Proc. Indian Acad. Sci. (*Chem. Sci.*), Vol. 114, No. 4, August 2002, pp 311–338

Inverted porphyrins and expanded porphyrins: An overview

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Abstract. Porphyrins and metallopophyrins have attracted the attention of chemists for the past 100 years or more owing to their widespread involvement in biology. More recently, synthetic porphyrins and porphyrin-like macrocycles have attracted the attention of researchers due to their diverse applications as sensitizers for photodynamic therapy, MRI contrasting agents, and complexing agents for larger metal ions and also for their anion binding abilities. The number of *p*-electrons in the porphyrin ring can be increased either by increasing the number of conjugated double bonds between the pyrrole rings or by increasing the number of heterocyclic rings. Thus, 22*p* sapphyrins, 26*p* rubyrins, 30*p* heptaphyrins, 34*p* octaphyrins and higher cyclic polypyrrole analogues containing 40*p*, 48*p*, 64*p*, 80*p* and 96*p* systems have recently been reported in the literature. These macrocycles show rich structural diversity where normal and different kinds of inverted structures have been identified. In this review, an attempt has been made to collect the literature of the inverted porphyrins and expanded porphyrins reported until December 2001. Since the *meso* aryl expanded porphyrins have tendency to form both inverted and non-inverted structures more emphasis has been given to *meso* aryl expanded porphyrins.

Keywords. Inverted porphyrins; N-confused porphyrins; rubyrins; heptaphyrins; octaphyrins.

1. Introduction

Porphyrins are the most widespread of all prosthetic groups found in nature [1,2]. These highly colored tetrapyrrolic pigments play such a diverse and critical role in nature ranging from electron transfer, oxygen transport, photosynthetic processes and catalytic substrate oxidation that they are aptly termed as 'pigments of life' [3]. Porphyrins are 22π electron systems whose main conjugation pathway contains 18π electrons, which explains the aromatic nature from which the intense colour associated with them stems. The parent form of these tetrapyrrolic macrocycles has structure **1** known as *porphine*. The ubiquity of its functions in nature led researchers around the globe to focus their attention on these macrocycles and this paved the way to the syntheses of porphyrin-like macrocyclic units, that differed from the naturally occurring porphyrins and related systems in a number of ways, but mimicked their properties and functions outside biological systems.

The interdisciplinary interest generated by the porphyrins resulted in the syntheses of modified porphyrins (scheme 1) and the most important modifications are as follows: (a)

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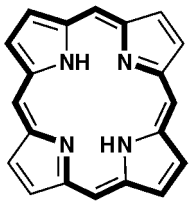

