1.1 Introduction

Porphyrins are ubiquitous molecules in nature and have been referred to as “pigments of life”. These macrocyclic molecules consist of four pyrrole rings connected by four methine carbon bridges which has 18π electrons in conjugation and are considered to be a Hückel aromatic molecule. Porphyrins and its derivatives play a critical role in living systems which form the basic unit for many functionally diverse enzymes and proteins like Hemoglobin, Myoglobin, Cytochromes, Peroxidases, Coenzyme B₁₂, etc, [1,2]. These respective proteins or coenzymes are performing various important processes such as oxygen transport, oxygen storage, photosynthesis and catalysis [3,4].

Last few decades, varieties of modified porphyrin derivatives were synthesized for an objective to mimic the biological processes and use them for diverse applications. These modifications in general can be classified into three categories such as i) peripheral modification ii) core modification and iii) contracted / isomer / expanded porphyrins [5].
a. **Peripheral modification**: Porphyrin meso position 1 and heterocyclic β- positions 2 & 3 are modified by using suitable substituents such as halogens or alkyl / aryl groups with electron donating and withdrawing behavior (Chart 1). Peripheral modification alters the global electron conjugation pathway of the macrocycle which in turn leads to change in the reactivity, aromaticity, photophysical and electrochemical properties of the macrocycle [6].

![Diagram of Peripheral Modification](image1)

b. **Core modification**: Normal porphyrin containing pyrrole rings in the macrocyclic skeleton, whereas in the core modified porphyrin, one or more pyrrole rings are replaced by other heterocyclic rings such as thiophene 4, furan, selenophene, benzene, pyridine or other heterocyclic and aromatic rings 5. Further, changing the linkage between meso position and pyrrole leads to core modified N-confused porphyrin 6 (Chart 2). Core modification in the porphyrin framework alters the coordination properties, electronic properties and aromaticity of the macrocycle [7].

![Diagram of Core Modification](image2)
c. **Contracted / Isomer / Expanded porphyrins:** Contracted porphyrin containing less numbers of heterocyclic rings and/or meso position 7. This can be obtained by removal of one or more meso and/or heterocyclic ring. Whereas isomeric porphyrins 8 can be obtained by reshuffling the pyrrole and methine bridges, which contains same number of heterocycle rings and meso carbon bridge as like normal porphyrin. [8]

![Chart 3](image)

Expanded porphyrin 9, on the other hand, contains more number of heterocyclic rings and/or meso position than the normal porphyrin. These macrocycles have more than 16 non-hydrogen atoms in their innermost periphery and more than $18\pi$ electrons in its conjugation pathway [9,10]. These modification leads to change in photo-physical, electrochemical properties, aromaticity, coordination properties, anion and cation binding properties.

### 1.2 Expanded Porphyrins

Among all the modifications depicted above, expanded porphyrins have received much attention due to its structural diversity and versatile applications. Sessler defined the expanded porphyrins as “*macrocycle that contain pyrrole, furan, thiophene or other heterocyclic subunits linked through either directly or through spacer atoms in such a manner that the internal ring pathway contains a minimum of 17 atoms*” [11]. Expanded porphyrins possess the excellent physical and chemical properties such as large red-shifted absorption spectrum, multi-metal coordination site, ability to adopt various conformations,
increased number of $\pi$ electrons conjugation pathway. These excellent properties led this molecule to potential application as sensitizer for photodynamic therapy (PDT) [12], magnetic resonance imaging contrasting agent (MRI-CA) [13], nonlinear optical materials (NLO) [14-18], model for aromaticity in annulene family compounds [5], near infrared (NIR) dyes, anion and cation complexing agents and so on [19-20].

In 1966, Woodward and co-workers have serendipitously synthesized the first expanded porphyrin derivative sapphyrin ($22\pi$ macrocycle) [21]. Even though it was synthesized long back, efforts towards the synthetic methodology in expanded porphyrin chemistry was made only in last decades mainly by the Vogel and Sessler groups. Vogel and co-workers have reported a series of octaphyrin derivatives in addition to normal porphyrin [22]. On the other hand, Sessler and co-workers mainly focused on the rational synthesis of $22\pi$ sapphyrin, $26\pi$ rubyrin, $24\pi$ rosarin, $24\pi$ amethyrin, $28\pi$ heptaphyrin, and $40\pi$ turcasarin using stable precursors in good yields [11]. They have not only reported developing efficient synthetic methods and also reported syntheses of stable building blocks, such as tripyrromethanes, dipyrromethanes, and quaterpyrroles required for the synthesis of expanded porphyrrins in simple and efficient way [10].

So far, expanded porphyrrins containing more than four pyrrole or heterocyclic rings were reported in literature, such as pentaphyrin (five heterocyclic rings with five meso carbons), sapphyrin (five heterocyclic rings with four meso carbons) [21], hexaphyrin (six heterocyclic rings with six meso carbons) [23], rubyrin (six heterocyclic rings four meso carbons) [24], heptaphyrin (seven heterocyclic rings with seven meso carbons) [25], octaphyrin (eight heterocycle) [22], nonaphyrin (nine heterocycle) [26], decaphyrin (ten heterocycle) [27] and dodecaphyrin (twelve heterocycle) [28] where in the last four derivatives the number of meso-carbon bridges varies depending on the size.
1.3 Conformation of Expanded Porphyrins

As mentioned in the previous section, the expanded porphyrins have more number of meso carbon bridges, hence it suffer from structural flexibility which leads to the molecule attain the various conformation in solution and solid state such as normal 10, twisted figure-eight structure 11, inverted heterocyclic ring structure 12, ring confused 13 [11,29].

