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Structural Diversity in Expanded Porphyrins

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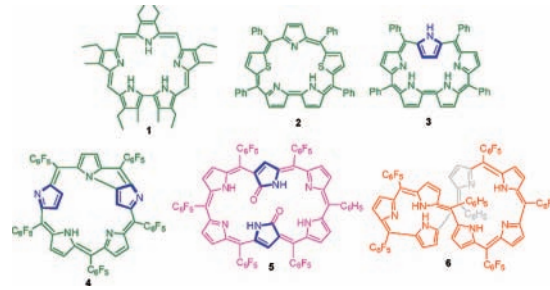

Inspired by the chemistry of porphyrins, in the last decade, a new research area where porphyrin analogues such as expanded, isomeric, and contracted porphyrins have been synthesized, and their chemistry has been exploited extensively. Expanded porphyrins are macrocyclic compounds where pyrrole or heterocyclic rings are connected to each other through *meso* carbon bridges. Depending on the number of pyrrole rings in conjugation or the number of double bonds linking the four pyrrole rings expanded porphyrins containing up to 64 π electrons are reported in the literature. The interest in these systems lies in their potential applications as anion binding agents, as photosensitizers for photodynamic therapy (PDT), in antisensing applications, as MRI contrasting agents, and more recently, as material for nonlinear optical application.

Expanded porphyrins containing more than four pyrrole or heterocyclic rings, such as sapphyrin (five pyrrole), rubyrin (six pyrrole), heptaphyrin (seven pyrrole), and octaphyrin (eight pyrrole), are reported in the literature. Furthermore, substituents on expanded porphyrins can be attached either at the *meso* carbons or at β-pyrrole positions. β-substituted expanded porphyrins generally adopt *normal structure* where all the pyrrole nitrogens point inward in the cavity **1**, while the *meso*-substituted expanded porphyrins exhibit normal **2**, *inverted* **3**, *fused* **4**, *confused* **5**, and *figure eight* **6** conformations. The conformation of expanded porphyrin is dependent on the nature of the linkage of the heterocyclic rings, the nature and the number of the heteroatoms present in the cavity, and the state of protonation. It is possible to change one conformation to another by varying temperature or by simple chemical modification, such as protonation by acids.

An understanding of the structure−function correlation in expanded porphyrins is an important step for designing these molecules for their potential applications. In this context, even though several *meso* aryl expanded porphyrins are reported in literature, there is no comprehensive understanding of structural diversity exhibited by them. In this Account, an attempt has been made to provide a systematic understanding of the conditions and circumstances that lead to various conformations and structures. Specifically, the structural diversities exhibited by five pyrrolic macrocycles to ten pyrrolic macrocycles are covered in this Account.

In pentapyrrolic systems, sapphyrins, N-fused, and N-confused pentaphyrins are described. It has been shown that the positions of the heteroatom affect the conformation and in turn the aromaticity.

In hexapyrrolic systems, rubyrins and hexaphyrins are covered. The conformation of core-modified rubyrins was found to be dependent on the number and nature of the heteroatom present inside the core. Further, in the hexapyrrolic systems, an increase in the number of *meso* carbons from four (rubyrin) to six (hexaphyrin) increases the conformational flexibility, where different types of conformations are observed upon going from free base to protonated form.

Heptapyrrolic and octapyrrolic expanded porphyrins also exhibit rich structural diversity. Octaphyrins are known to exhibit figure eight conformation, where the macrocycle experiences a twist at the *meso* carbon, losing aromatic character. By suitable chemical modification, it is possible to avoid the twist, and planar 34 π core-modified octaphyrins have been reported that show aromatic character and obey the $(4n + 2)$ Hückel rule. The structural diversity exhibited by nine pyrrolic macrocycles (nonaphyrins) and ten pyrrolic macrocycles (decaphyrins) are also described.

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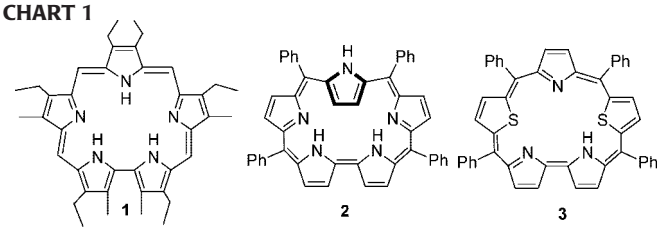
Introduction

Even though the first expanded porphyrin, a 22 π macrocycle named "sapphyrin", **1**, was serendipitously discovered[1] by Woodward and co-workers in 1966, significant advancement in expanded porphyrin chemistry was made only after the early 1980s because of the nonavailability of efficient methodologies to synthesize them in decent yields.[2,3] The synthetic advances were spearheaded by the groups of Vogel in Köln and Sessler in Austin laboratory.[2] Vogel et al. have reported a diverse range of expanded porphyrin analogues, tetraoxa, tetrathia, and tetraselena dications containing 22 π, 26 π, and 30 π conjugated electrons.[4] On the other hand, Sessler et al. pioneered the rational synthesis of 22 π sapphyrin, 26 π rubyrin, 24 π rosarin, 24 π amethyrin, 28 π heptaphyrin, and 40 π turcasarin using stable precursors in good yields.[5] They not only have succeeded in developing efficient synthetic methods but also have pioneered synthesis of stable building blocks, such as tripyrranes, dipyrromethanes, and quaterpyrroles, required for the construction of expanded porphyrins. The interest in the chemistry of expanded porphyrins is many fold. They are (a) used in biomedical applications,[6a] (b) potential molecules to complex larger cations in free base form and anions in protonated form,[6b] (c) fundamentally ideal models to test the limit of the ($4n + 2$) Huckel rule for aromaticity,[2] and (d) potential molecules for application as nonlinear optical materials.[7]

This significant growth in expanded porphyrin chemistry in the last two decades has resulted in a few excellent reviews on various aspects of their chemistry. Recently, Sessler et al. have reviewed various synthetic methods[5] and their anion binding abilities comprehensively.[6b] Osuka and co-workers have reviewed confusion, inversion, and creation aspects of expanded porphyrins.[8] We have recently reviewed synthesis and spectroscopic aspects of core-modified expanded porphyrins.[9]

Most of the above reviews have concentrated on synthetic methodologies, spectroscopic properties, coordination chemistry of anions and cations, reactivities, and some structural aspects.[5,6,8,9] However, several expanded porphyrins reported in the last five years (especially *meso*-aryl derivatives) show fascinating structural diversity and exhibit conformational flexibility. It has been shown that the structure and the conformation of expanded porphyrins are very sensitive to the nature of the linkage of the heterocyclic rings, the nature and the number of the heteroatoms present in the cavity, the temperature at which measurement was made, and the state of protonation. It has been possible to change one conformation to another by varying temperature or by simple chemical modification, such as protonation by acids.[9] To the best of our knowledge, there are no reviews on the fascinating structural diversity exhibited by expanded porphyrins. Hence an attempt has been made in this Account to review the structural diversity aspect of expanded porphyrins. Specifically, emphasis has been given on expanded porphyrins containing five to ten pyrrolic or heterocyclic rings. The material covered in the porphyrin handbook has also been excluded for constraints of space. Emphasis has been given to the work published in last five years, and the materials published up to March 2007 have been included in this Account. Furthermore the material covered in our earlier review[9] has been excluded.

CHART 1



Sapphyrins

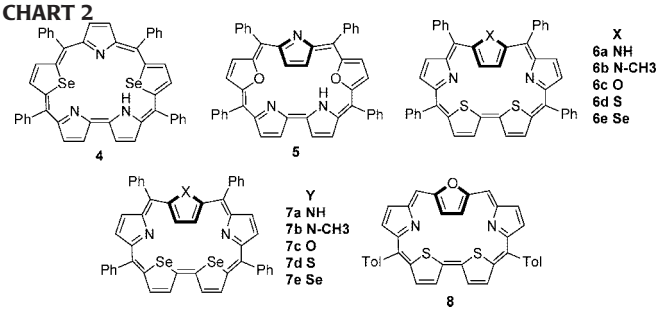
The first expanded porphyrin was named sapphyrin (**1**) because of its brilliant blue color. Sapphyrin contains five pyrrole rings linked to each other with four *meso*-carbons and one direct pyrrole−pyrrole bond.[10] Two different types of sapphyrins are known in the literature (Chart 1) depending on the location of substituents: (a) β-substituted sapphyrins (**1**), which contain alkyl substituents on β-pyrrole positions with *meso*-free carbons; (b) *meso*-substituted sapphyrins (**2** and **3**), where *meso*-carbons have aryl groups and β-pyrroles have no substituents.[6b]

It is seen from the structure that the β-substituted sapphyrin **1** exhibits a *normal structure* where all the pyrrole rings are pointing inward, while the *meso*-aryl sapphryins show structural diversity.[6b] For example, **2** exhibits an *inverted structure* in which the pyrrole ring opposite to the bipyrrole subunit has undergone a 180° ring flipping, while the *meso*-aryl sapphyrin **3** exhibits a normal structure without any ring inversion.[11,13]

To understand the reason and circumstances that lead to ring inversion, a range of sapphyrins (**4**−**8**) were synthesized (Chart 2).[12,14] Interestingly sapphyrins **5**, **6**, **7**, and **8** show inverted structure, whereas sapphyrins **3** and **4** exhibit normal structure.