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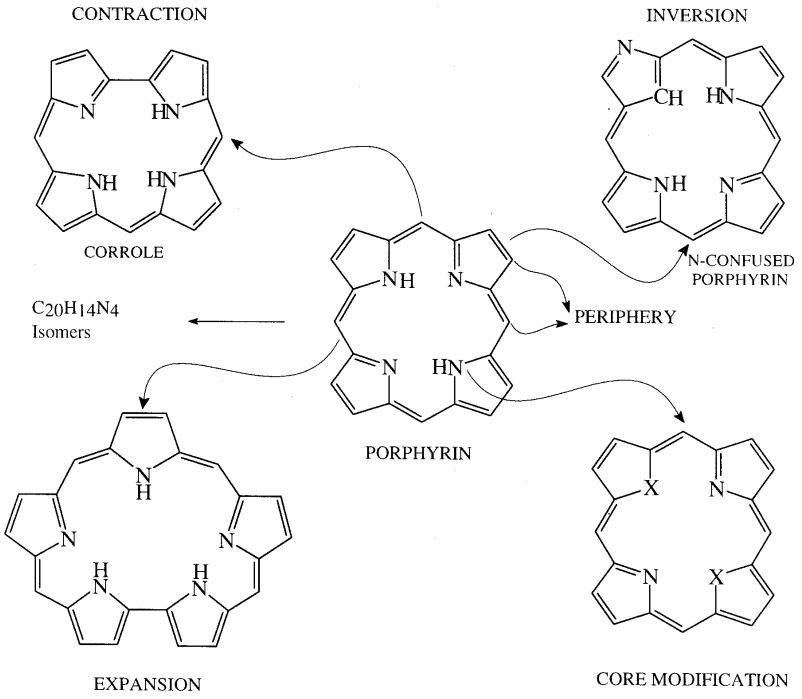
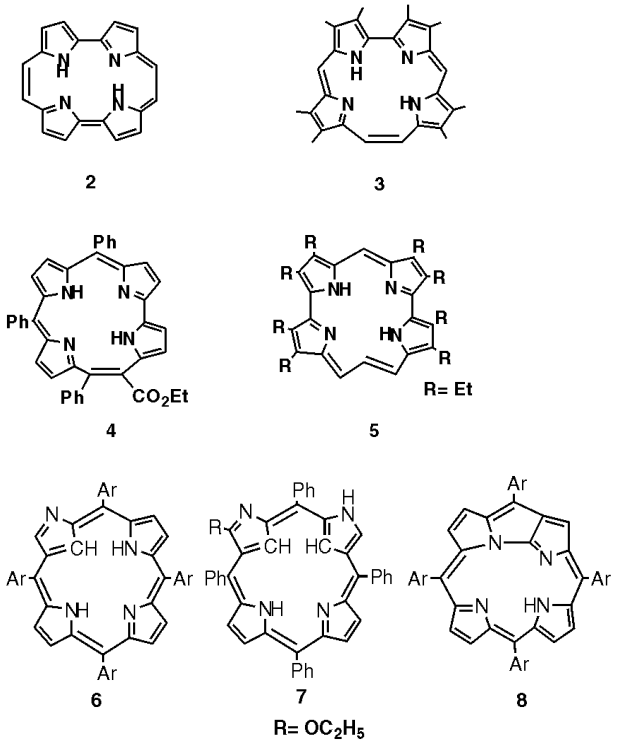
Periphery modified porphyrins – where the modifications are done on the periphery, which includes ***b*** and *meso* positions of the parent tetrapyrrolic macrocycles; (b) *Core modified porphyrins*[4] – where one or more core nitrogen atoms of parent porphyrin are substituted with chalcogen atoms; (c) *Contracted porphyrins*[5] – obtained by removing one of the meso carbons resulting in the formation of corroles; – (d) *Isomeric porphyrins*[6] – structures which have same molecular formula $C_{20}H_{14}N_4$ obtained by scrambling the four pyrrolic subunits and the four bridging carbon atoms which are shown as structures **2–5**; (e) *Inverted porphyrins*[4] – which can also be considered porphyrin isomers which have one or more of the core nitrogens pointing out of the ring and hence and called '*N-confused porphyrins*' or '*mutant porphyrins*' and are treated as a different class (shown as structures **6** and **7**); and (f) *Expanded porphyrins*[7] – which result from the expansion of the ***p***-electron conjugation by increasing the number of heterocyclic rings. The resulting chromophores show strong absorptions in the red region compared to those of normal 18***p*** porphyrins.



Scheme 1.



There are a variety of expanded porphyrins reported in the literature. They are sapphyrins [8], smaragdyrins [9], isosmaragdyrins [10], pentaphyrins [11], hexaphyrins [12], orangarins [13], amethyrins [13], octaphyrins [14–16], rosarins [17], rubyrins [18], ozaphyrins [19], bronzaphyrins [20,21], heptaphyrins [22], turcasarins [23], dodecaphyrins [24], and hexadecaphyrins [24]. There are citations in the literature that these giant macrocycles can act as anionic, cationic and neutral complexing agents, which are substrate-specific and hence can be used in a variety of ways in medicine and industry[7a]. Their photosensitizing ability to convert triplet oxygen to highly reactive and toxic singlet oxygen makes them indispensable in the field of photodynamic therapy [25–27]. The complexing ability to trap lanthanide metals make these macrocycles potent candidates as contrast agents in magnetic resonance imaging (MRI) [28,29]. Thus, these modifications result in the control of the electronic structure, and the geometry of the system and its surroundings, associated with rich, diverse and exotic chemistry.

These properties have generated considerable interest in synthesizing new macrocycles in high yields with different core atoms and cavity size that can reveal interesting spectroscopic, chemical and physical properties, which can find applications in biology [30], medicine [31], material science [32] and catalysis [33].

A brief survey of the earlier literature earlier in the field of porphyrin isomers and expanded porphyrin systems is given in the following sections.