Surprisingly, depending on the site of substitution (either at meso carbons or at β-pyrrole positions) the expanded porphyrin exhibits different structural diversity. For instance, β-substituted expanded porphyrins shows normal structure where all the pyrrole rings point inward in the cavity, while the meso-substituted derivatives exhibit the structural diversity such as normal 10 and inverted conformations 12. Overall in expanded porphyrins, the conformation is dependent on the nature of the linkage of the heterocyclic rings, the nature and the number of heteroatoms present in the cavity, measurement temperature and the state of protonation. However, it is also possible to change one conformation to another by varying
temperature, simple chemical modification, protonation by acids, metallation, changing the bulkiness of meso substitutions, varying the number of meso positions, modifying the heteroatom in core, etc [29-31]. For instance, octaphyrins are known to exhibit figure eight conformation due to more number of meso positions where the macrocycle undergoes a twist at the meso carbon, hence losing aromatic character. So, it was remains challenge to prepare the planar expanded porphyrin.

However, Chandrashekar and co-workers have synthesized two kinds of octaphyrins (Chart 5), one of them has eight meso positions and adopts figure-eight conformation 14 and another octaphyrin 15 has six meso positions and exhibits the planar structure both in solution and solid state. This study unambiguously proved that by suitable chemical modification such as decreasing the number of meso carbons enhancing the planarity of the macrocycle [32].

1.3 Aromaticity of expanded porphyrins

Aromaticity is one of the most important and basic concept of the organic molecules in chemistry. Because, the chemical and physical properties of the molecule fully depending on the aromatic nature of the molecules. In general, aromaticity of the molecule can be classified into three categories such as i) aromatic ii) antiaromatic and iii) nonaromatic. According to Hückel concept, aromatic molecules are defined as the molecule should possess
(4n+2)π electrons in conjugation pathway with planar structure. Recently, continuous attempts to quantify the degree of aromaticity by various parameters, such as structural, energetic, reactivity, and spectroscopic criteria have been made [5,11].

Normal porphyrins possess 18π electrons in conjugation, so it is considered to be a (4n+2)π Hückel aromatic molecule. Expanded porphyrins, on the other hand, exhibit versatile aromatic properties such as (4n+2)π Hückel aromatic 16, (4n)π Hückel antiaromatic 17 and nonaromatic 18 (Chart 6). The expanded porphyrin derivatives containing 22π, 26π, 30π and 34π electron in its conjugation framework exhibits Hückel aromatic character [29]. Aromaticity of the porphyrin unit can be easily predicted from the NMR chemical shifts of inner and outer protons. An aromatic compound shows the diatropic ring current (the peripheral protons resonate in the downfield region while inside protons resonate in the up
field region) whereas antiaromatic shows paratropic ring current (the peripheral protons resonate in the up-field region while inside protons resonate in the downfield region). However, expanded porphyrins with more than six heterocyclic rings have flexibility and attain figure-eight conformation. Hence, it losses planarity and attain nonaromatic behavior [11]. Further, there have been continuous efforts to synthesize antiaromatic porphyrins. For instance, the \([4n]n\)-electronic freebase [20]isophlorin would be expected as antiaromatic on the basis of Hückel’s \([4n]\) electronic configuration but turned out to be nonaromatic as a consequence of its non-planar saddle structure [33]. However, there are other approaches which describe the syntheses of stable antiaromatic porphyrins. [34]

Recently expanded porphyrins attracted attention of researchers for its ability to form Möbius aromatic molecules 19. The concept was first proposed by Heilbronner in 1964, predicts an electronically delocalized aromatic circuit for a \([4n]\)annulene when lying on a single-sided, non-orientable Möbius strip [35]. However, the concept was extensively challenged from both the theoretical and experimental viewpoints, as it is theoretically simple and difficult to make such a compound in practical. The first stable neutral Möbius aromatic molecule was reported by Herges and co-workers in 2003, in which the correct combination of a normal conjugated system and a belt-shaped conjugated system were employed to enforce a twist in the molecule, however, the reported [16]annulene of Möbius topology shows weak aromaticity as inferred from the ring current and NICS values [36]. Recently, by using the expanded porphyrins Latos–Grażyński and co-workers reported the temperature-dependent topology change between Möbius conformations 20 and Hückel 21 in di-\(p\)-benzi[28]hexaphyrin(1.1.1.1.1.1) (Scheme 1). [37]
After that, Osuka and co-workers have introduced series of Möbius aromatic molecules. Initially they have described the facile metalation of a series of meso-aryl substituted expanded porphyrins led to conformationally rigid, single sided twisted structures with distinct Möbius aromaticity. Moreover, it has fast equilibrium between different Möbius conformers of freebase [28]hexaphyrins(1.1.1.1.1.1), which was frozen on the NMR time scale at 173K.[38,39]

