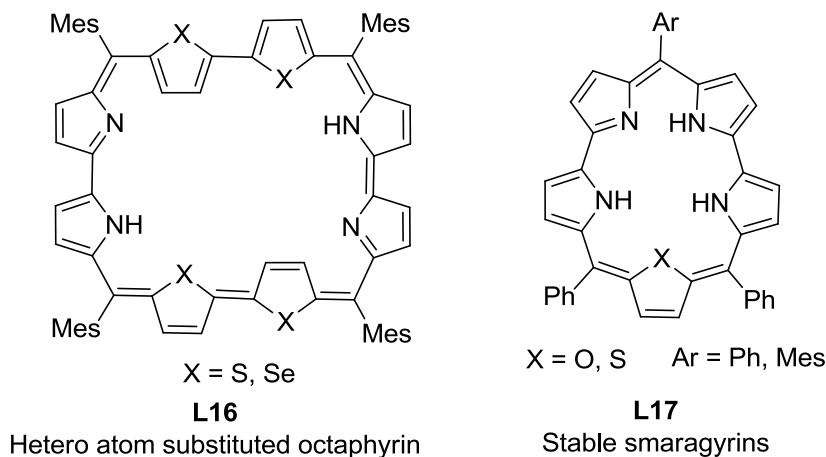


Figure 1.7 Few core modified expanded porphyrins.

Expanded porphyrin containing heteroatoms other than nitrogen are of great importance because of their unusual structural as well as photophysical properties in comparison to their nitrogen analogue. Contribution from Chandrashekar group in the development of this interesting area of research is noteworthy.²⁵ In general larger expanded porphyrin such as octaphyrin(1.0.1.0.1.0.1.0) are found to exist in figure eight conformation and shows non-aromatic behavior. In 2001, Chandrashekar and coworkers reported first core modified planar 34π octaphyrin **L16** that displays aromatic character.^{25c} Subsequently, they reported a planar core modified aromatic dodecaphyrin that exhibits record two photon absorption cross section ($\sigma_2 = 108000 \text{ GM}$).²⁶ In another important contribution, Chandrasekar group reported synthesis of core modified stable smaragdyrins **L17** which made possible for further exploration of this 22π aromatic macrocycle in detail.²⁷ Much of this later development was done by the same research group.^{28a} Recently, Ravikanth group reported synthesis of boron complexes of smaragdyrins and evaluated them as fluoride ion sensor.^{28b} The same group also reported the synthesis of porphyrin-expanded porphyrin dyads and especially, the porphyrin–smaragdyrin dyad was found to be an efficient fluorescent anion sensor.^{28c,d} They also synthesized a series of covalently linked trichromophoric systems composed of BODIPY, smaragdyrins and porphyrin.^{28e} Efficient energy transfer from central BODIPY to macrocycle was observed in these triads, hence holds great promise in the design and synthesis of suitable multichromophoric systems for material application.^{28e}

1.4 π -Extended porphyrinoids

Annulated porphyrins, wherein additional aromatic rings are fused onto the porphyrin periphery, have received much attention recently. Extension of π -conjugation through additional aromatic ring often leads to bathochromically shifted absorption spectra relative to their non-annulated counterpart.²⁹ Thus these materials are promising for various applications such as dye stuffs, optical materials, nonlinear optics, organic semiconductors, photosensitizers for photodynamic therapy (PDT), and dye-sensitized solar cells.³⁰ Fused systems are generally synthesized by

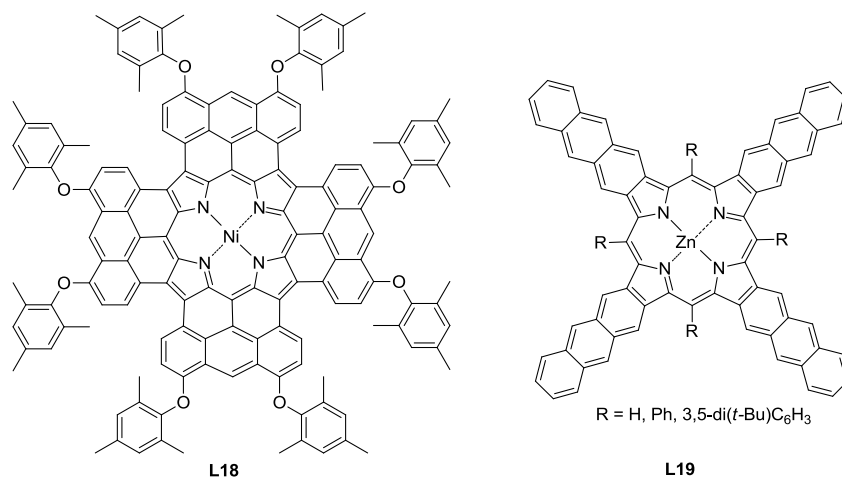


Figure 1.8 Examples of π -extended porphyrins.

