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Aromatic core-modified expanded porphyrinoids with *meso*-aryl substituents*

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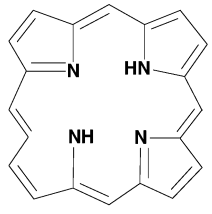
Abstract: Porphyrins are the most widespread of all prosthetic groups found in Nature. The ubiquity of their functions in Nature led researchers around the globe to focus their attention on these highly colored macrocycles. The interdisciplinary interest generated by porphyrins resulted in the syntheses of modified porphyrins, which can be put to a variety of uses in medicine and industry. A brief overview of the synthetic methodologies resulting in the formation of aromatic *meso*-aryl-substituted core-modified aromatic heterocyclic ring-inserted expanded porphyrinoids like sapphyrins, smaragdyrins, rubyrins, hexaphyrins, heptaphyrins, and octaphyrins reported to date are discussed in this article.

INTRODUCTION

Porphyrins are highly colored tetrapyrrolic pigments that play a diverse and critical role in biology, ranging from electron transfer, oxygen transport, photosynthetic processes, and catalytic substrate oxidation; they are aptly called "pigments of life" [1]. They are 22π electron systems whose main conjugation pathway contains 18π electrons, which explains the aromatic nature from which their associated intense color stems. The parent form of these tetrapyrrolic macrocycles has structure **1**, known as "porphine" [2,3]. The ubiquity of its functions in Nature led researchers around the globe to focus their attention on these macrocycles, and it paved the way for the syntheses of modified porphyrins that differed from the naturally occurring porphyrins and related systems in a number of ways.



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The most important modifications resulted in the formation of the following porphyrin-like macrocycles: (a) *periphery-modified porphyrins*, where the modifications are done on the periphery, which includes the β and meso positions of the parent tetrapyrrolic macrocycles; (b) *core-modified porphyrins* [4], where one or more core nitrogen atoms of parent porphyrin is substituted with chalcogen atoms; (c) *contracted porphyrins* [5], where removal of one of the *meso* carbons results in the formation of corroles; (d) *isomeric porphyrins* [6], structures which have the same molecular formula $C_{20}H_{14}N_4$ as the parent porphyrin, obtained by scrambling the four pyrrolic subunits and the four bridging carbon

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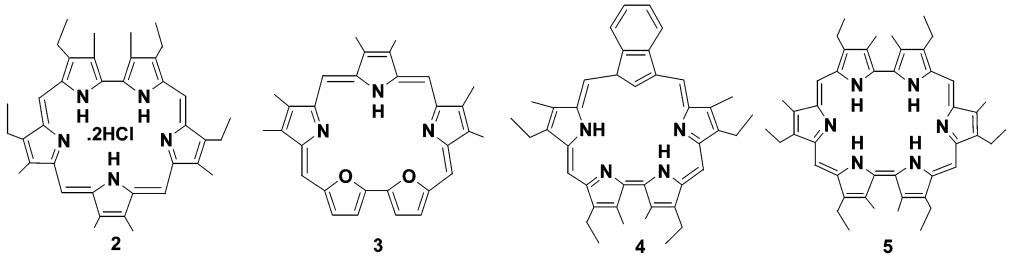
atoms; (e) *inverted porphyrins* [4], which can also be considered as porphyrin isomers that have one or more of the core nitrogens pointing out of the ring and hence considered as "*N*-confused porphyrins" or "mutant porphyrins" and are treated as a different class; and (f) *expanded porphyrins* [7,8], which result from the expansion of the π electron conjugation by increasing the number of heterocyclic rings/methine bridges connecting those heterocyclic rings. There are citations in the literature that some of these macrocycles, especially the expanded porphyrinoids, can act as anionic, cationic, and neutral complexing agents, which are substrate-specific and hence can be put to a variety of uses in medicine and industry [7]. In this article, we discuss only the synthetic methodologies and a brief overview of studies done on aromatic core-modified expanded porphyrinoids, which are obtained by incorporating more heterocyclic rings into the porphyrin macrocycle. These macrocycles are important from the point of view of metal coordination due to the increased number of heteroatoms, varying cavity sizes, and the *aromaticity* of these macrocycles, which in turn depends on the nature and number of links bridging the heterocyclic units. The complexing ability to trap lanthanide metals makes these macrocycles potent candidates for contrast agents in magnetic resonance imaging (MRI) [9]. Furthermore, such macrocycles are used as RNA-cleaving catalysts for antisense applications and enzyme models [7,8]. Thus, these modifications result in the control of electronic structure, geometry of the system, and its surroundings associated with rich, diverse, and exotic chemistry. Their photosensitizing ability to convert triplet oxygen to highly reactive and toxic singlet oxygen makes them indispensable in the field of photodynamic therapy [7,8,10]. One of the macrocycles, namely, a core-modified sapphyrin discussed in this article, was made water-soluble, and its preliminary evaluation as a potent photosensitizer in the field of photodynamic therapy has been discussed in detail in a recent publication [11].