The same group have also reported π octaphyrin with a twisted figure-eight conformation 22 in its freebase form changes into an open extended Möbius structure upon protonation 23 (Scheme 2).
The driving force for such a structural change is attributed to breaking intramolecular hydrogen-bonds in freebase form and formation of intermolecular hydrogen-bonds with TFA in the dicationic form. Detailed photophysical studies revealed increase in excited singlet and triplet state lifetimes which are attributable to the rigidity of the macrocycle in the dicationic form. Further, two-photon absorption (TPA) values increases more than four times in the dicationic form proved that the macrocycle attaining Möbius aromatic character of with open extended structure [40].

1.4 Photophysical properties of expanded porphyrins:

Porphyrins have unique absorption characteristic in UV-Vis spectrum which exhibits the strong intense Soret band in higher energy region and very weak Q-bands in lower energy region. Expanded porphyrins on the other hand, have extended π-electron conjugation pathway hence the electronic structures of expanded porphyrins give rise to considerably red-shifted absorption bands relative to those of normal porphyrins [11,41]. The π-conjugation pathways become longer and longer going from porphyrin to expanded porphyrin, hence the HOMO–LUMO energy gap becomes smaller. However, on increasing the number of heterocyclic rings in the macrocycle (e.g. hexaphyrin and/or higher analogue) deviation from planarity is observed due to the intrinsic conformational distortion in the meso positions. Upon non-planar conformations due to the flexibility of their molecular frameworks, they exhibit (i) only broad Soret band without Q-like bands, (ii) no emission intensity, (iii) short singlet and triplet excited (π,π*) state lifetimes, and low triplet state quantum yields and (iv) small TPA values. This clearly indicates that there is a close relationship between the photophysical properties and geometrical structure of expanded porphyrins. Further, aromatic, nonaromatic and antiaromatic characters of the expanded porphyrin also have effect on photophysical properties. For instance, the aromatic derivatives have relatively long
singlet excited ($\pi$, $\pi^*$) state lifetimes and large $\sigma^2$ values. However, the antiaromatic and nonaromatic derivatives have the broad Soret band, low excited state lifetime and TPA values. [41,42]

The materials with high TPA values are found suitable for commercial NLO applications. Among these, porphyrins with 18$\pi$-electrons are quite promising, but high TPA performance has only been achieved when the $\pi$-electron networks have been considerably enlarged by conjugation with peripheral substituents and/or by covalent and non-covalent assembling, because normal porphyrin monomers only exhibit small TPA values of less than 100 GM. In this aspect, expanded porphyrins can be good candidates as new NLO materials with large TPA values, because expanded porphyrins possess a greater number of $\pi$-electrons along the extended $\pi$-conjugation pathway [14,17]. In the next section we would like to highlight such materials and their brief mechanical background.

1.4.1 Nonlinear Optical Materials (NLO)

Nonlinear optics deals with the interactions of applied electromagnetic fields with materials to generate new electromagnetic field altered in phase, frequency, amplitude or other physical properties [43]. NLO processes can be viewed as dielectric phenomena. Electrons that are bound to the nearby nuclei in the medium gets slightly perturbed by the external applied electromagnetic field and begin oscillating at the applied frequency. The magnitude of such an induced polarization (P) at modest field strengths will be proportional to the applied field and expressed as

$$P = \chi^{(1)} E \quad \text{(1.1)}$$

Where E is the magnitude of the applied electric field and $\chi^{(1)}$ is the polarizability of the material.
The NLO phenomena occur at sufficiently intense fields. As the applied field strength increases (e.g., lasers) the polarization response of the medium is no longer linear as shown by the eq (1.1). The induced polarization (P) becomes a function of the applied field and given by the equation,

\[ P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots \ldots \ldots \quad (1.2) \]

Where the \( \chi^{(2)} \) and \( \chi^{(3)} \) coefficients represent the second and third order susceptibilities of the medium respectively.

At the molecular level eq. 1.2 is expressed as

\[ P = \sum \alpha_{ij}E + \sum \beta_{ijk}E^2 + \sum \gamma_{ijkl}E^3 + \ldots \ldots \quad (1.3) \]

\[ i < j < k < l \]

Where \( \alpha_{ij} = \) Polarizability

\( \beta_{ijk} = \) First hyperpolarizability (second order effects)

\( \gamma_{ijkl} = \) Second hyperpolarizability (third order effects)

\[ i, j, k, l \quad = \text{corresponds to the molecular coordinates.} \]