2. Porphyrin isomers

Porphyrin isomers [6], as the name indicates are tetrapyrrolic macrocycles, having a $C_{20}H_{14}N_4$ skeleton and 18π electrons in the cyclic conjugated pathway. They are

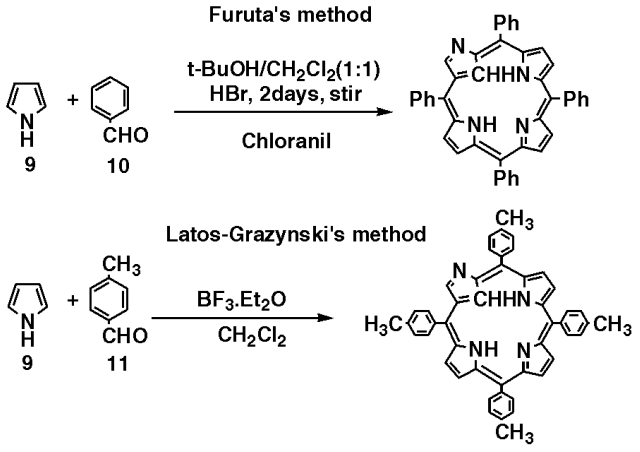
differentiated by the way the four-pyrrole units are interconnected. The first isomer of a porphyrin 'Porphycene' **2** [18] porphyrin-(2.0.2.0) was reported by Vogel's group in 1986[34], followed by a gap of eight years in 1994, two more of its isomers 'corrphycene' **3** [18] porphyrin-(2.1.0.1)[35], and 'hemiporphycene' **4** [18]porphyrin-(2.1.1.0)[36] were reported. This period also marked the successful synthesis of N-confused porphyrin (NCP) or inverted porphyrin **6** [18] porphyrin (1.1.1.1) (C_a, N, N, N) by two independent groups across the globe[37]. The fifth porphyrin isomer 'isoporphycene' **5** [18] porphyrin-(3.0.1.0) was reported in 1996[38]. More recently Furuta and coworkers reported the synthesis of another isomer, 'doubly N-confused porphyrin' (N_2CP) **7** [18] porphyrin-(1.1.1.1) (C_a, C_b, N, N)[39] and 'N-fused porphyrin' **8**[40] derived from N-confused porphyrin by appropriate synthetic modifications.

3. Inverted porphyrins (NCP)

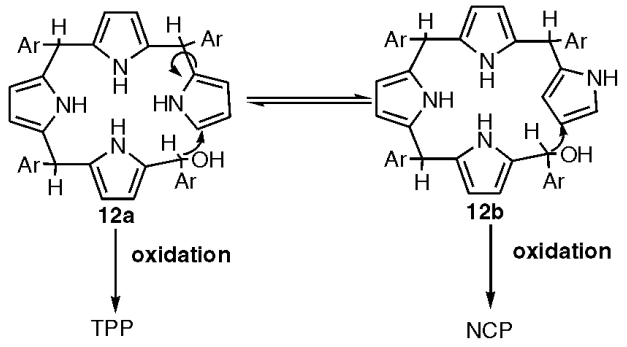
Latos–Grazynski and coworkers reported inverted (mutant or N-confused or carba) porphyrin (NCP) **6** i.e. 2-aza-21-carba-tetraaryl porphyrin, by the Rothemund reaction between tolualdehyde **11** and pyrrole **9** in presence of $BF_3.Et_2O$ in CH_2Cl_2 followed by oxidation with chloranil in 4% yield[37a]. Simultaneously Furuta and coworkers also reported the formation of NCP in the reaction with pyrrole **9** and benzaldehyde **10**, in presence of *t*-BuOH/CH_2Cl_2 (1:1) and conc. HBr (1equivalent), stirring in dark for two days, followed by oxidation with chloranil in 5–7% yields (scheme 2)[37b].

The mechanism for formation of porphyrin and carba porphyrin macrocycle was suggested by Latos–Grazynski and coworkers that two helical conformations of tetrapyrromethane **12** differing only by the rotation of the terminal pyrrole moiety with respect to the C_a–C_{meso} bond during the porphyrinogen ring closure (scheme 3)[37a].