The inversion of the heterocyclic ring in *meso*-aryl sapphyrin can be inferred from the measurement of chemical shift of the β-pyrrole protons of the inverted ring by ^{1}H NMR in solu-

CHART 2



tion and by solving the single-crystal X-ray structure in the solid state.[12] For example, if the ring is inverted in the solution, the β-pyrrole protons of the inverted ring resonate in the shielded region (−1.49 ppm for **2**), while in the normal structure the β-pyrrole proton resonate in the deshielded region (8.96 ppm for **4**).[13] This large difference in the chemical shift can be used as a marker to identify inverted structure in sapphyrins.

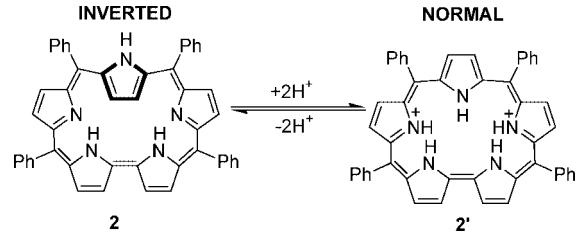
The ^{1}H NMR and X-ray structure (of few of the sapphyrins) analyses reveal that larger core size and the presence of smaller heteroatoms (N or O) adjacent to the heterocyclic ring leads to inverted structure, while the presence of bigger heteroatoms (S or Se) leads to normal structure.[12] For example, when the adjacent ring next to the inverted ring contains a small heteroatom like N and O, the ring is inverted as in **2**, **5**, **6**, **7**, and **8**, while in **3** and **4**, which show a normal structure, the adjacent ring contains bigger S or Se atoms (Figure 1).

Further, Lee et al. looked at the effect of removal of *meso*-aryl substituents on the conformation of sapphyrin.[15] The ring inversion observed for **8** clearly confirms that the presence of a smaller heteroatom like N and O adjacent to the inverted ring is important for the observation of inverted structure.

It is possible to convert an inverted structure to a normal structure in favorable cases by simple chemical modification. For example, Latos-Grazynski et al. using ^{1}H NMR have shown that the free base form of **2**, which shows an inverted structure, can be converted to a normal structure by simple diprotonation[11] (Scheme 1). Here, the inverted pyrrole ring undergoes a 180° ring flipping upon protonation of the

FIGURE 1. X-ray structure of **6d** and **4**.

SCHEME 1



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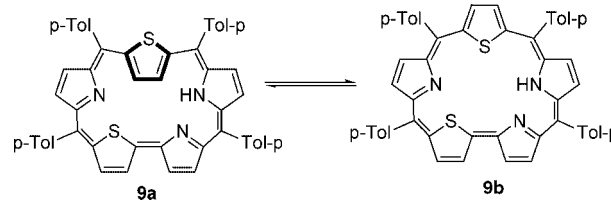

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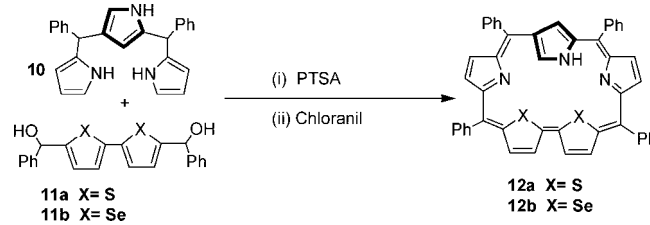


adjacent pyrrole nitrogens. The chemical shift difference, $\Delta\delta$ (the difference between the chemical shift of the most shielded and the most deshielded proton), of 11.6 ppm clearly reveals the aromatic nature of **2**. On the other hand, the core-modified sapphyrins (**3**−**8**) do not exhibit such ring flipping upon protonation, and the structures remain inverted or normal as the case may be.[12]

An analysis of ^{1}H NMR data indicates that inverted structures show reduced diatropic ring current; that is, the aromaticity in the macrocycle is reduced due to ring inversion. The inverted sapphyrins show smaller $\Delta\delta$ values as compared with normal sapphyrins probably caused by nonplanar structure resulting in the disruption of π-conjugation. A comparison of $\Delta\delta$ values of a few normal and inverted sapphyrins reveals the above fact. For example, the $\Delta\delta$ value for **3** is 14.87 ppm, that for **2** is 11.60, that for **5** is 10.64, and that for **6a** is 9.70 ppm.

Interestingly Latos-Grazynski et al. have shown the presence of equilibrium between the normal and inverted forms in unsymmetrical dithiasapphyrins (Scheme 2). This equilibrium has been found to be temperature dependent in the range 193−342 K, and the predominant species is the inverted form (**9a**).[16]

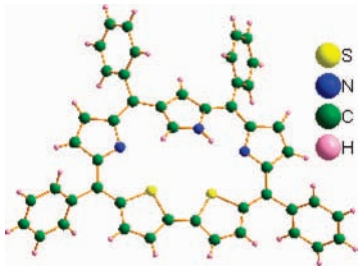


FIGURE 2. X-ray structure of **12a**.

N-Confused and Doubly N-Confused Sapphyrins

Recently, we have reported the modified N-confused sapphyrins **12a** and **12b**.[17] The synthetic strategy here was a MacDonald-type condensation reaction of N-confused tripyrrane **10** with bithiophene/biselenophenediol **11a**/**11b** (Scheme 3). In the resulting sapphyrin, the NH of the N-confused pyrrole is inside the cavity. Usually, in N-confused porphyrins the NH of the N-confused pyrrole points outward.[8] The single-crystal X-ray structure confirms the proposed structure (Figure 2).

The $\Delta\delta$ values of 7.06 and 8.79 ppm for free base and protonated forms of **12a** clearly exhibit reduced aromaticity in N-confused sapphyrins as compared with all-aza *meso*-tetraarylsapphyrin.

Very recently, Sessler et al. have used a [3 + 2] approach to generate doubly N-confused sapphyrin **16** (Scheme 4), where the two pyrroles of the bipyrrole unit are inverted.[18]

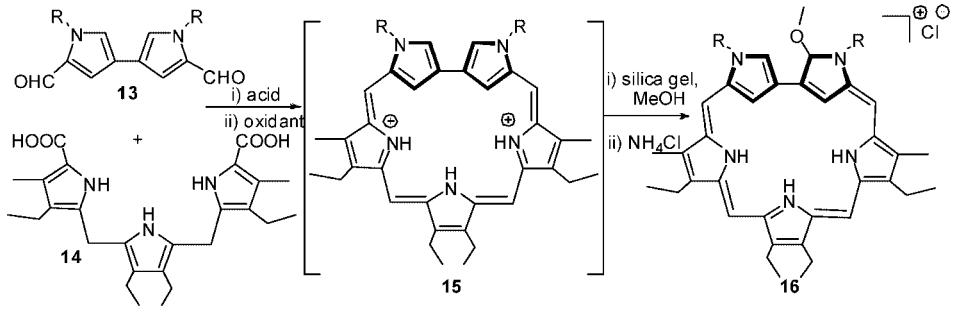
In the synthesis of N-confused sapphyrins **12a** and **12b**, the synthetic strategy involves N-confused tripyrrane **10**, while in doubly N-confused sapphyrin **16** the confusion was incorporated in the bipyrrolic unit **13**, and the tripyrrane **14** has β-alkyl substituents. The idea for incorporation of double confusion was excellent because the inversion of the pyrrolic nitrogen was configurationally executed. The $\Delta\delta$ values of 4.79 and 4.52 ppm indicate moderate aromaticity in **16**. A comparison of $\Delta\delta$ values of *meso*-aryl sapphyrins and N-confused sapphyrins indicates a gradual reduction in the aromaticity upon N-confusion (Scheme 5).

N-Fused and N-Confused Pentaphyrins

Osuka et al. first reported that the *meso*-aryl pentaphyrin exists in the form of an N-fused pentaphyrin.[19] The Rothemund-type condensation reaction of pyrrole with pentafluorobenzaldehyde resulted in oxidized and reduced forms of N-fused pentaphyrin along with other products. A fused tripentacyclic ring with one inward and one outward pointing pyrrole nitrogen was found in N-fused pentaphyrin (Figure 3). The oxidized form of N-fused pentaphyrin **18** shows aromatic behavior, while the reduced form **17** shows antiaromatic behavior, and they are interconvertible (Scheme 6).