Modified expanded porphyrins

Modified heterocyclic ring-inserted expanded porphyrins constitute a different class of porphyrins due to the incorporation of heteroatoms into the core of the macrocycle, leading to the significant alteration of the cavity size and electronic structure, leading to interesting spectroscopic, chemical, and physical properties, which can find applications in biology [12], medicine [13], materials science [14], and catalysis [15]. These properties have generated considerable interest in the field of synthesizing such new macrocycles in high yields with different core atoms and cavity size and analyzing their properties.

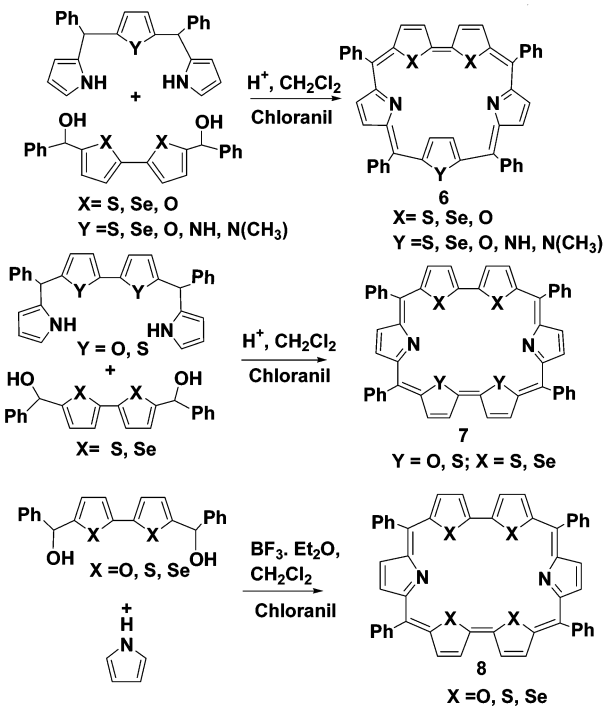
Aromatic core-modified pentaphyrins and hexaphyrins

R. B. Woodward and coworkers serendipitously discovered the first expanded porphyrin, sapphyrin **2** or [22]pentaphyrin (1.1.1.1.0), in the course of the synthesis of vitamin B_{12} in 1966 [16]. A perusal of literature reveals that there are only limited reports on the synthesis and characterization of core-modified expanded porphyrins. Johnson and coworkers developed the first example of such a system, dioxasapphyrin **3**, when they tried to generate heteroatom analogs of corroles starting from diformylbifuran and dipyrromethane, synthesizing it along with the sought after dioxacorrole [17]. Sessler and coworkers have synthesized a series of β-substituted sapphyrins containing one or more heteroatoms by the usual 3+2 methodology, selecting appropriate precursors [18]. The first carba sapphyrin **4** was reported by Lash and coworkers through a (4+1) MacDonald condensation between a tetrapyrrole dicarboxylic acid