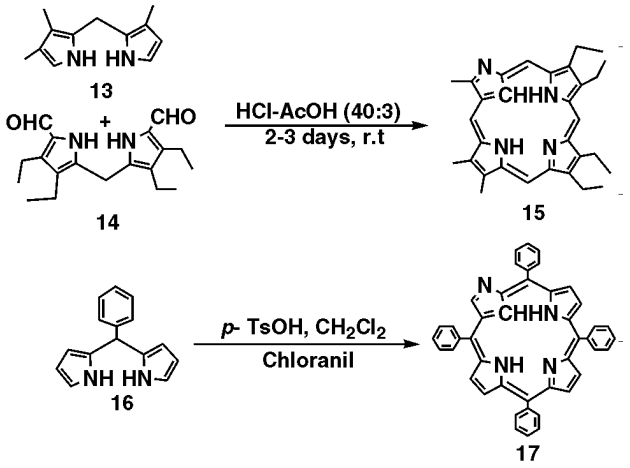
Many research groups have recently synthesised N-confused porphyrins (NCP). Dolphin and coworkers prepared periphery modified NCP **15** by the acid catalysed condensation of modified dipyrromethane **13** and dipyrromethanedialdehyde[41] **14** while Chandrashekar and coworkers[42] reported the formation of *meso*-tetraaryl NCP by oxidative coupling reaction of appropriate dipyrromethane **16** in presence of 0·1 eq. *p*-TsOH (scheme 4). Recently Lindsey and coworkers[43] reported the formation of NCP **17**



Scheme 2.



Scheme 3.



Scheme 4.

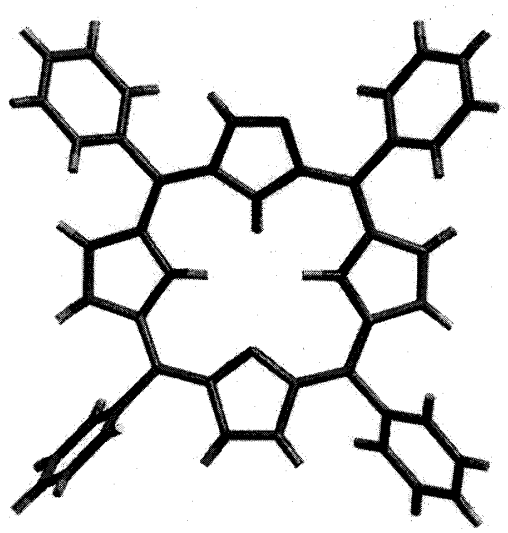


Figure 1. Crystal structure of N-confused porphyrin (reproduced from ref. 37b).

as one of the products in a one flask synthesis of a acid-catalysed reaction of pyrrole and aldehyde and this reaction is similar to that described earlier in scheme 2. Lash and coworkers reported the syntheses of hexa and heptaalkyl substituted inverted porphyrins by a 3+1 condensation involving tripyrranedicarboxylic acid and pyrrole-2,4-dicarboxaldehyde [44].

The remarkable ability to act as tetra coordinate ligands to form transition metal complexes involving a metal–carbon bond inside the porphyrin cavity has resulted in the formation of divalent simple and organometallic Ni(II) and Ni(III) complexes [37a,45], rare organo Cu(II) complexes [46], Ag(III) [47] complexes with metal–carbon bonds. Recently, Furuta and coworkers have reported the formation of three types of Pd (II) complexes [48], one involving inner co-ordination sites and the other two involving both inner and outer N-coordination sites, resulting in the formation of double-decker complexes. In the reaction of N-confused tetratolyl porphyrin and $Pd(OAc)_2$, the formation of products was found to be solvent dependent [48]. Macrocycle **6** was also found to complex Sb(V) and the resulting metal complex was found to be a potential candidate for molecular wire component [49]. The surprising ease of formation of metal–carbon bonds is attributed to the presence of an Arduengo-type aromatic carbene-like structure [50], which makes the *b*-carbon inside the porphyrin cavity 'exotic' since it stabilizes a variety of oxidation states for transition metals, like Ni, used for complexation, which is otherwise difficult to obtain with the parent tetraphenyl porphyrin. Thus, owing to the inner core carbon and outward-pointing nitrogen, the coordination chemistry of **6** and **7** differs greatly from that of normal porphyrins. This characteristic multivalent nature of NCP is explained by the stabilization of the polarized metal–carbon bond by the deprotonation of the outward pointing NH in the confused pyrrole. NCP can act both as a divalent (NCP^{2-}) and trivalent (NCP^{3-}) ligand with d^8 metals like Ni^{2+} and Ag^{3+} as shown as type **I** and type **II** in figure 2, while in presence of Pd^{2+} salts it gives type **III** and type **IV** complexes, where metal coordination occurs both inside and outside the macrocycle [51].