In another attempt for the synthesis of N-confused pentaphyrin, Furuta et al. conducted the [3 + 2] acid-catalyzed condensation reaction of N-confused tripyrrane **19** and

SCHEME 4



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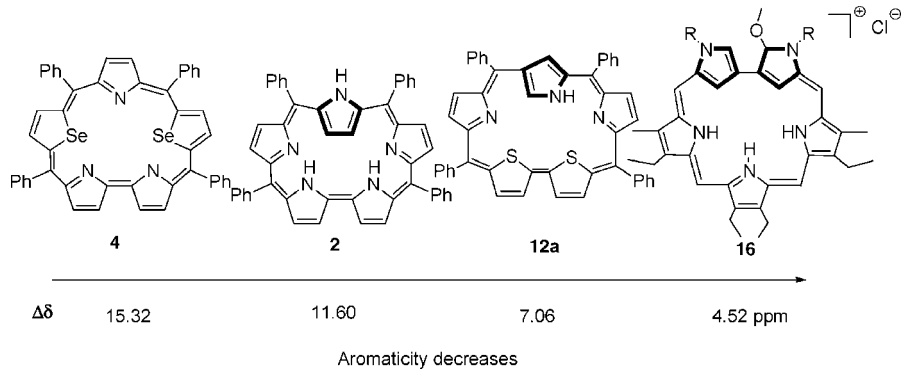


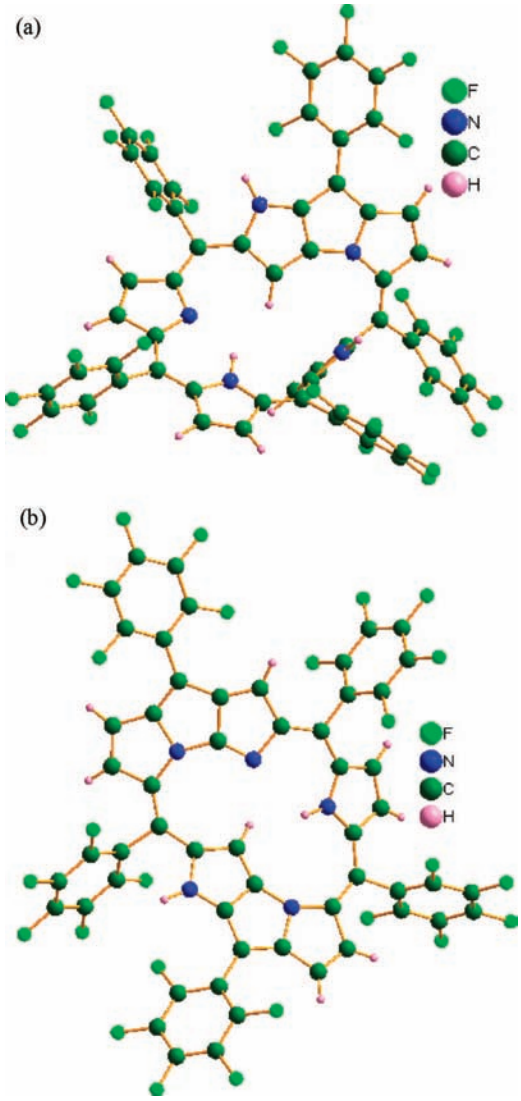
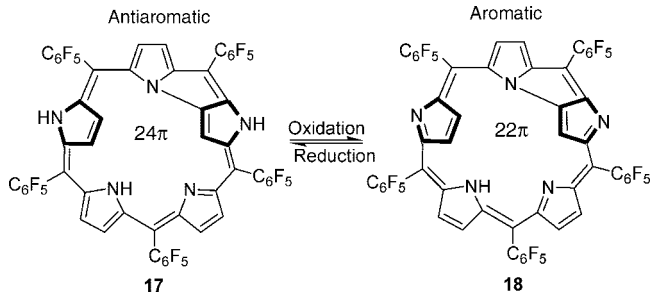


FIGURE 3. X-ray structure of (a) **18** and (b) **23**.

SCHEME 6



dipyrromethanedicarbinol **20** (Scheme 7).[20] The resultant product **21** contained the fused tripentacyclic ring with all nitrogens pointing inward. Further, oxidation of **21** resulted in formation of **22**, which isomerized into doubly N-fused pentaphyrin **23**. Interestingly isomerization takes place with loss of aromaticity and the resultant pentaphyrin **23** is nonaromatic. The single-crystal X-ray structure of doubly fused pentaphyrin **23** reveals the presence of two tripentacyclic rings and a pyrrole ring in the macrocycle (Figure 3).

SCHEME 7

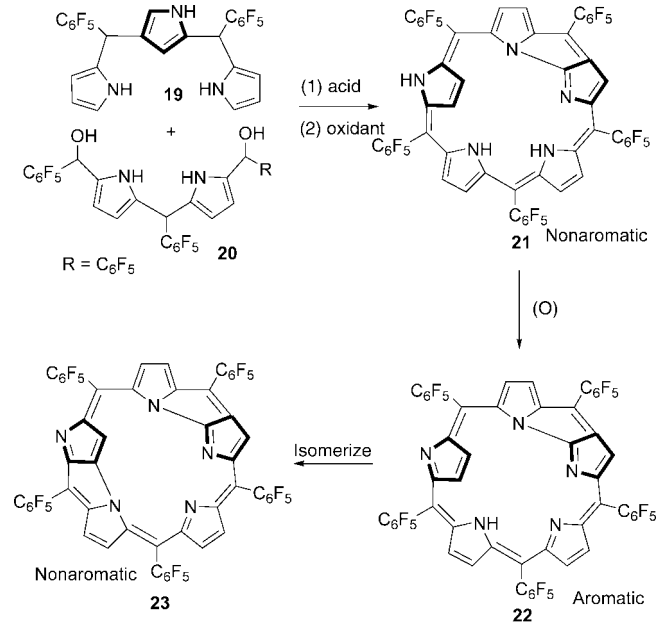
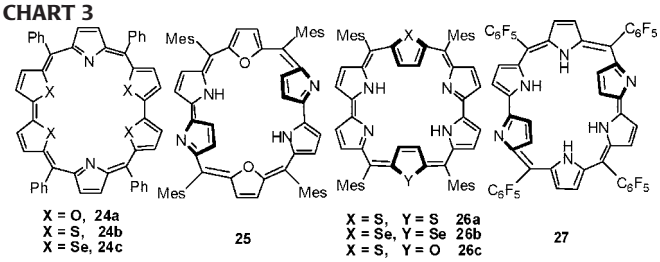


CHART 3

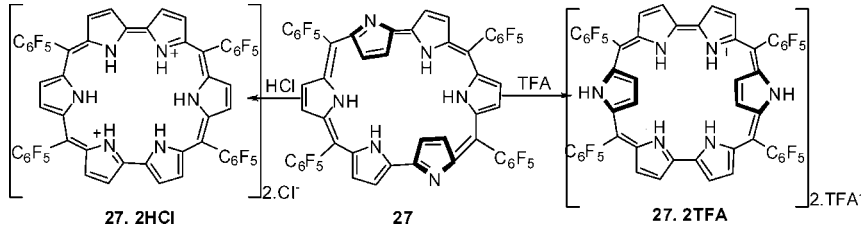


Hexapyrrolic Systems

(a) Rubyrins. In contrast to pentapyrrolic systems, the hexapyrrolic systems exhibit more structural diversity, and the structure of the resulting macrocycle is influenced by the nature of the link, the number of *meso*-carbons linking the six pyrrole/heterocyclic rings, and the nature of heteroatom.[5] For example, amethyrin (1.0.0.1.0.0) in which six pyrrole rings are linked with two *meso*-carbons and rosarin (1.0.1.0.1.0) linked by three *meso*-carbons do not exhibit any structural diversity.[3] On the other hand, the *meso*-aryl rubyrins in which six heterocyclic rings are linked with four *meso*-carbons exhibit rich structural diversity.[13] The core-modified rubyrin shows three different types of structures, described as normal in which all the heterocyclic ring points toward the macrocycle as in **24** (Chart 3).[13]

Normal structure is always observed when there are four heteroatoms and two pyrrole nitrogens present in the cavity. However, in rubyrin containing four pyrrole nitrogens and two

SCHEME 8



27. 2HCl **27** **27. 2TFA**

heterocyclic rings, two different ring inverted structures are observed.[9] When the heteroatom present is either S or Se, the middle heterocyclic ring of each tripyrrane unit is inverted as in **26**, while when the heteroatom is smaller (oxygen), one pyrrole ring of each bipyrrole unit is inverted as in **25**. The all-aza rubyrin **27**, reported by Osuka et al. also shows inversion of one pyrrole ring in each bipyrrole unit as in **25**.[21]

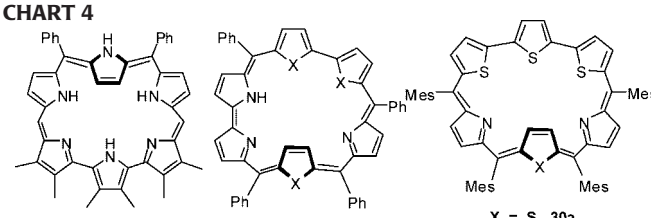
Like sapphyrins, in rubyrins also, it is possible to convert an inverted structure to a normal structure, and these are shown to be temperature dependent.[9] For example, Chandrashekar et al. have shown that the dithia- and diselena-rubyrin (**26a**, **26b**), which show an inverted structure in the free base form, can be converted into a normal structure upon diprotonation of the pyrrole rings.[13] Interestingly, all-aza *meso*-aryl rubyrin **27** shows similar behavior upon protonation. For example, it has been shown that the ring flipping in the all-aza rubyrin **27** upon protonation depends on the nature of acid used (Scheme 8). Protonation by HCl leads to 180° ring flipping of two inverted pyrrole rings, while use of TFA leads to simultaneous flipping of two inverted rings to normal and two normal rings to inverted as depicted in Scheme 8.[21]

UV–vis spectral changes upon addition of acid also support the attainment of different conformations. Protonation of **27** with TFA leads to red shift of the Soret band by 18 nm with respect to the free base congener, while protonation with HCl results in blue shift of the Soret band by 19 nm, suggesting different structures in the dication.