A medium exhibiting such a NLO response might consist of a crystal composed of molecules with symmetric charge distribution, which are known as second order NLO materials. However, if the medium (or molecule) is centrosymmetric, then first order hyperpolarizability (\( \beta \)) is zero, indicating that centrosymmetric media do not show second harmonic generation. This can be explained as follows, if a field +E is applied to the medium, eq (1.3) predicts the first nonlinear term as +\( \beta E^2 \). If a field –E is applied, the polarization is still predicted to be +\( \beta E^2 \). Yet if the medium is centro-symmetric the polarization should be –\( \beta E^2 \). Thus the centro-symmetric medium has zero \( \beta \)-value. In the case of third order NLO susceptibility, if +E field produces polarization +\( \gamma E^3 \) and –E field produces –\( \gamma E^3 \), so the
second order hyperpolarizability ($\gamma$) is the first nonzero nonlinear term in centrosymmetric media. These materials are known as 3rd order NLO materials. The value of 3rd order nonlinear coefficient is measured in terms of $\sigma^2$ known as the two photon absorption coefficient.

$$\sigma^2 = \frac{4\pi^2 \hbar \omega L^4 \text{Im} (\gamma)}{n^2 c^2}$$  \hspace{1cm} (1.4)

1.4.2 Materials for Non-Linear Optics

Currently, inorganic solids such as LiNbO$_3$, KH$_2$PO$_4$ and semiconductors are the most popular NLO materials for commercial applications. These are ionic bulk materials where the optical nonlinearity is a bulk effect. However, the rigidity of these systems, their high cost and their poor response time to the electromagnetic radiation had been a hurdle in the further development of these materials and has limited their applications. Moreover, phase matching is not satisfied for these inorganic crystals. [14]

On the contrary, organic materials are emerging as an alternative to inorganic materials because of their low cost, ease of fabrication and integration into devices, and intrinsic tailorability which allows one to fine tune the chemical structure and properties for a given NLO process. Conjugated polymers, polyacetylenes, polythiophenes were considered to be a good candidates for NLO applications but these systems showed a very low $\gamma$ value (3rd order) to replace the inorganic materials commercially. [44]

However, in the last few years, expanded porphyrins have turned out to be excellent candidates for this purpose. These systems can be easily tailored to obtain highly $\pi$ conjugated systems and also show a drastic change in the properties on metallation. Recently, our groups synthesized series of expanded porphyrins ranging from 22$\pi$–50$\pi$ and
demonstrated the aromaticity, coordination properties of these derivatives and also used them as a potential commercial material for NLO applications. [45-46]

1.5 Topologically controlled expanded porphyrins

Merits and applications of expanded porphyrins are as a result of enlarged $\pi$ electron conjugation. However, structural distortion in expanded porphyrins leads to disturbed delocalization of $\pi$-electrons along the molecular framework. Thus, while the absorption bands of a series of representative planar expanded porphyrins show a continuous red-shifted absorption spectrum, but some of the larger expanded porphyrins with distorted topologies exhibit (i) broad and ill-defined Soret banded absorption spectra without Q bands or very weak bands (ii) low singlet and triplet life time and (iii) low NLO coefficient. Considering these demerits, the overall molecular structure is an important factor to determine the electronic structures of expanded porphyrins for understanding the molecular structure–property relationship in expanded porphyrins. [11,15,47]

It is obvious that topology control is become the one of important solution for maintain the planarity and aromaticity in expanded porphyrin. So far, various attempts has been made to rigidify the expanded porphyrins such as metal coordination, temperature control, solvent change, protonation with appropriate acids, and functional group modifications [48]. Fused and bridged strategies to control the topology become an interesting topic which does not alter the porphyrin intrinsic properties.

1.5.1 Fused porphyrins

In 2000, Furuta and co-workers have reported the first N-fused porphyrin (NFP) 25 where the new fusion bond is formed between the pyrrole nitrogen and $\beta$-CH of another pyrrole. The 25 was synthesized from the self-condensation reaction of $\alpha$-bromo substituted
N-confused tetraaryl porphyrin 24 in presence of base, pyridine solution at room temperature. From the mechanistic point of view, the reaction has been initiated by the inversion of the confused pyrrole ring, followed by the nucleophilic attack of the adjacent pyrrole and HBr elimination. The X-ray diffraction analyses clearly shows that the porphyrinoid like core containing a fused tri-pentacyclic ring, the whole molecule is completely flat in nature. This unique structure of fused tri-pentacyclic ring in the macrocyclic core leads the molecule to show unusual long wavelength absorption near 1000 nm. [49]

![Diagram](image)

The next higher homologue of fused porphyrin, N-fused pentaphyrin (NFP₃) 30 was reported by Furuta, Osuka and co-workers, where the pentaphyrin ring contains a fused tripentacyclic ring in the macrocyclic framework. The 30 was synthesized through two different strategies. In the first case, they have performed the Rothmund type condensation reaction, where the pyrrole and pentafluorobenzaldehyde reacted in the presence of Lewis acid (BF₃·OEt₂) followed by DDQ oxidation afforded normal porphyrin and 30 along with series of expanded porphyrins. In the second strategies, they have also adopted step-wise synthesis, where [2+3] acid-catalyzed condensation of tripyrromethane 28 and dipyrrromethane dicarbinol 29 afforded 30 (Scheme 4). [50]

In both the synthetic methodology, they observed both oxidized (30-R, R represents for Red color solution) and reduced form (30-Y, Y represents for Yellow color solution) of 30. Depending on the amount of oxidizing agent used, the yield varies accordingly. Further, they have also demonstrated that the CH₂Cl₂ solution of 30 was treated with DDQ, the yellow
solution changed to red color and afforded the quantitative conversion into oxidized form. Similarly, the obtained oxidized form is quantitatively converted into reduced form in the presence of reducing agent, such as NaBH$_4$ (Scheme 5).