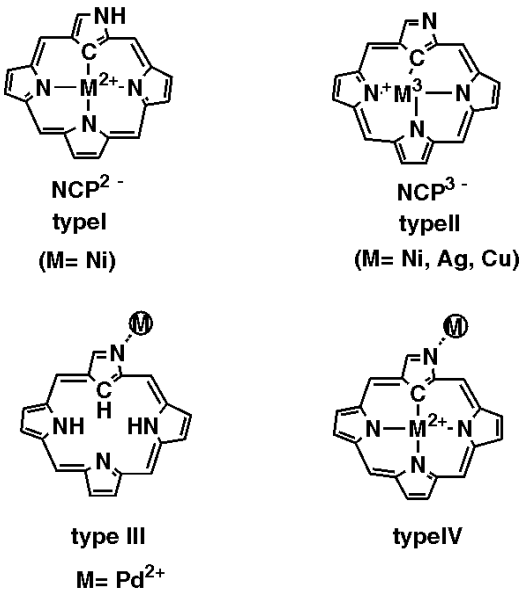


Figure 2. Metal binding modes of NCP.

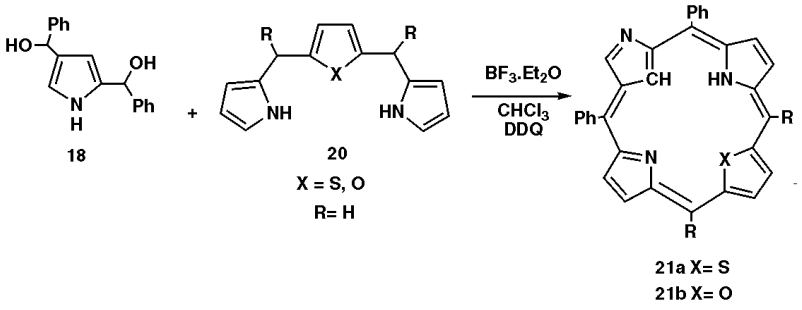
Core-modified inverted porphyrin, 2-aza-2-methyl-5,10,15,20-tetraphenyl-21-carba-porphyrin bearing a methyl group on the inverted pyrrolic nitrogen was formed from the methylation involving methyl iodide[52]. Apart from trying to obtain various mutant porphyrins, attempts were made to core-modify NCP by substituting one of the core NHs with O, S groups. Scheme 5 describes the synthetic methodology adopted for the formation of the products. Thus the isomers of 21-oxaporphyrin and 21-thiaporphyrin, **21a** and **21b**, with an inverted pyrrole ring in the position trans to the furan or thiophene rings were synthesized by the reaction between 2,5-*bis*(phenyl *α*-hydroxymethyl) pyrrole **18** and modified tripyrrin **20** and in 5·5–8% yield respectively[53].

Very recently Latos-Grazynski and coworkers reported a pyrrole-inverted isomer of 5,10,15,20-teraaryl-21-selena porphyrin i.e. 5,10,15,20-tetraaryl-22-selenaporphyrin **24** in 1% yield where the selenophene ring is *cis* with respect to the inverted pyrrole ring (scheme 6) from the precursor diol **22** and tripyrrin[54] **23**.

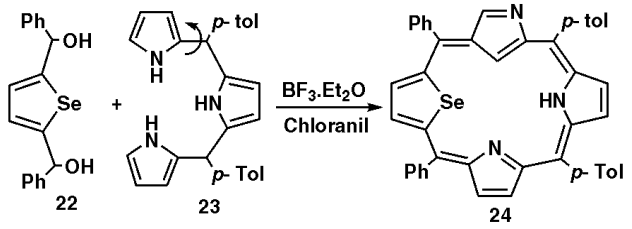
Latos–Grazynski and coworkers also reported the formation of a new isomer of 5, 10,15,20-tetraphenyl-21-thiaporphyrin with an inverted thiophene ring, i.e. 2-thia-5,10,15,20-tetraphenyl-21-carbaporphyrin **27** resulting from the condensation reaction of 2,4-*bis*(phenyl hydroxymethyl) thiophene **25** with pyrrole and benzaldehyde via a one-pot two-step reaction in 4% yield or by the 3+1 condensation of the thiophene precursor and 5,10-diphenyl tripyrrin **26** in 2% yield as shown in scheme 7[55].