The structural diversity in rubyrins also depends on the nature of the links. For example, **28** reported by Sessler et al. is an interesting one.[22] Here, one part of tripyrrane has *meso*-aryl substituents and another part of tripyrrane has β-alkyl substituents. The ring inversion happens only in the tripyrrane part containing *meso*-aryl substituents. In compounds **29** (1.1.1.0.1.0) and **30** (1.1.1.1.0.0) where the link is unsymmetrical, only one heterocyclic ring is inverted (Chart 4).[23,24]

(b) Hexaphyrins. Hexaphyrin (1.1.1.1.1.1) **31** can be considered a real homologue of porphyrin in terms of a conjugated cyclic π-system with alternate arrangement of heterocyclic rings and methine bridges.[2] The presence of six *meso*-carbon bridges makes the molecule flexible, and hence

CHART 4



28 **X = S, 29a** **X = Se, 29b** **X = S, 30a** **X = Se,30b**

the hexaphyrins generally adopt different conformations. Hexaphyrins reported in the literature (Chart 5) were found to exhibit normal structure as in **33**, inverted structure as in **31**, **34**, and **35** and *figure eight* conformation as in **32**.

All-aza hexaphyrins reported by Cavaleiro, Osuka, and Anderson, exhibit rectangular conformations, which consist of two opposite, inverted pyrroles with nitrogen atoms pointing outward and the four corner pyrroles with nitrogen atoms pointing inward. Further, they show both normal and figure eight conformation depending on the nature of *meso*-substituents and β-substituents.[25] In general, hexaphyrins exhibiting normal or inverted structure show aromatic character, while hexaphyrins with figure eight structure are nonaromatic. Interestingly, 28 π all-aza hexaphyrin **35** reported by Anderson et al., which has two different *meso*-substituents, does not show aromatic character despite its inverted structure.[25] These observations reveals that the subtle changes on the periphery of hexaphyrin can affect the aromatic nature as well as the conformation.

Core-modified hexaphyrins **36–38** (Chart 6) exhibit interesting structural diversity as compared with all-aza hexaphyrin. The conformation of **36–38** was found to be highly dependent on the temperature, the nature of the heteroatom, and the state of protonation.[26]

For example, all three hexaphyrins exhibit dynamic structure, where the heterocyclic rings are undergoing rotation at room temperature.[26] However; at low temperature, they show static structure. At 218 K, in **36**, two pyrrole rings of each tripyrrane unit exhibit a 180° ring flipping, while **37** and **38** exhibit partial ring inversion of two pyrrole and two heteroatom rings as shown in Chart 7.[26] However, the trithiahexa-

CHART 5

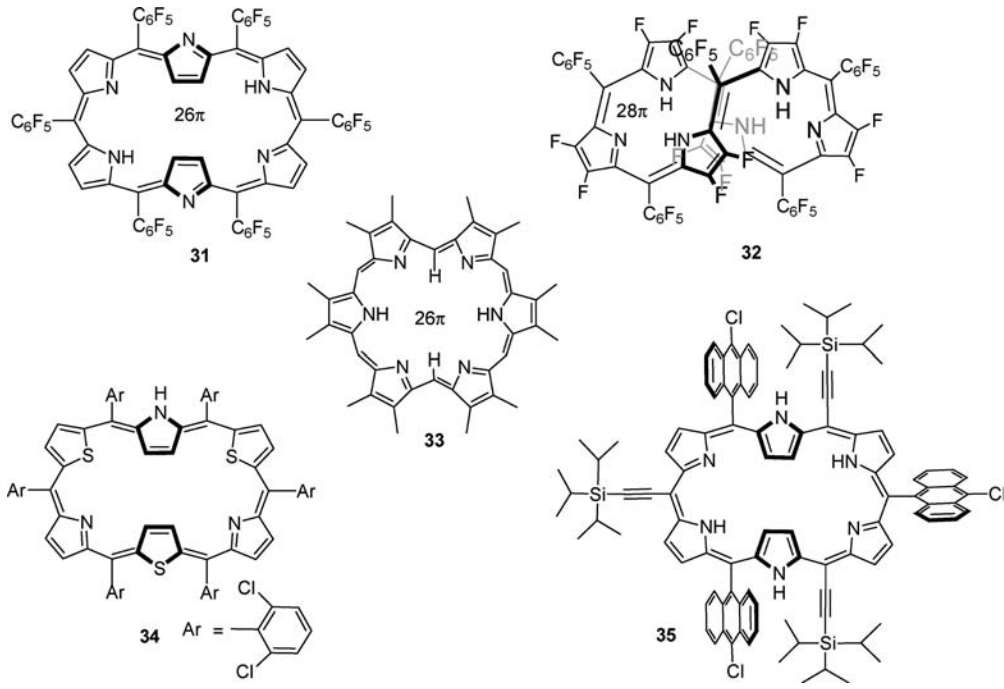


CHART 6

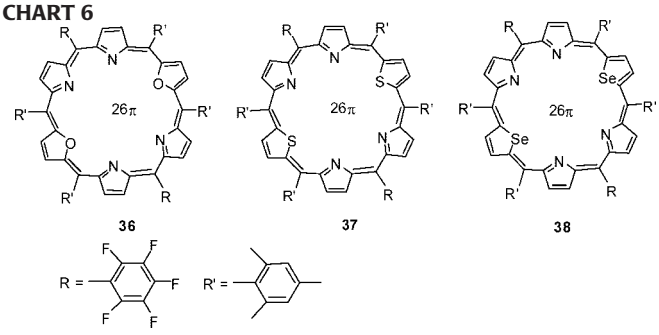
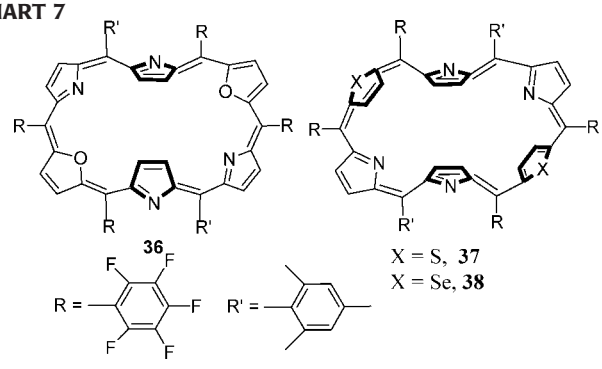


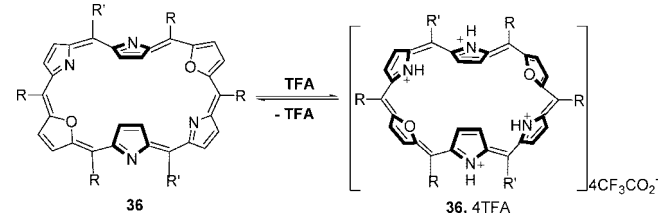
CHART 7



phyrin **34** reported by Hung et al. show inversion of pyrrole and thiophene ring at room temperature.[27]

Upon protonation of the pyrrole nitrogens, interesting conformational changes were observed for **36**, **37**, and **38**. Specifically, protonation of **36** leads to further ring inversion, and in the fully protonated form, **36** exhibits 180° ring inversion of two central pyrrole rings and partial ring inversion of

SCHEME 9



the remaining heterocyclic ring as shown in Scheme 9.[26a] This is also supported by UV–vis spectroscopic studies (Figure 4), where distinct color changes and large shifts of the Soret band were observed. Compounds **37** and **38** also exhibit ring inversions upon protonation. Specifically, partial protonation of **37** and **38** arrests the ring rotation, and only two pyrrole rings of each tripyrrane unit exhibits 180° ring flipping as observed by the X-ray crystal structure of partially protonated **37**.[26b] Further protonation, by two additional protons leads to inversion of two more heterocyclic rings leading to hexaphyrin having four inverted rings (Scheme 10).