1.5.2 Fused precursor approach for Fused Porphyrins

The fused tripentacyclic ring was formed through step-wise strategies in the synthetic scheme-3 has the control over the reaction, however, in the second methodology (scheme 4), there is no control for the formation of fused tripentacyclic ring formation. In addition, in the later methodology, the overall yield of the fused derivative reduced drastically and also the site of fusion is not specific. In order to overcome these problems, C. H. Lee and co-workers synthesized the benzobipyrrrole based fused sapphirin 34. The [3+2] acid-catalyzed condensation of diformyl benzodipyrrole 32 and tripyrromethane 33 followed by aerial oxidation afforded 34 in 18% yield, respectively (Scheme 6) [51]. Similarly, Sessler and co-
workers have synthesized the benzodifuran 37 macrocycle by condensation reaction of 35 and 36 (Scheme 7) [52]. The effect of fusion led to: (a) red-shifted Soret band absorption and (b) extended $\pi$-conjugation and aromaticity as compared to non-fused sapphyrin. The single crystal X-ray analysis of salt of 34 and 37 confirmed the planar structure in the solid state.

In 2010, our group has reported the dithienothiophene modified singly 40 and doubly fused rubyrin 42. The [4+2] Mac-Donald type condensation of DTT-diol 38 with modified tetrapyrranes 39 or 41 in the presence of 1 equiv of trifluoroacetic acid (TFA) as a catalyst followed by oxidation with $p$-chloranil in air afforded singly fused 40 and doubly fused rubyrins 42 in good yield as single product (Scheme 8). [53]

The single crystal X-ray analysis of both 40 and 42 revealed the planar structure defined by four meso carbon atoms. However, two or more heterocyclic units were tilted in the case of non-fused rubyrin derivatives (all aza and core-modified) reported earlier. The
effect of conformational restriction was further reflected by electronic spectral analysis which inferred the following physical characteristics; (i) the red shifted Soret band absorption; (ii) the increase in the molar extinction coefficient by four times upon fusion; (iii) enhanced aromaticity, probably due to the planar structure. The introduction of fusion in the macrocyclic framework resulted in conformational restriction, where the inversion was avoided in the singly and doubly fused rubyrin.

1.5.3 Bridged porphyrins

There are several reports described the syntheses and characterization of porphyrin dimers, trimers and etc, by bridging spacer groups [54]. Recently, Osuka and co-workers demonstrated the syntheses of highly conjugated porphyrin arrays such as β-to-β 2,5-thienylene-bridged porphyrin dimer 44, a triangular trimer 45, and a ladder like trimer. The β,β’-diborylporphyrin was cross-coupled with 2,5-dibromothiophene under Suzuki–Miyuara
coupling conditions resulted doubly 2,5-thienylene-bridged diporphyrin was obtained in 29% yield. [55]

The π-conjugation through thienylene linkages was quite effective because of their relatively strong aromaticity as well as their small rotational barriers. Although several thienylene-bridged porphyrin systems have been reported, the doubly linked diporphyrin (44) showed a large TPA cross-section values. However, the respective values are not significant in the cyclic trimer system. On the other hand, the ladder like trimer showed a very large TPA cross-section value. The effective electronic delocalization through the thienyl bridge to porphyrin array led to large TPA cross-section value.

In 2012, Dongho Kim and co-workers have synthesized two types of thieno-bridged porphyrins 46 & 47 incorporating a thiophene group across the meso and β-positions with different directions of the thiophene ring to investigate the aromaticity of these porphyrins
with extended π-systems. The 2,3-thieno bridged porphyrin 46 showed a larger antiaromatic contribution than the 3,4-thieno-bridged porphyrin 47. The antiaromatic contribution in 46 was based on a 20-π-electron conjugated circuit. In addition to regular spectral and structural analysis, the two thieno-bridged porphyrins were further analyzed by electrochemical studies, time resolved excited state analysis, TPA cross-section measurements and also theoretically calculated the NICS value and the AICD plot. [56]

Nucleus independent chemical shift (NICS), which has been successfully used as a measure of aromaticity. At the five-membered ring between the porphyrin and thiophene moieties, the NICS(0) values for both 46 and 47 are positive (+30.5 and +13.1 ppm, respectively). The large positive NICS(0) value for 46 indicates a large contribution from the antiaromatic 20π circuit. A smaller contribution from the antiaromatic 24π circuit of 47 is also possible, judging from the positive value at the five membered rings between the porphyrin and thiophene moieties of 47. The NICS(0) values at the porphyrin macrocycle of
46 are more positive (−10.1 to −13.6 ppm) than those of 47 (−14.6 to −16.1 ppm; suggesting that the antiaromatic network makes a larger contribution to the overall electronic structure in 46 than in 47.