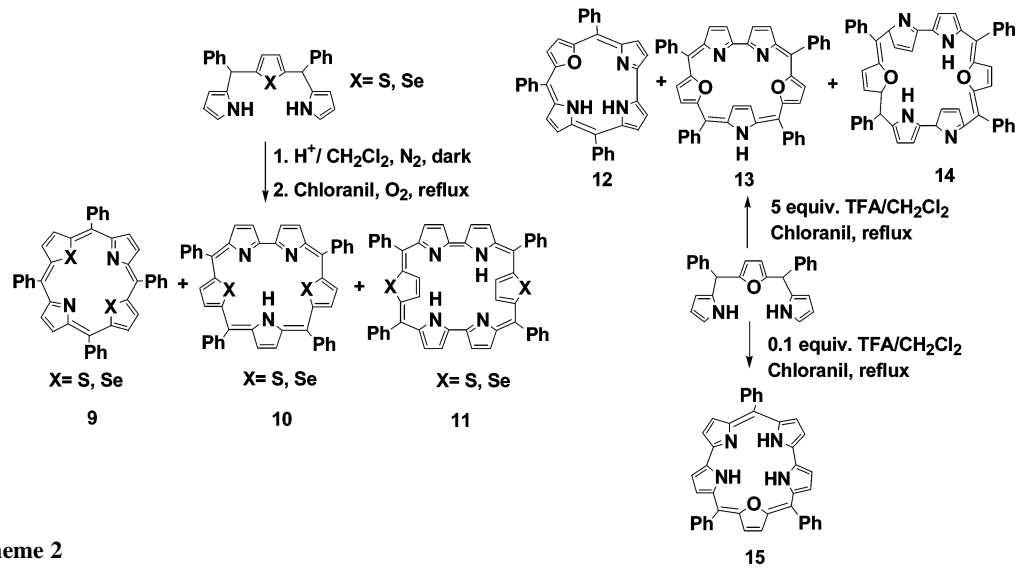


and diformyl indene [19]. Rubyrin **5**, which is [26]hexaphyrin (1.1.0.1.1.0), was reported by Sessler et al. in 1991 by condensing tetrapyrrolic precursor with diformylbipyrrole under acid catalysis and subsequent air oxidation [20], and the β-substituted hexathiarubyrin was synthesized by Vogel and coworkers [8].

We were particularly interested in *meso*-aryl-substituted analogs and have recently reported a series of *meso*-aryl sapphyrins **6** and rubyrins **7** and **8**, where O, S, and Se replaced two or three core nitrogens by easy and efficient MacDonald (3+2, 4+2, 2+1) condensations involving appropriate precursors in comparatively high yields as shown in Scheme 1 [21,22]. We also reported diheteroatom-substituted *meso*-aryl sapphyrins **10** and **13**, and rubyrins **11** and **14**, and in the case of oxygen containing