4. Doubly N-confused porphyrins

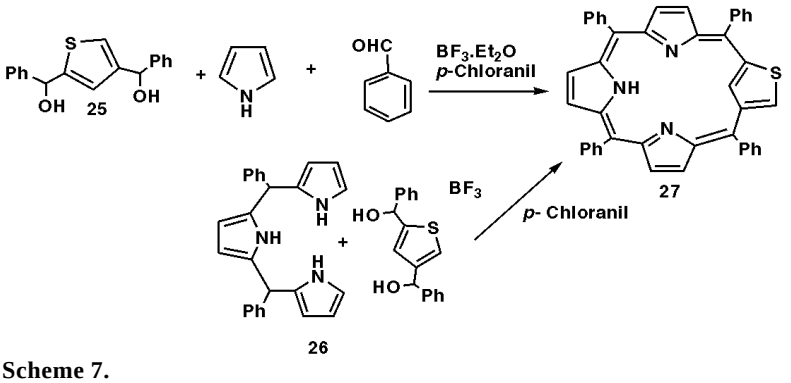
Doubly N-confused porphyrin (N_2CP) **7** was synthesized in 2% yield by Furuta and coworkers[39] via the acid catalysed condensation of perfluorobenzaldehyde **29** with N-confused dipyrromethane **28** in $CHCl_3$ containing a trace of EtOH followed by oxidation



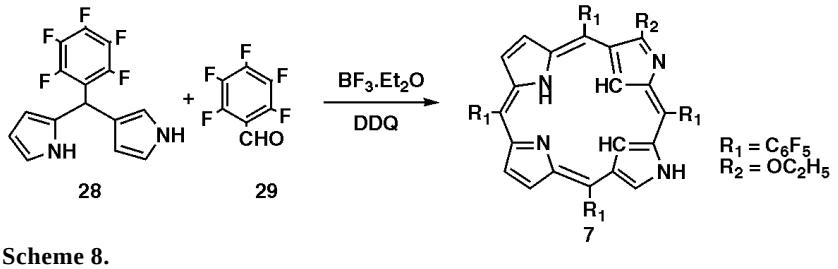
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

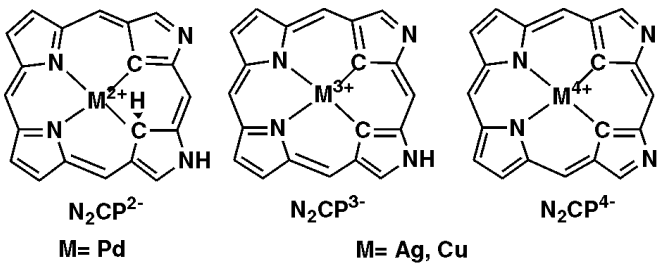


Figure 3. Metal binding modes for N_2CP.

with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as described in scheme 8. Small amounts of EtOH and bromide were found to be effective for this reaction. An attempt using EtOH-free dry $CHCl_3$ to avoid generating products containing ethoxy substituents led to trace amounts of N_2CP.

This macrocycle was found to stabilize complexes containing rare Ag(III) and Cu(III) centres [39]. Furuta *et al* have shown that similar reaction with 2-ethoxy-5,10,15,20-*tetrakis* (pentafluorophenyl) derivative of **7** in toluene, unexpectedly yielded inner C-tolylated Pd(II) complex instead of the expected Pd(IV) or Pd(III) complex [56]. The multivalent property is common for all members of the NCP family and hence N_2CP exhibits divalent nature (N_2CP^{2-}) in the case of Pd(II), trivalent nature (N_2CP^{3-}) in the case of Ag(III) and Cu(III), while tetravalent nature can also be expected as shown in figure 3 [39]. The crystal structure of N_2CP is shown in figure 4.