1.5.4 Internally Bridged porphyrins

Although several reports describe the synthesis of dimer porphyrin by spatial bridging group, only three reports in the literature discussed the synthesis of internally bridged porphyrins. Osuka and co-workers synthesized the internally 1,4-phenylene bridged octaphyrin 51 and decaphyrin 50. The main objective of this bridged system was to maintain the planarity. [57]

A solution of one mole equiv of 1,4-phenylene-bridged bis(dipyromethane) 48 and two mole equiv of tripyrromethane diol 49 in CH$_2$Cl$_2$ in the presence of $p$-TSA followed by oxidation with DDQ afforded 50 in 10% yield (Scheme 10).

They have also demonstrated the reversible redox inter-conversion between [46]decaphyrin and [44]decaphyrin by simple oxidation and reduction. Treatment of [46] decaphyrin with 10 equiv of DDQ resulted in quantitative conversion into [44]decaphyrin, with a color change from dark red to dark green. Similarly, it was reduced quantitatively with NaBH$_4$. 
Both [46]decaphyrin and [44]decaphyrin were confirmed by single crystal X-ray diffraction analysis. Decaphyrin showed C$_2$-symmetric nonplanar, but not a figure-eight structure in which the two twisted pentapyrrole subunits were interconnected by the central 1,4-phenylene bridge. Each pentapyrrole arm, has dipyrrromethene and a tripyrroldimethene unit, maintained the near planar structure.

The same group also reported the vinylene bridged hexaphyrin 53. Cross-bridging reaction of 5,20-diethynyl substituted [26]hexaphyrins (1.1.1.1.1.1) 52 under reflux condition in ethylacetate for 36h resulted in a quantitative conversion to trans-vinylene bridged [26]hexaphyrins(1.1.1.1.1.1) with vivid color change from indigo blue to magenta purple (Scheme 12) [58].
The electronic absorption and emission spectral analyses of 52 and 53 showed remarkable differences where the bridged compound exhibited unique features: (i) relatively broad and weak Soret-like bands in the 400-600 nm region; (ii) smeared Q-like bands in the 620-850 nm region; (iii) an extremely weak and broad NIR absorption band in the 900-1800 nm region; and (iv) a lack of emission in the NIR region [59].

As observed in the case of 30 and 45, the compound 53 was also shown to be interconvertible into its reduced form 54 by using NaBH$_4$ and oxidized back to 53 by using DDQ (Scheme 13). Single crystal X-ray analysis confirmed the trans-vinylene-bridged [28]π hexaphyrin. The overall conjugated electronic systems of 53 and 54 were characterized as 26- and 28-π circuits respectively, while a resonance form that contributes to 53 was regarded as [16]diazaannuleno[16]diazaannulene. However, this contribution should be lower due to the perpendicular arrangement of the central vinylene bridge. This [16]annuleno[16]annulene was regarded as [4n]annuleneo[4n]annulene which consists of two annulated antiaromatic[4n]annulenes with a total of (4n + 2) π-electrons have been extensively studied to examine a possibility that such conjugated molecular systems could possess overall aromaticity.

1.6. Calixphyrins

The definition of calix[4]phyrins comprise systems with one, two, and three sp$^2$-hybridized bridging meso carbons in the macrocycle. They are divided into three types;
porphomethenes, porphodimethenes, and porphotrimethenes, based on the number of sp² hybridized meso carbon (Chart 8). [60]

![Chart 8](image)

Porphomethenes 55 contain only one sp² hybridized meso carbon atom and are names as calix[4]phyrins-(1.1.1.1) (The numbering system refers as follows: bold numbers refer to sp² meso centers, and italicized numbers refer to sp³ meso centers [60]). Porphodimethenes are containing two sp²-hybridized meso carbon atoms. There are two types of porphodimethenes; 5,15-porphodimethene type calix[4]phyrin-(1.1.1.1) 56a and 5,10-porphodimethene type calix[4]phyrin-(1.1.1.1) 56b. Porphotrimethenes are containing three sp² hybridized meso carbon bridges. They are further divided into two, based on the number of –NH protons; isoporphyrins 57 (one NH hydrogen atom) and Phlorins 58 (three NH hydrogen atoms). [61]

Porphyridins are long well known as cation coordinating ligands, while calixpyrroles have emerged as anionic receptors. The introduction of both sp² and sp³-hybridized meso carbon bridges in calixphyrin leads to partial interruptions in the conjugation pathway of the molecule and hence introducing novel structural features and anion and cation recognition properties. Today, the field of calix[n]phyrin chemistry is growing rapidly and is opening up
new opportunities in the porphyrin analogue area. Recently, the step-wise synthesis and binding process of calixphyrins are exploited by Sessler and co-workers. [60-62]

1.7. Expanded and core-modified calixphyrins

Sessler and co-workers have demonstrated the synthesis of first expanded calixphyrin. The acid-catalyzed condensation of mesityl dipyrromethane 59 with acetone followed by oxidation with DDQ, along with normal calixphyrins, such as diaryl tetraalkyl porphodimethenes, affords higher order homologues 60 and 61 in 13% and 08% yield, (Scheme 14) respectively. [63]

![Scheme 14](image)