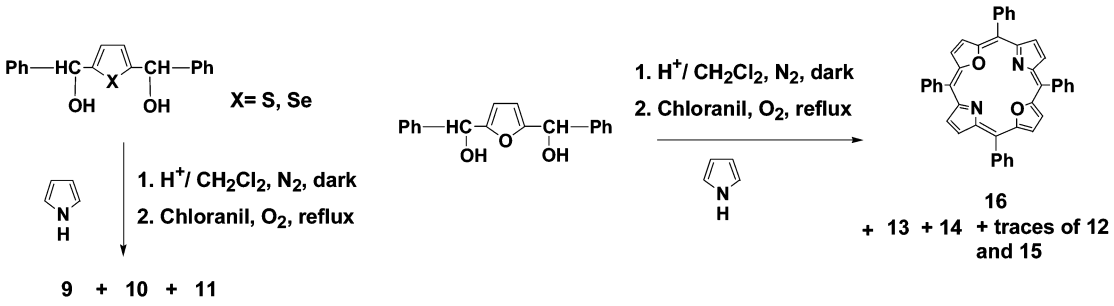


Scheme 1



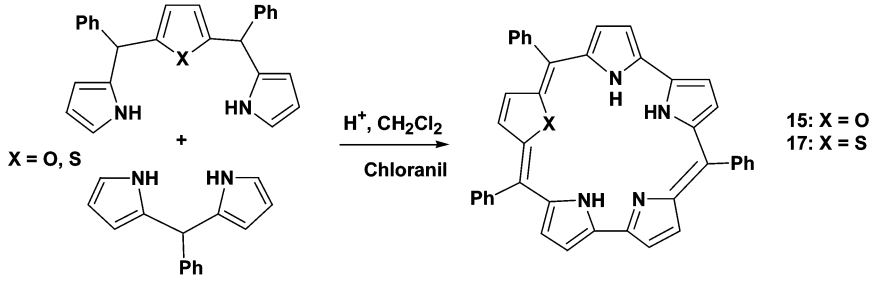
Scheme 2

tripyrrane, additional products such as monooxacorrole **12** and monooxasmaragdyrin **15** were also formed from an unprecedented coupling of modified tripyrranes (Scheme 2) [23]. The formation of porphyrins in the oxidative self-coupling reaction of modified tripyrranes as shown in Scheme 2 reveals that the precursor undergoes acidolysis. Hence, we particularly wanted to reexamine the reaction reported by Ulman and coworkers [24], which yielded *meso*-tetraphenyl porphyrins containing heteroatoms S and Se, in a new light by using protic acid as catalyst, and we tried to obtain the modified tripyrrane in situ, thus formulating a new methodology for the syntheses of expanded porphyrins. The methodology adopted here involves condensation of diol with excess pyrrole in presence of protic acid catalysts like TFA, HBr, and *p*-TsOH (Scheme 3). The product distribution and isolated yields were dependent on the nature and concentration of the protic acid catalyst used [25]. Here it is noted that the formation of tripyrrane in situ is the key step, and this further reduces the already existing methodology reported earlier from our group [23]. This method has drastically reduced the number of steps involved in the preparation of diheteroatom-substituted expanded porphyrins and is the simplest method to date to arrive at the desired expanded porphyrins. Other literature methods involve multistep synthesis to obtain sensitive precursors, and the yields of the macrocycles were also poor. Even though there was a mixture of products in the reaction, the ease of chromatographic separation of these compounds due to their differing polarity, moderately good yields, and easily available precursors make this method versatile. During the course of this work, Latos-Grazyński and coworkers reported the formation of furan/thiophene-substituted *meso*-aryl sapphyrin in low yields as a by-product of the Rothemund reaction of 2,5-disubstituted thiophene diol and pyrrole [26].

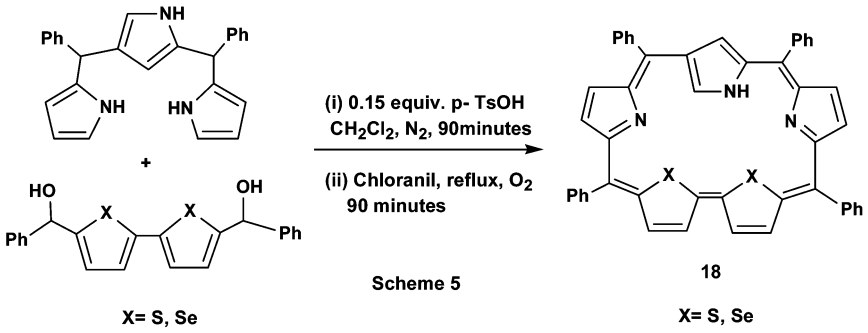


Scheme 3

Another pentaphyrin with a trivial name, "smaragdyrin or norsapphyrins" or [22]pentaphyrin (1.1.0.1.0), that has only three *meso* carbons that bear a structural relationship to sapphyrins as corrole does to porphyrin, was first reported as a β-substituted dioxasmaragdyrin [27]. A facile and efficient synthesis for the formation of first *meso*-aryl smaragdyrin **15** and **17**, bearing one O or S by an oxidative coupling reaction involving modified tripyrrane and dipyrromethane (Scheme 4), was reported from our group [28]. Our experience with core-modified *N*-confused porphyrins [29] prompted us to extend the methodology used, to generate first examples of *N*-confused sapphyrins. We have reported an easy



Scheme 4



Scheme 5

and efficient synthesis and characterization of the first core-modified, stable, aromatic *N*-confused *meso*-aryl core-modified sapphyrins **18** with an inverted *N*-confused ring by (3+2) MacDonald condensation methodology by carefully selecting the nature and concentration of acid catalyst used (Scheme 5) [30].