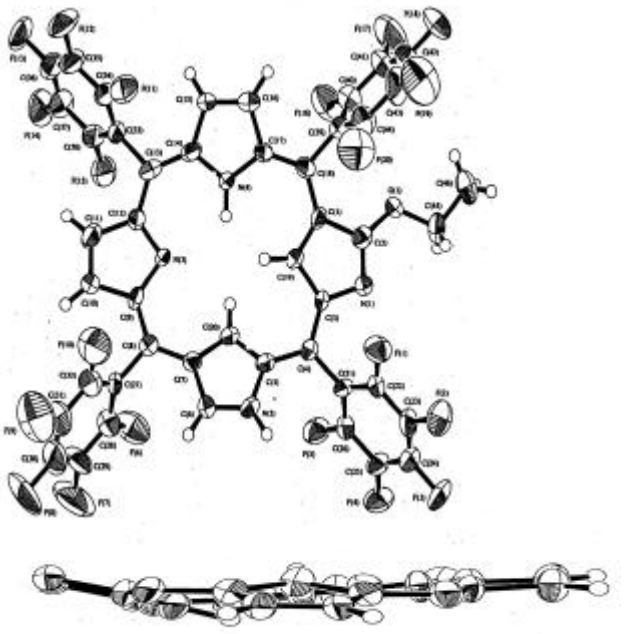
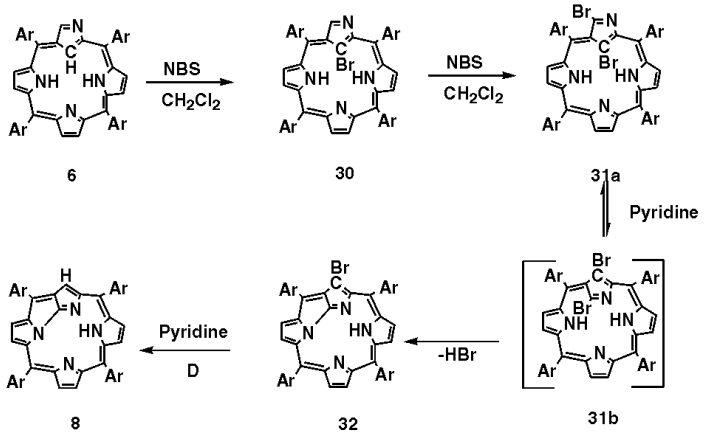


Figure 4. Crystal structure of **7** plane view (top) and side view (bottom) (pentaflourophenyl, ethoxy groups were omitted for clarity) (reproduced from ref. [39]).



Scheme 9.

5. N-fused porphyrin

N-fused porphyrin[40] (NFP) **8** was accidentally obtained from a pyridine solution of brominated N-confused porphyrin. When a solution of NCP was treated with N-bromosuccinimide (NBS) for 5 min at room temperature monobrominated-NCP **30** in 90% yield was formed which on further bromination by addition of 2 eq. NBS afforded

dibrominated NCP **31** in 70% yield. The monobrominated derivative of NFP **32** was formed at room temperature after 8 h in pyridine and the substituented bromine was replaced by hydrogen resulting in the formation of NFP **8** simply by refluxing in pyridine as shown in scheme 9. Figure 5 shows the crystal structure of NFP.

6. Pentapyrrolic systems

Expanded porphyrins[7] containing five pyrrolic units are connected by different numbers of methine bridges, which can be either maintained as four or increased or decreased. These conjugated pentapyrrolic macrocycles reported till date can be classified into two groups, namely aromatic pentaphyrins (**33–38**) and nonaromatic pentapyrrolic system **39** shown in chart 1.