oxidative fusion of porphyrin with aryl moiety at the periphery or by using annulated pyrrolic precursors. For instance fused tetraanthracenylporphyrin **L18** synthesized by FeCl₃ mediated oxidative ring closure reaction shows exceptionally small HOMO-LUMO gap with a λ_{\max} extending up to 1417 nm.³¹ Similarly tetraanthroporphyrins **L19** synthesized via the retro-Diels-Alder reaction of bicyclo-[2.2.2]octadiene-fused precursors have strong absorption and emission in the near-IR region.³² However, π -extension in isomeric and expanded porphyrins is still in its infancy stage. Only a few examples appear very recently.³³ Nonetheless these molecules show unprecedented optical and structural properties compared to their non-annulated counterparts. It has been well documented that electronic, optical, and coordination properties of expanded porphyrins are dependent upon their conformations and hence control over their conformations is very crucial. Use of rigid fused bipyrolic precursor or fusion of aromatic ring on periphery of expanded porphyrin has twofold advantages, because this not only increases π -conjugation but

also imparts structural rigidification to the resulting macrocycle. For example rosarin i.e. hexaphyrin(1.0.1.0.1.0) with 24π electrons are formally expected to be antiaromatic. However, rosarin **L20** derived from simple bipyrrrole exhibit very weak antiaromatic character owing to non-planarity of this molecule as it is conformationally flexible. However, rosarin **L21** derived from naphthobipyrrole is planar and is antiaromatic.³⁴ Another interesting feature displayed by **L21** is that it undergoes proton coupled reduction to produce its corresponding 26π aromatic cationic counterpart when exposed to proton source. In this process an intermediate 25π -radical

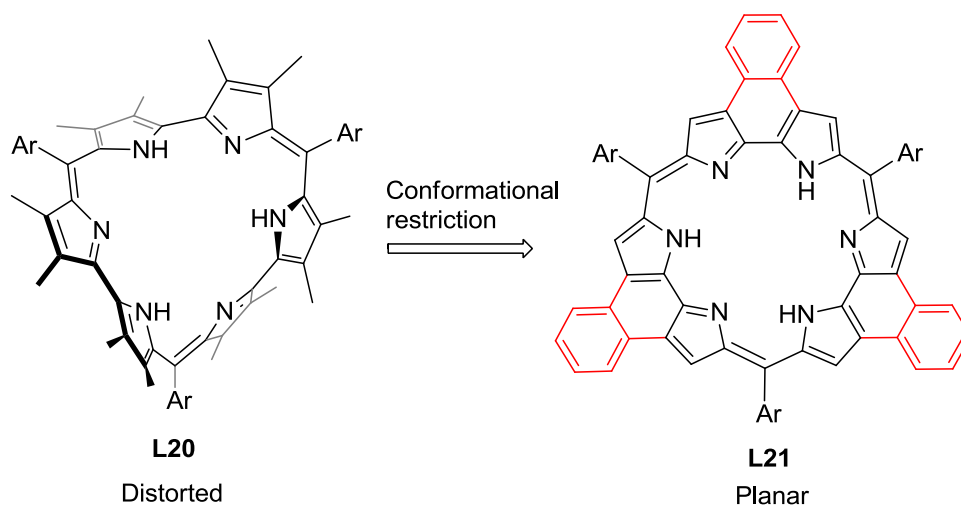


Figure 1.9 Conformationally flexible and rigid rosarins.

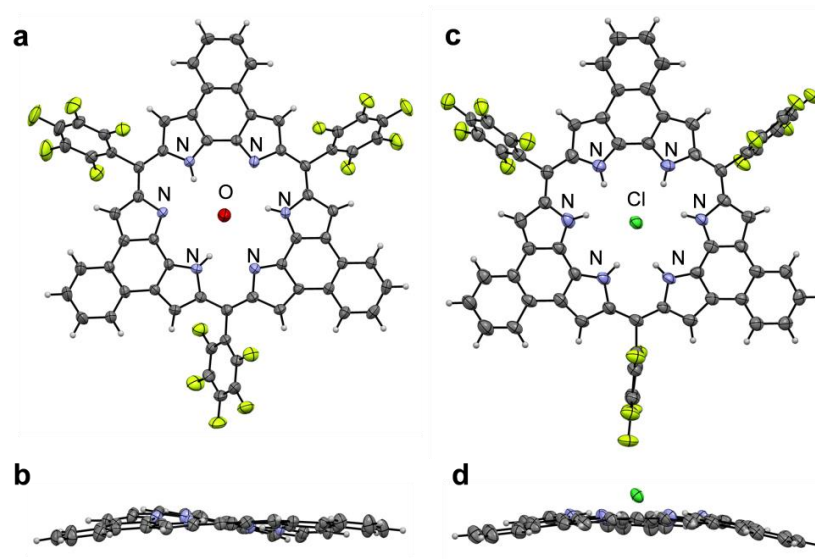


Figure 1.10 X-ray structure of **L21** (a, b) and its aromatic cationic counterpart (c, d).

dicationic species was also isolated and characterized. This interconversion between antiaromatic, radical and aromatic forms of **L21** are reversible. However, similar treatment with **L20** does not show this kind of behavior. Recently, Osuka and coworkers reported bis(Au^{III}) complex of [26]hexaphyrin fused to two anthracenes, which displays a remarkably red-shifted and sharp Q-band-like band at 1467 nm, multicharge storage ability, and a large TPA cross-section value owing to its flat and elongated rectangular conjugated network.³⁵ Similar π -extension in expanded porphyrins, in particular in cyclo[8]pyrrole and sapphyrin systems will be discussed in chapter 4 and 5 of this thesis.

1.5 References

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