Apart from sapphyrins or [22]pentaphyrins (1.1.1.1.0), smaragdyrin or norsapphyrins or [22]pentaphyrin (1.1.0.1.0), and rubyrins or [26]hexaphyrin (1.1.0.1.1.0), there are some reports of other aromatic pentaphyrins and hexaphyrins (Chart 1). In 1983, Gossauer and coworkers obtained β-substituted pentaphyrin **19**, which has a Franck nomenclature [22]pentaphyrin (1.1.1.1.1), and more recently, *meso*-diphenyl pentaphyrin was reported by trifluoroacetyl (TFA)-catalyzed (3+2) condensation by Dolphin and coworkers [31]. Pentathiapentaphyrin and pentaselenapentaphyrin were reported by Vogel's group [32]. Very recently, Furuta and coworkers reported the formation of *N*-fused, normal-type 22π electronic pentaphyrin **20** containing a fused tripentacyclic ring from the Rothemund reaction of aldehyde and pyrrole [33]. Other reported aromatic pentaphyrins are **21**, having the trivial name "isosmaragdyrin" or [22]pentaphyrin (1.1.1.0.0) [34], [22]pentaphyrin (2.0.2.0.0) or ozaphyrin **22** [35], and [22]pentaphyrin (2.1.0.0.1) **23** [36]. β-substituted [26]hexaphyrin (1.1.1.1.1.1) was prepared by

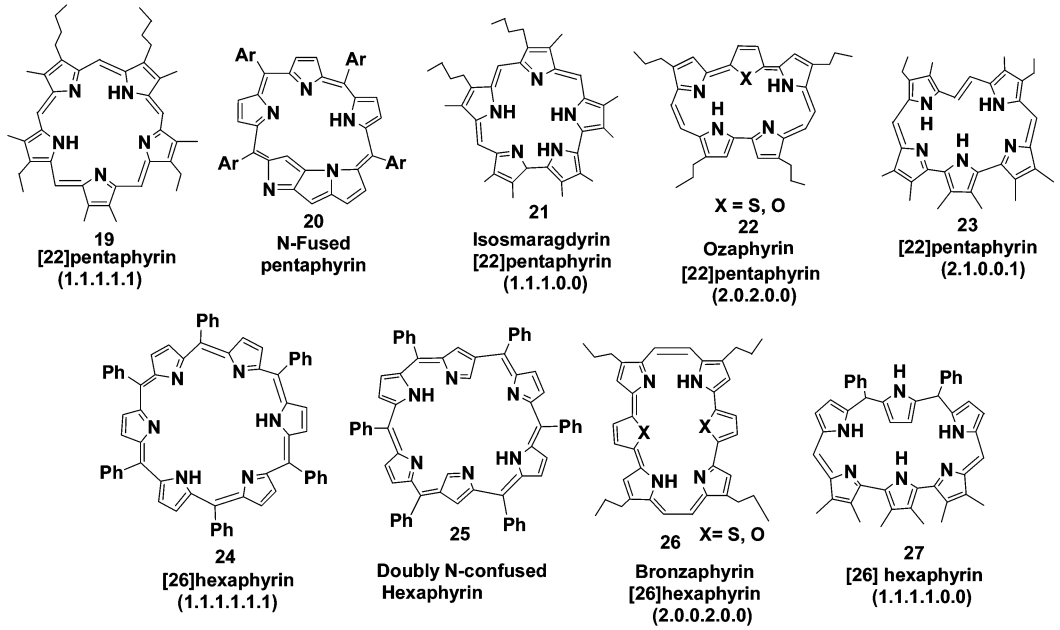
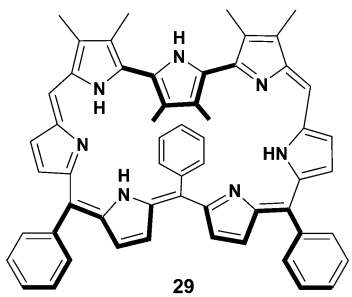