Recently, Furuta et al. have reported doubly N-confused hexaphyrins **39**–**42**.[28] The nature of hexaphyrin was found to be dependent on the nature of oxidant used in the reaction. When N-confused tripyrrane was treated with pentafluorobenzaldehyde in presence of acid catalyst followed by oxidation with *p*-chloranil, doubly N-confused hexaphyrins (**39** and **40**) were obtained (Scheme 11). Spectroscopic studies reveal that **39** is a nonaromatic 28 π system, while **40** is a 26 π aromatic system. However, aromatic system **40** was found

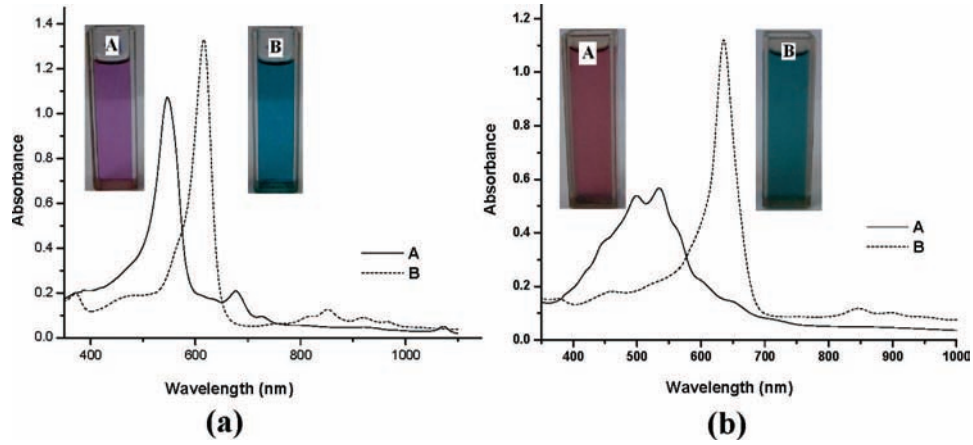
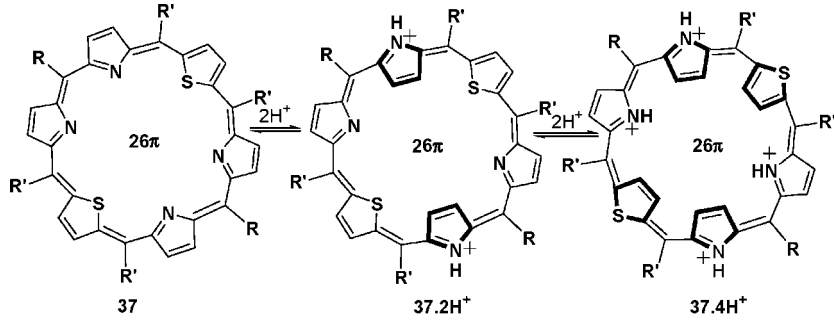
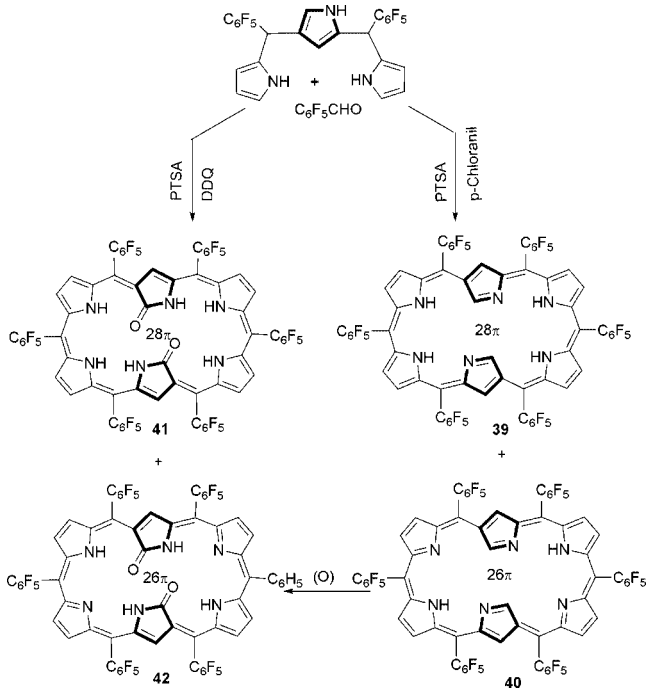


FIGURE 4. Electronic absorption spectra of (a) **36** and (b) **38** in CH_2Cl_2. **A** and **B** represent free base and protonated forms of the corresponding hexaphyrins.

SCHEME 10



SCHEME 11



to be unstable and gradually oxidized into the dioxo derivative **42** in CH_2Cl_2 solution at room temperature. On varyiation of the oxidizing agent from *p*-chloranil to DDQ, again two different products (**41** and **42**) were obtained. Spectroscopic studies reveal that **41** is a nonaromatic 28 π system while **42** is a 26 π aromatic system. The X-ray analysis reveals that confused pyrrole rings are inverted and two oxo groups are attached at the inner α carbon atom affording the CONH group (Figure 5).

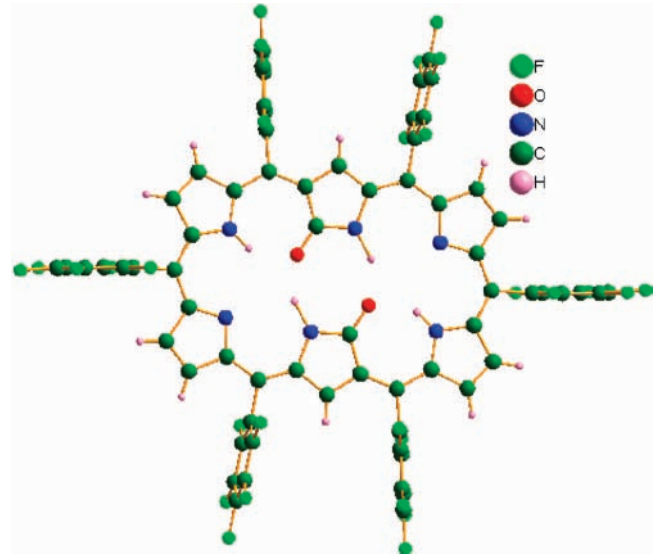
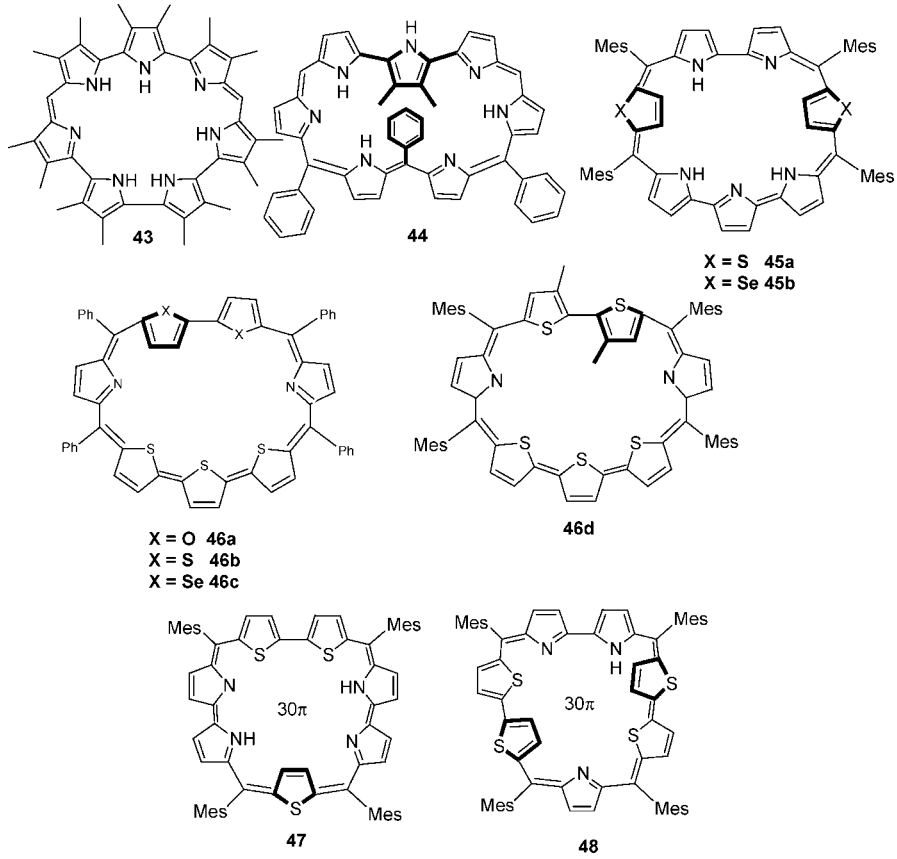


FIGURE 5. X-ray structure of **42**.