In 2004, Latos Grażyński and co-workers described the synthesis of core modified calixphyrin, thus, they introduced benzene ring in the macrocyclic framework. The acid-catalyzed condensation of 1,5-bis(diphenylhydroxymethyl)benzene, pyrrole and p-nitrobenzaldehyde followed by oxidation afforded benziporphodimethene in 14% yield. The coordination chemistry was further performed by using divalent metal complexes such as Ni(II), Zn(II) and Cd(II), where the NMR spectral analyses of Ni(II) complex reflected the paramagnetic nature of the complex and single crystal X-ray analysis showed the weak agostic metal-arene interactions. [64]
In 2007, C. H. Hung et al. have also reported similar type of porphodimethenes, where the acid-catalyzed condensation of 1,5-bis(dimethylhydroxymethyl)benzene 62 with pyrrole and aryl aldehyde gave 63 in 27% yield (Scheme 15). The Zn$^{2+}$ complex of 63 showed the long wavelength absorption and also the turn-on fluorescent emission at 672 nm with the quantum yield of 0.34 reflects the chemosensor properties of 63. [65]

![Scheme 15](image)

Recently, Ravikanth and co-workers have also synthesized thia-analogue of calix[4]phyrin-(1.1.1.1) 66 starting from 2,5-bis(diphenylhydroxymethyl)thiophene 64 with tripyrromethane 65 afforded in 15% yield (scheme 16). [66]

![Scheme 16](image)

Interestingly, in 2003, Sessler and co-workers have synthesized the cryptand like three dimensional calixphyrin 69 from diformyl tripyrromethane 67 and tripyrromethane 68 precursors, in the presence of acid-catalyst followed by oxidation afforded in 08% yield, respectively (Scheme 17). The single crystal X-ray analysis confirmed the proposed novel calixphyrin like three dimensional structure for 69. Also, revealed the presence of H$_2$O molecule inside the cavity, which supported that such system could have a role to play in the area of substrate specific molecular recognition. [67]
In the year 2006, Matano and co-workers demonstrated the phosphole-containing hybrids which exhibited characteristic coordination behavior derived from both the phosphole ring and the π-conjugated pyrrole-heterole-pyrrole (N-X-N) subunits. The synthesis of phosphole-containing hybrid calixphyrin was done by treatment of 2,5-bis[pyrrol-2-yl]methyl]phosphole 70 and 2,5-bis[phenylhydroxymethyl]thiophene 71 in the presence of acid-catalyst such as BF$_3$.OEt$_2$ followed by oxidation with DDQ afforded 72 in 15% yield (Scheme 18), respectively. Further, they introduced the new class of calixphyrin transition metal catalysts by synthesizing a Pd(II) complex and was found to catalyze the Heck reaction with high efficiency. The coordination number and the oxidation state at the metal center are controllable by the flexible calixphyrin framework. Similarly, they reported the thiophene analogue of calixphyrin as well (Scheme 19). [68,69]
1.8. Molecular Receptors

Molecular receptors are host molecules which specifically and selectively recognize certain guest molecules and ions such as anions, cations and neutral substrates. Interactions between host and guest can be donor-acceptor interaction, hydrogen-bonding, dipole-dipole interaction, electrostatic interaction. The size and shape of the ions play a major role where cations are normally spherical in shape and anion of different shapes like $\text{CO}_3^{2-}$ has a planar shape, $\text{SO}_4^{2-}$ has a tetrahedral shape, $\text{N}_3^-$ has a linear shape while $\text{F}^-$ and $\text{Cl}^-$ are spherical in shape. For cation recognition, the size of the cation has to be considered. However, for the anion receptor both size and shape has to be considered when designing the receptor for the anions. Some of the examples of molecular receptors are crown ethers, cryptands, cyclodextrins, calixpyrroles, calixarenes and expanded porphyrins. [70]

1.9. Anion Binding

Anions play an important role in biological, medical, chemical and environmental processes. Hence, the anion recognition and sensing continue to attract the researchers because of its challenges in the mentioned areas. Therefore the ability to detect and quantify such anions is of particular importance [70]. While designing molecular receptors, should have the significant binding affinities and selectivity like by naturally occurring biological anion receptors such as proteins, so that it can be used for real world applications. These systems possesses multiple balancing hydrogen-bonding interactions to bind their target guest anions within complicated three-dimensional cavities buried deep below the surfaces of the proteins [71,72].

Recently, Sessler and co-workers proved that calixpyrroles are best suited for selective binding of anions in sensing mode or for purification/removal of anions from mixtures when bound to solid supports [60]. However, compared to calixpyrroles,
calixphyrins are less explored for anion binding studies. This may be explained by the fact that the more reduced calixphyrins have less N–H bonds to interact via electrostatic hydrogen bonds with anions [61-63]. However, protonation of the basic di or oligopyrrin units in the macrocycle significantly increases the anion binding. An advantage of calixphyrins is that they (and certainly their protonated forms) contain a strong chromophore which helps to visualize the binding experiments by simple analytical the binding experiments in simple analytical techniques such as Uv-Vis spectroscopy and photometry. Initial reports on calix[n]phyrins, Sessler et al. demonstrated the synthesis of three calixphyrins and performed the receptor properties by using various anions and monitored the binding event by electronic spectral analysis. The “deep cavity” calix[6]phyrin was not bind with anions unless it was protonated. The single crystal X-ray analysis confirmed that the chloride was firmly located in the cavity [60,63]. Recent years various calixphyrins with expanded, core-modified and functional group attached were reported for anion binding studies, such details, which we have discussed further in the respective chapter.