Chart 1

Gossauer and coworkers [31b–d], but first *meso*-aryl hexaphyrin **24** was reported by Dolphin and coworkers through Lindsey-type condensation between 5,10-diphenyl tripyrrane and benzaldehyde, and was found unstable [31e]. Cavaleiro and coworkers, through the Rothemund-type synthesis involving pentafluorobenzaldehyde and pyrrole, reported the first stable *meso*-aryl hexaphyrin [37]. Furuta's group, in one of their recent publications, have revealed that they have synthesized doubly *N*-confused hexaphyrin **25** bearing *meso*-aryl substituents by the acid-catalyzed condensation of *N*-confused tripyrrane and pentafluorobenzaldehyde [38]. Another aromatic β-substituted hexaphyrin is **26**, with the trivial name "bronzaphyrin", which is [26]hexaphyrin (2.0.0.2.0.0), both normal and core-modified versions owe their existence to the synthetic efforts of Johnson and Ibers [39], Cava and coworkers [40], and the groups of Merz and Neilden [41]. An all-aza isomer of rubyrin **27** with an inverted pyrrole ring and bearing aryl substituents in two of its *meso*-positions, where the pyrrolic units are connected in a 1.1.1.1.0.0 fashion, was reported very recently by Sessler and coworkers [42]. Other aromatic hexaphyrin systems reported are a hexathia [34]hexaphyrin (2.2.2.2.2.2), where each thiophene unit is connected by two bridging carbon atoms [8]. Very recently, we were able to report the synthesis of another isomer of rubyrin **28**, where the six pyrrole/heterocyclic rings are linked in a [1.1.1.0.1.0] fashion, in which the heterocyclic ring opposite the bithiophene/biselenophene unit remains inverted both in the free-base and the diprotonated form (Scheme 6). It was formed as one of the by-products of the reaction where the 30π heptaphyrin was the main product [43].

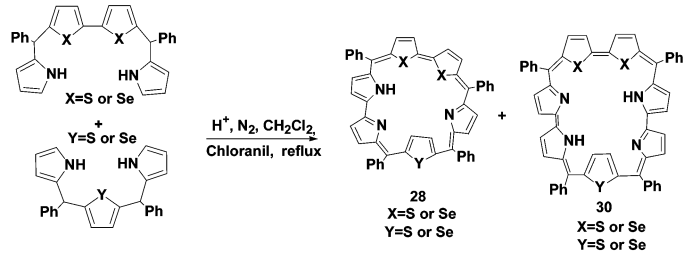
Aromatic core-modified heptaphyrins and octaphyrins

There are only a few reports on the expanded porphyrins containing more than six heterocyclic units. They are 28π heptaphyrin, 30π, 32π, and octaphyrin reported by Sessler and coworkers [44]; 34π, 36π, and 38π octaphyrins containing eight heterocyclic units [45,40c]; 40π decapyrrolic turcasarin [46]; 48π 12 pyrrolic dodecaphyrin and 64π 16 pyrrolic hexadecaphyrin [47]; 80π icosapphyrin and 96π tetracosapphyrin [48]. Furuta and coworkers reported Rothemund-type condensation of pyrrole and pentafluorobenzaldehyde, resulting in the formation of an array of expanded porphyrins, including a TFA salt of nine pyrrolic nonaphyrin [49]. Even though all these expanded porphyrins are important from a structural point of view and are shown exhibiting various nonplanar or figure-eight twisted conformations, they all turned out to be nonaromatic in their free-base form. Sessler and coworkers have reported the synthesis of a 30π aromatic heptaphyrin (1.1.1.1.1.0.0) **29**, bearing five meso bridging carbons of which three are aryl-substituted, and the compound exhibits a flat structure in solution and a figure-eight nonplanar structure in the solid state [50]. The aromaticity in these compounds depends on the number and nature of links between the heterocyclic rings as well as the flexibility of the ring. It is found that the adaptation of the figure-eight conformation disrupts the π electron pathway and thereby decreases the aromaticity of the octaphyrins. Thus, characterization of aromatic systems containing 30π and higher still remains a challenge not only from the synthetic point of view, but also from an understanding of molecular and electronic structures of the macrocycle, which can give more insight into the π conjugation pathway. Thus, currently (2+3) [21a,51], (4+1) [52], (3+1+1) [53], or a (3+3) [42] condensation