CHART 8



Heptaphyrins

In the past few years, the chemistry of the heptaphyrins has grown rapidly (Chart 8). Sessler's group reported the first planar 28 π heptaphyrin **43** with two *meso*-carbons.[29] The single-crystal X-ray structure of **43** reveals a fairly planar structure with no ring inversions due to its rigidity. However, **43** turned out to be antiaromatic, and the single-crystal X-ray structure of the sulfate salt of **43** reveals the presence of a SO_4^{2-} group inside the cavity with N−H---O hydrogen-bonding interactions (Figure 6).

Another paper from Sessler's group reported 30 π aromatic heptaphyrin **44**, which exhibits unusual behavior.[30] The X-ray structure of **44** reveals figure eight conformation (Figure 6). However, in solution, detailed ^{1}H NMR studies show that the macrocycle **44** is aromatic with unusual behavior. It was observed that the pyrrole rings containing β-methyl substituents are inverted and one of the *meso*-phenyl rings is pointing inward, toward the cavity. This is the first example of a heptaphyrin that is nonaromatic in the solid state but exhibits aromatic features in solution.

We reported a range of 30 π aromatic heptaphyrins **45**−**48**. Interestingly all the core-modified heptaphyrins reported by us exhibit unique inverted structure in which one or more heterocyclic rings have undergone 180° ring flipping. For example, in **45** only two opposite thiophene or selenophene rings of tripyrrane moiety are inverted. In **46**, one heterocyclic ring of the biheterocyclic ring is inverted. The ^{1}H NMR spectrum of **46b** shows a well-resolved "doublet of doublets" in the region −0.5 to −2 ppm, assigned to one of the inverted heterocyclic rings.[31] Upon protonation, these resonances experience much more shielding (−5 to −5.2 ppm), and the pyrrole NH proton resonates in the region −6.5 to −7 ppm, indicating that the ring inversion was retained after protonation.

In order to confirm that the ring inversion is taking place in the bithiophene unit instead of the terthiophene unit, an analogue of **46b** bearing a methyl group on the β-position of the bithiophene unit **46d** was synthesized.[31] The ^{1}H NMR of **46d** resolved the doubts concerning the ring inversion in the macrocycle. In the ring inversion state, of the two β-methyl groups, one experiences diatropic ring current and the other does not. Therefore, the methyl groups should have different chemical shifts. In **46d**, the two methyl groups resonate at −3.86 and 2.7 ppm, thus confirming one ring inversion of the bithiophene unit and not the terthiophene unit. This was further confirmed by the observation of two different ^{77}Se sig-

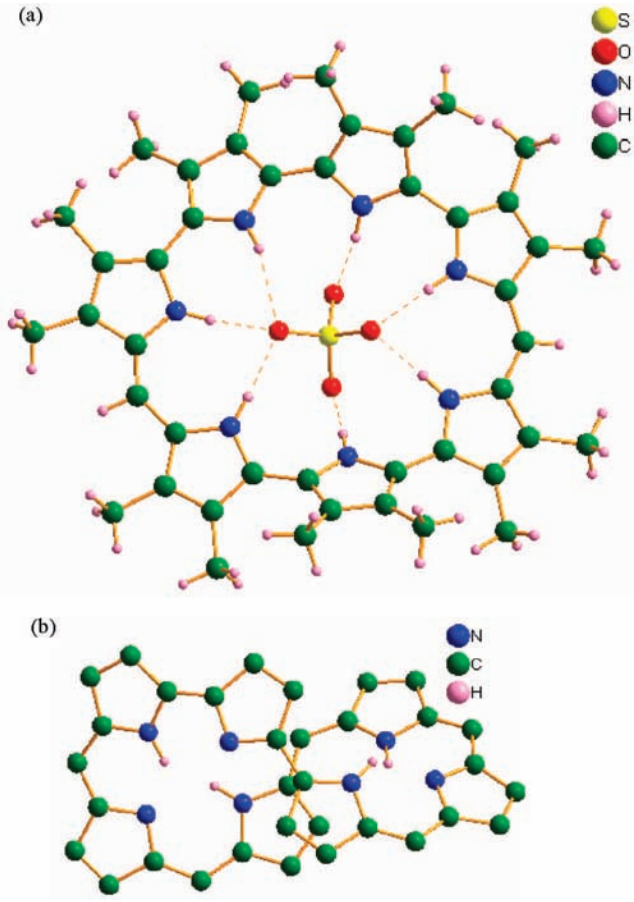


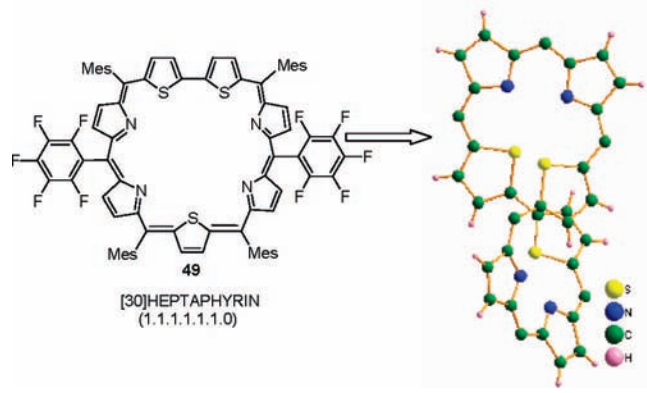
FIGURE 6. X-ray structure of (a) **43** and (b) **44**.

nals of **46c** in the ^{77}Se NMR of 557 and 537 ppm with respect to dimethyl selenide.[31]

The oxidative coupling reaction of tetrapyrrane with tripyrrane resulted, in addition to the expected heptaphyrin **47**, new isomer **48**. In **47**, the thiophene ring of the tripyrrane part is inverted, whereas in **48** one heterocyclic ring of each bithiophene is inverted.[31] As the number of *meso*-carbons in the expanded porphyrin increases, the flexibility also increases. Very recently, we have reported core-modified heptaphyrin **49** with six *meso*-carbons. Compound **49** exhibits a twisted conformation in the solid state and aromaticity in solution.[32] The $\Delta\delta$ value of 16 ppm and Δ_{redox} of 1.18 V reveals aromaticity of **49** in solution. This observation clearly reveals that there is a structural transformation upon going from solid state to solution state (Scheme 12).

Very recently, in the condensation reaction of pyrrole and pentafluorobenzaldehyde, Osuka's group obtained heptaphyrins **50** and **52** with four and six *meso*-carbons.[33] Heptaphyrin **50** with four *meso*-carbons exhibits inverted structure, where one pyrrole ring opposite to the quaterpyrrole ring is inverted. Interestingly, after protonation two pyrrole rings

SCHEME 12



SCHEME 13

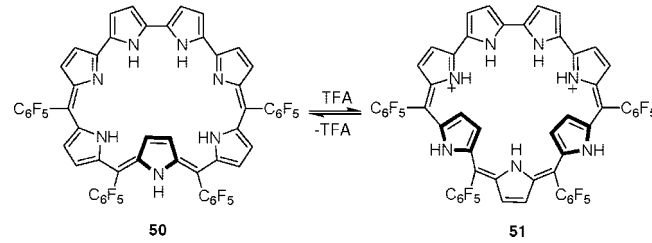
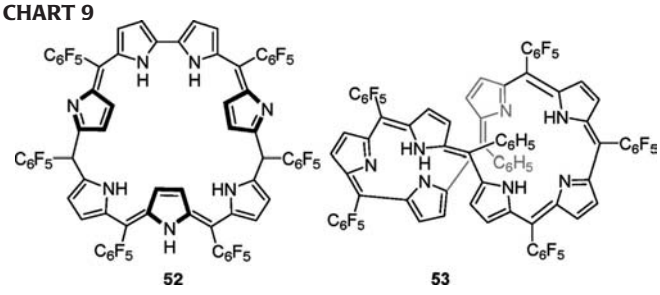


CHART 9

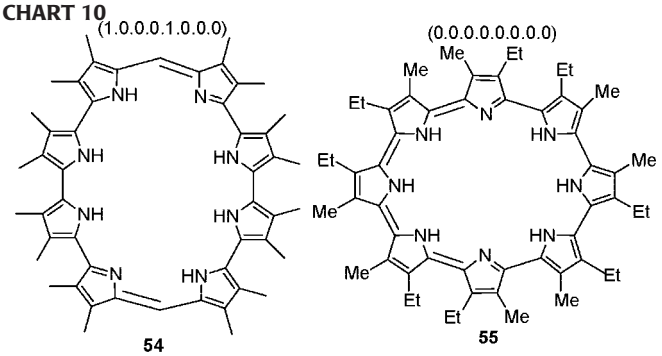


undergo inversion and the inverted pyrrole ring flips back and points inward toward the cavity, **51** (Scheme 13). After protonation this type of behavior was previously seen in the case of rubyrins.[9,21]

Heptaphyrin **52** with six *meso*-carbons is more flexible and was expected to exhibit a figure eight conformation in the solid state. However, to our surprise **52** exhibits almost planar structure with three rings inverted in the solid state and shows aromatic behavior in solution. The X-ray structure of the protonated form of **52** with TFA justifies such a conclusion (Chart 9).