1.10. Aggregation Induced Enhanced Emission

Recent years, the design and synthesis of potential luminophores is an attractive research topic in the field of molecular imaging technology, photonics and electronic devices, as fluorescent probes in molecular biology, photosensitizers in dye-sensitized solar cells and dye lasers, and many more. In general, many fluorophores are emissive when it is in solution state. However, when they are fabricated into solid state or films for devise applications, which undergo the well-known effect of aggregation caused quenching (ACQ) [73,74]. Planar luminophores tend to aggregate in solid state or in film or in a higher concentrated solution like as discs pile up due to strong π-π stacking interaction as shown in the below
Figure 1.1, which commonly turns non-emissive because these stacking often induces non-radiative energy transfer [75].

This ACQ effect is the hurdle for luminophores to use them for real world applications. Moreover, as we know, most of our biological system deal with water is major component, and since water is not a good solvent for almost all organic fluorophores. So, the molecules get aggregated due to which they can not act as a good and effective sensors in biological system. However, there are molecules, which are weakly emissive or nonemissive in dilute solution but when they are in aggregated state, they show intense emission. This phenomena is known as aggregation induced enhanced emission (AIEE) or aggregation induced emission (AIE) respectively. [74,76]

Tang and co-workers and other researchers proposed the following effects need to be taken into consideration with respect to the luminophore moiety in the aggregated states: [74]

(i) Conformational planarization

(ii) Prevention of close intermolecular interaction that leads to emission quenching

(iii) Restriction of intramolecular rotation (RIR).
Scope of the present thesis:

In light of the extensive literature discussion covering the chemistry of fused and bridged expanded porphyrins and also the receptor properties of expanded calixphyrins, it is clear that the synthesis of new bridged and fused variants has been a growing area of highly interdisciplinary research over the last decade. In the present thesis, an attempt has been made to carry out a simple novel precursor in order to maintain the planarity and aromaticity of the expanded derivatives, which are difficult to maintain for more than six heterocyclic rings present in the expanded porphyrins framework. The main content of the thesis includes synthesis, spectral, structural and photodynamic studies of such novel expanded porphyrins. The goal, therefore, is to provide easy and simple synthetic methodologies to prepare fused, bridged expanded porphyrins and expanded calixphyrins.

In the second chapter, the synthesis of novel dithienothiophene precursor (DTT) is discussed, which is the important building block for the synthesis of bridged and fused expanded porphyrin. The other precursors required for the synthesis of expanded porphyrin and calixphyrin such as heterocyclic diol and tripyrromethane are also discussed in this chapter.

In the third chapter, we have demonstrated the synthesis of core-modified analogues of internally bridged expanded porphyrins with dual aromatic character. The synthetic methodology adopted here is simple and straight-forward. Interestingly, depending on the heteroatom present in the core such as Sulfur or Selenium atom, the participation of bridging thiophene ring in the \( \pi \) electron conjugation pathway are different and exhibit hybrid aromatic character revealed by spectroscopic studies. The structural analyses further confirm that the hexaphyrin macrocycle is planar and aromatic and that the internal bridging thiophene ring deviates from the mean plane of \textit{meso} carbon atoms. The spectral data of these
bridged hexaphyrins are more planar, thus facilitating better a \( \pi \) conjugation pathway and therefore increasing the aromaticity, as compared to its core-modified congeners. The preliminary photophysical studies reveal an increase of singlet lifetime by two times upon introduction of bridge, which is presumably due to increased rigidity of the macrocycle.

The fourth chapter describes the synthesis, spectral, structural and photophysical characterization of fused derivative of expanded porphyrin such as doubly fused octaphyrins. These are synthesized by simple acid-catalyzed condensation of appropriate precursors followed by oxidation with DDQ. The single-crystal X-ray structure shows a figure-eight twisted conformation. Spectroscopic and quantum mechanical calculations reveal that both the octaphyrin conform to a \([4n] \pi\) nonaromatic electronic structure. Protonation of the pyrrole nitrogen atoms results in dramatic structural change from twisted figure-eight to extended open structure. The spectral analysis, photodynamic studies, NICS values and AICD plot reveal the paratropic ring-currents with \([4n] \pi\) Hückel antiaromatic and further confirm by single-crystal X-ray structural analysis. The second part of this chapter discusses the synthesis and structural characterization of mono-fused sapphyrins and antiaromatic heptaphyrins.

Fifth chapter demonstrates the core-modified expanded calixphyrin synthesis and their important properties such as aggregation induced enhanced emission (AIEE) and anion receptor properties. The presence of \( meso \) phenyl substitution on the \( sp^3 \) carbons not only restricts the intramolecular rotations and inducing AIEE. Further, it also forces the macrocycle to adopt a distorted chair like conformation in the solid state. Furthermore, the anion binding properties reported here suggest that macrocycle has stronger affinity for tetrahedral ions.