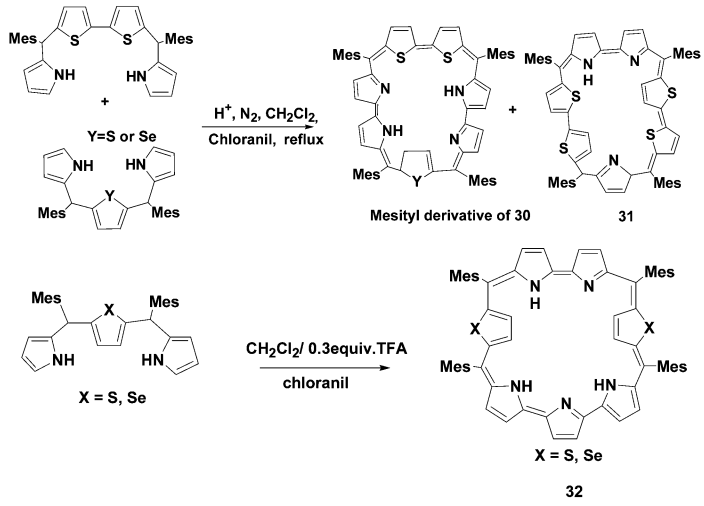


29
[30]heptaphyrin
(1.1.1.1.1.0.0)

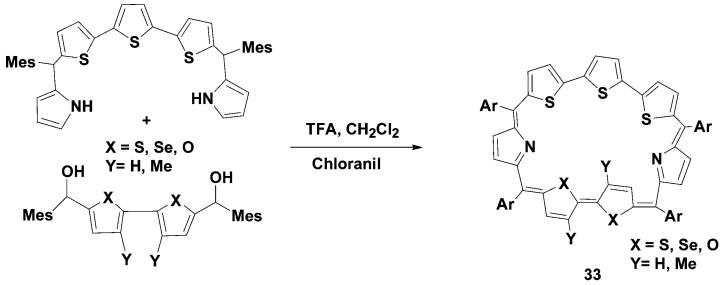
and self-coupling of small molecules are widely used to synthesize aromatic expanded porphyrins. We have very recently reported successful synthesis of a range of aromatic core-modified 30π *meso*-aryl heptaphyrins by oxidative coupling and condensation methodology. (4+3) Oxidative coupling gave rise to **30**, **31** (by carefully varying the substituents at the *meso* position and acid catalyst concentration, we could control the product formation effectively in this oxidative coupling reaction), while (3+3+1) gave **32** as shown in Schemes 6 and 7 and (5+2) and (4+3) condensation (Schemes 8 and 9) gave rise to **33** and **34**, respectively [54], and 34π octaphyrins **35** by (4+4) acid-catalyzed oxidative coupling (Scheme 10) [55] by judiciously selecting the precursors. These synthetic steps show that minor variations in the precursors and reaction conditions are crucial for obtaining novel macrocyclic ligands.