Osuka et al. reported the synthesis of a unique heptaphyrin **53** with seven *meso*-carbons. Compound **53** exhibits a figure eight structure.[34] However, **53** is found to be conformationally flexible and was susceptible to unique N-fusion reactions, leading to formation of singly, doubly, and quarterly N-fused heptaphyrins.

CHART 10



54 [32]Octaphyrin

55 [30]Octaphyrin

Octaphyrins

Octaphyrins with eight pyrrole rings in conjugation reported by Vogel's group turned out to have figure eight conformation, leading to loss of aromaticity in the macrocycles.[35] Sessler et al. adopted a strategy to reduce the *meso*-carbons linking the eight pyrrole rings to avoid the figure eight twist in the resulting macrocycle. Using this strategy, they synthesized two octaphyrins **54** and **55** (Chart 10), which have nontwisted structures (Figure 7).[29,36] Compound **54** had only two *meso*-carbons and **55** had none. Compound **54** despite its nontwisted structure turned out to be nonaromatic. The lack of ring current was explained due to strong deviation from planarity. However, **55** exhibits planar structure with 30 π electrons in conjugation and shows aromatic features. No ring inversion was observed in **55**, probably due to lack of flexibility.

We were successful in synthesizing planar octaphyrins with four *meso*-carbons that exhibit strong aromatic behavior using two strategies: (a) by introducing a sterically bulkier group at the *meso*-carbon bridges; (b) by replacing a few pyrrole rings with other heterocyclic rings such as furan, thiophene, and selenophene. Such modification leads to core-modified octaphyrins **56** and **57** (Chart 11), and the X-ray structure of **56** clearly shows a completely flat structure (Figure 8).[37] ^{1}H NMR studies reveal the strong aromatic nature of **56** and **57**. The interesting features of these structures are the site of ring inversion. In **56**, one of the heterocyclic rings of the each biheterocyclic unit was inverted, when the *meso* substituent was a mesityl group. However, on changing the *meso*-substituents from mesityl to *m*-xylyl as in **57**, the site of ring inversion was shifted to the bipyrrole unit, with one pyrrole ring inverted in each.[38] This observation clearly suggests that the subtle changes in the substituents can alter the conformation of resulting octaphyrin.

Another way of avoiding figure eight conformation of the octaphyrins containing four *meso*-carbons is to increase the rigidity in one of the precursors used for coupling or condensation reactions. By using a rigid quaterthiophene subunit **58** and modified tetrapyrrane **59**, we succeeded in synthesis of planar octaphyrin **60** (Scheme 14).[39] The X-ray structure of **60** indicates almost planar conformation with

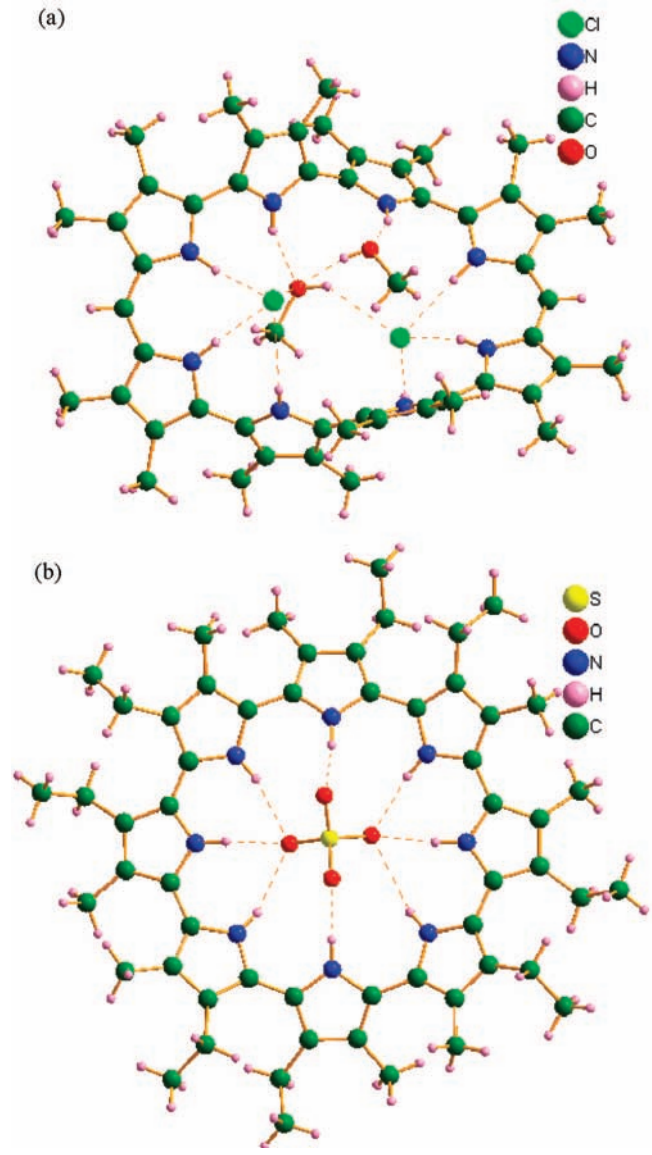
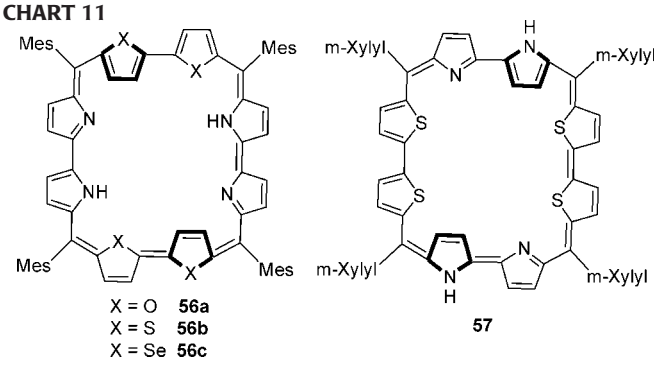


FIGURE 7. X-ray structure of (a) **54** and (b) **55**.

CHART 11



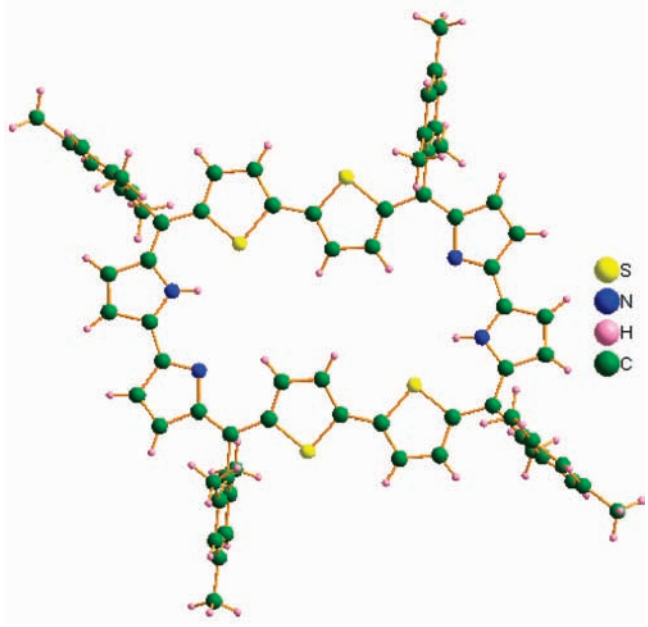


FIGURE 8. X-ray structure of **56b**.

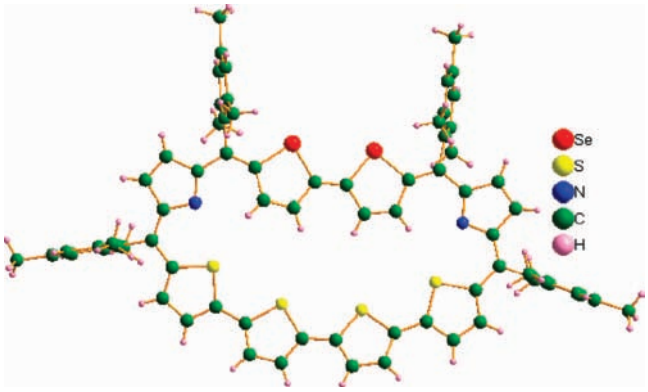


FIGURE 9. X-ray structure of **60a**.

two inverted rings (Figure 9). Solution studies reveal the aromatic nature of **60**.