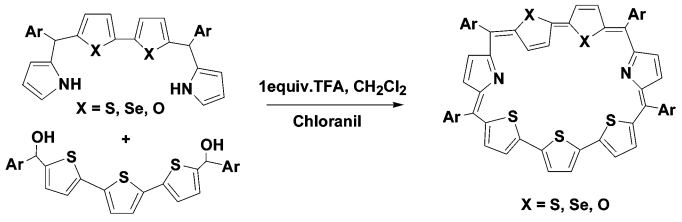
Scheme 6



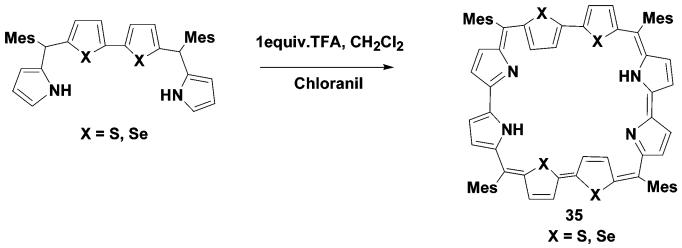
Scheme 7



Scheme 8



Scheme 9



Scheme 10

Spectral characterization

It has been shown that the aromatic *meso*-aryl-substituted core-modified expanded porphyrinoids like sapphyrins, smaragdyrins, rubyrins, hexaphyrins, heptaphyrins, and octaphyrins reported to date exhibit rich structural diversity. This interesting phenomena was characterized thoroughly with the help of detailed 1D and 2D NMR techniques, and in most of the cases, X-ray crystal structural evidence was also provided. In some cases, two different structural conformers were observed, and both of them exhibited an aromatic nature [54b,55]. Wherever crystal structural data could not be obtained, ab initio calculations were relied on, and they are in perfect agreement with NMR solution data, which explains the observed structural diversity such as heterocyclic inversion in terms of stabilization energies [54b].

A comparison of crystal structures of modified expanded porphyrins reported from our laboratory [22a] suggests that the inversion of heterocyclic ring depends upon the nature of the heteroatom present in the heterocyclic ring adjacent to it. For example, when the adjacent ring contains bigger heteroatoms such as S and Se, the ring will be planar due to the smaller cavity inside the core of the macrocycle and hence will hinder the ring inversion, while a smaller atom like N/O will create space inside the core to accommodate the β-CH protons of the heterocyclic ring adjacent to it, thereby allowing the ring inversion. From the literature, it can be hypothesized that two important parameters responsible for sustaining the diatropic ring current in expanded porphyrins are the number of heterocyclic rings and the number of bridging carbons present in the macrocyclic ring. Altering the number of either one of them has invariably led to successful synthesis of aromatic expanded porphyrins. The recent report of planar aromatic 34π octaphyrins support such a hypothesis [55]. It has been observed that simultaneous variation of both the parameters disrupts the aromaticity either due to flexibility of the molecule or due to increased number of direct pyrrole–pyrrole links found in octaphyrins and higher-order cyclopolypyrroles in its free-base form.

All the expanded macrocycles reported were found to have typical optical spectra with strong Soret-type bands and four Q-bands confirming the porphyrinic nature of the macrocycles. Aromatic *meso*-aryl-substituted, core-modified, expanded porphyrinoids are red-shifted with respect to that of normal porphyrins due to the presence of increased number of π electrons in the aromatic conjugative pathway. The cyclic voltammetric studies on these core-modified expanded porphyrinoids were performed, and the energies of the Soret maxima and the highest occupied molecular orbital–lowest occupied molecular orbital (HOMO–LUMO) gap vary linearly, with the increase in π electrons justifying

the aromatic nature of these macrocycles. In addition to these properties, these macrocycles, by virtue of their varying cavity size and coordinating atoms, are considered multipurpose macrocycles, which can selectively recognize and transport neutral, anionic, and cationic substrates under a variety of conditions. Exploration of their intriguing mechanistic details with the experiments performed on model systems is one of the most pursued topics of research.

CONCLUDING REMARKS

It is hoped that the availability of new methodologies for high-yield syntheses of these new core-modified expanded porphyrins will allow further exploitation of their rich chemistry in terms of their coordination behavior toward transition metals, and their use as catalysts for organic transformations and could also be potent new candidates for biomedical applications. These results have given strong impetus in the positive direction to carry out reactions to obtain huge aromatic macrocycles that are still elusive and may prove to be a daunting task, but can now not only be dreamt of but also can be attained by a judicious retrosynthetic approach.

ACKNOWLEDGMENTS

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