Recently, we reported the synthesis of octaphyrin **61** with six *meso* links.[40] As expected **61** turned out to have figure eight conformation because of increasing flexibility on going from four to six *meso*-carbons. However detailed ^{1}H NMR and

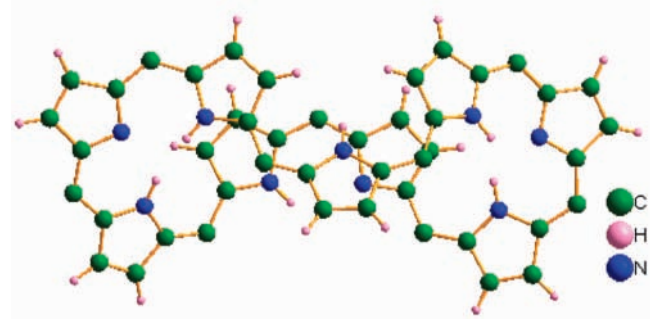


FIGURE 10. X-ray structure of **64**.

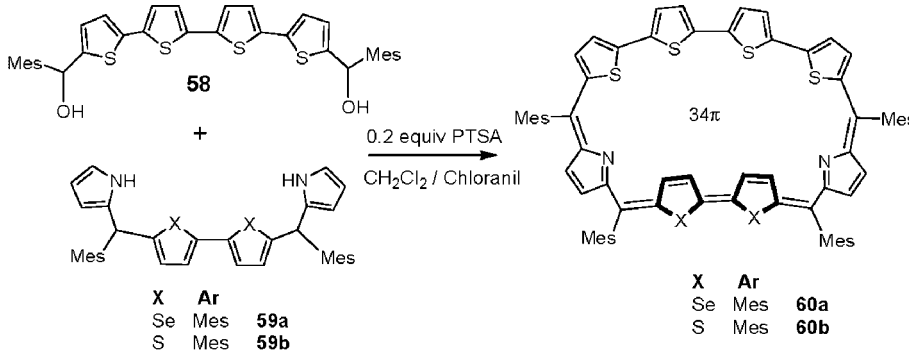
UV–vis studies reveal aromatic features in solution. This observation clearly suggests a possible change of conformation upon going from solution state to solid state (Scheme 15).

Nonaphyrins

Osuka et al. were successful in isolating expanded porphyrins having an equal number of pyrroles and *meso*-carbons.[41] Reacting pyrrole and pentafluorobenzaldehyde under modified Lindsey conditions yielded porphyrinoids having four to twelve pyrroles and a corresponding number of *meso* bridges. The monoprotonated TFA salt of nonaphyrin **62** was found to adopt a twisted helix-like conformation with a near mirror plane and a large cleft wherein the TFA counterion is bound. A different chemical shift for the β-pyrrole protons suggests aromatic electronic character for **62**, in accordance with 42 π electrons. As expected, here there are three pyrrole rings that show ring inversions (Chart 12).

Recently, Osuka et al. reported free base nonaphyrins **63** and **64**.[42] The free base 40 π nonaphyrin **63** exhibits twisted asymmetric structure consisting of a helically arranged porphyrin-like tetrapyrrolic core and hexapyrrolic core with two inverted pyrroles. Reduction of **63** results in **64**, 42 π nonaphyrin, which exhibits nonaromatic features. The single-crystal X-ray structure of **64** (Figure 10) revealed a distorted asymmetric butterfly-like conformation, which is similar to that of **62**. Osuka et al. recently reported synthesis of *meso* aryl substituted [38]nonaphyrin (1.1.0.1.1.0.1.1.0) **65**, from oxi-

SCHEME 14



SCHEME 15

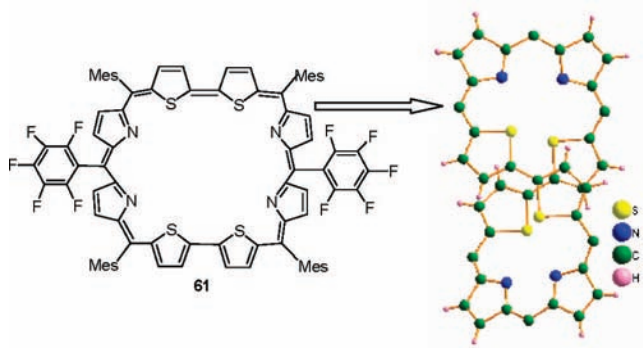


CHART 12

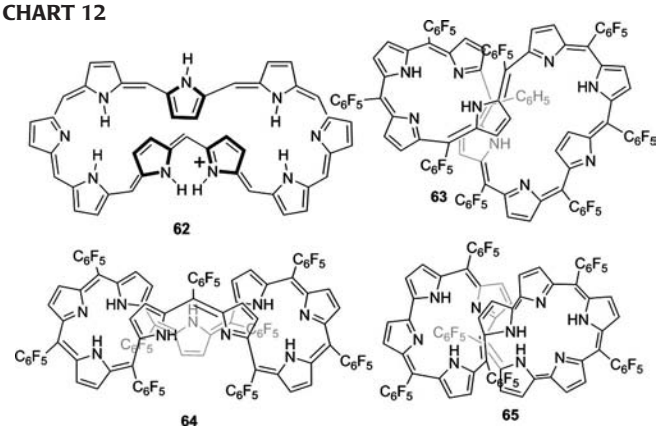
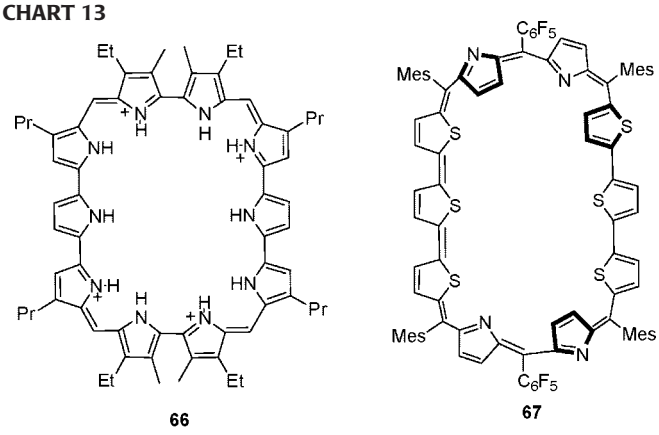


CHART 13



dative coupling of a tripyrrane.[21] The structure reveals a twisted figure eight conformation.

Decaphyrins

There are only two reports on decapyrrolic decaphyrin. One, which is named turcasarin **66** (Chart 13) due to its intense turquoise color in solution, was reported by Sessler et al.[43]

This macrocycle exhibits helical form, where four methine carbons link ten pyrrole rings in a cyclic fashion. The conjugated pathway has 40 π electrons and hence is nonaromatic. Recently, we have reported core-modified decaphyrin **67**, with six *meso* links by an acid-catalyzed [5 + 5] MacDonald-type condensation of modified pentapyrrane.[44] The geometry-optimized structure at B3LYP/3-21G level shows that **67** attains nonplanar geometry with two pyrrole rings and one thiophene ring inverted.

Concluding Remarks

Expanded porphyrins have been reported to have diverse applications ranging from biomedical to materials for electronic devices.[2,9] An understanding of the structure–function correlation in these systems is important for designing materials for specific application. In this direction, it has been recently shown that expanded porphyrins exhibit large two-photon absorption cross sections ($\sigma^{(2)}$) values, and the observed $\sigma^{(2)}$ values depend on the flexibility of the macrocycle, the number of π electrons in conjugation, and the conformation it adapts in solid and solution states.[7] Thus, it is hoped that a systematic analysis of structure–function correlation in these systems eventually will lead to design of these materials for nonlinear optical applications.

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Rajneesh Misra was born in Gorakhpur, India, in 1980. In 2007, he received his Ph.D. from the Indian Institute of Technology, Kanpur, under the supervision of Prof. T. K. Chandrashekar. Presently, he is a Postdoctoral fellow with Prof. Seth. R. Marder, Georgia Institute of Technology, Atlanta, GA, U.S.A.

Tavarekere K. Chandrashekar was born in Shimoga, India, in 1956. He received his Masters from the University of Mysore in 1978. He earned his Ph.D. from the Indian Instiitute of Science, Bangalore, under the supervision of Prof. V. Krishnan in 1982. After postdoctoral work with Prof. Hans Vanwilligen (1982–84) at University of Massachusetts, Boston, and with the late Prof. G. T. Babcock (1984–86) at Michigan State, East Lansing, he joined the faculty at Indian Institute of Technology, Kanpur, where he has been a full professor since 1995. He spent a year (1993–1994) on sabbatical with Prof. E. Vogel at University of Köln, Germany, as an Alexander van Humboldt Fellow. Since November 2003, he has taken over as Director, NIIST. He has been recently awarded J. C. Bose fellowship from DST for his contribution.

FOOTNOTES

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