6.1 *Aromatic systems*

6.1a *Sapphyrins-[22] pentaphyrins-(1.1.1.1.0):* Sapphyrins **33** are [22] pentaphyrins (1.1.1.1.0), which are aromatic and are the first expanded porphyrins to be reported[57]. RB Woodward coined the trivial name 'sapphyrin' for this macrocycle due to its intense blue-green colour in organic solvent. Woodward and coworkers[57] isolated this

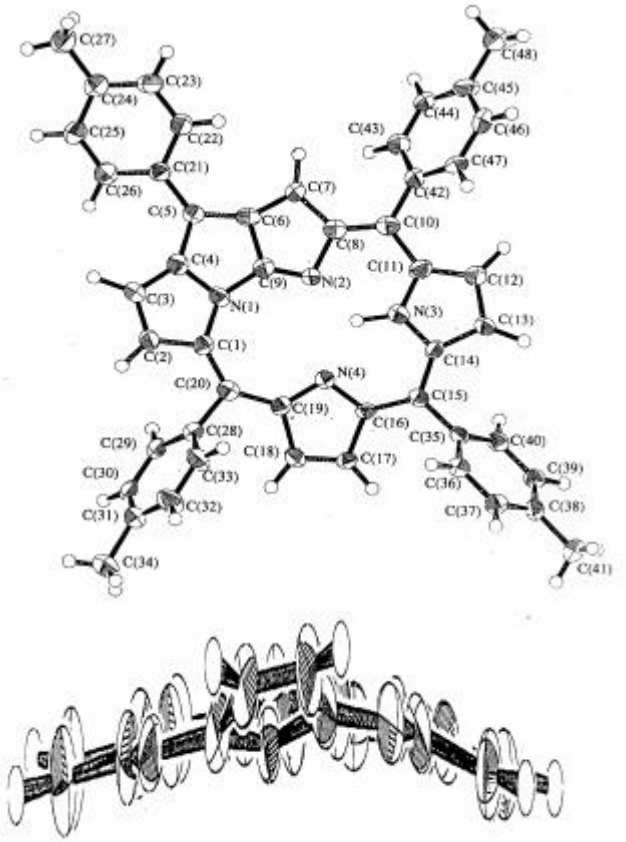


Figure 5. Crystal structure of **8** taken from ref. [40].

serendipitously during the course of synthesis of the corrin core of vitamin B_{12} in 1966. Sapphyrin was obtained in the 4+1 condensation reaction between the linear tetrapyrrolic precursor, bipyrrolyldipyromethane [8] **40** and 2,5-diformyl-3,4-dimethyl pyrrole **41** in acid medium as shown in scheme 10. This synthesis involved multi steps and the key precursors were hard to make.

Later, Woodward's group [8] and Johnson and coworkers [58] independently tried a 3+2 condensation involving bipyrrole dialdehyde **42** with a tripyrrane **43** catalysed by acid followed by air oxidation, which went on to become the most widely used methodology for the synthesis of sapphyrin **44** (scheme 11). Woodward and coworkers, using a pyrrolyl bipyrrole and diformyl dipyrromethane to produce the desired sapphyrin in 35% yield, implemented an alternative 3+2 methodology but the difficulty in precursor synthesis limited the utility of the above methods.

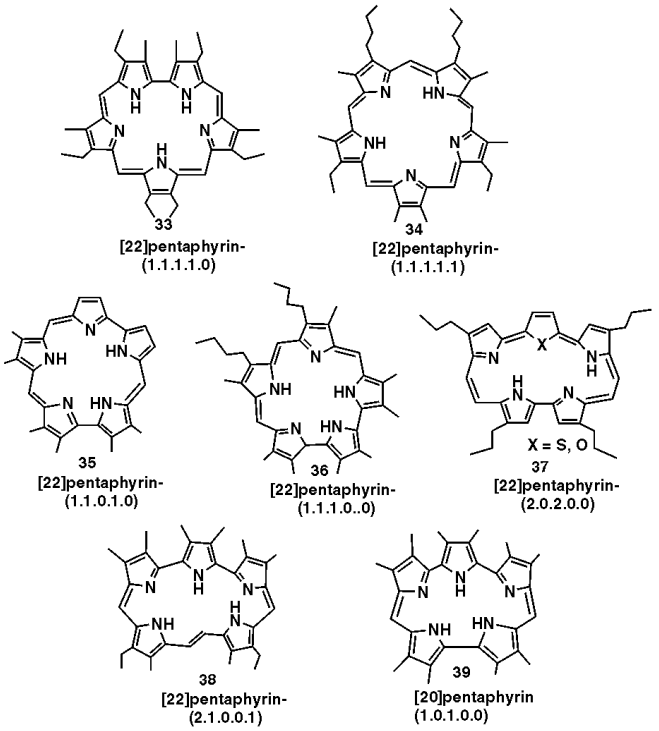
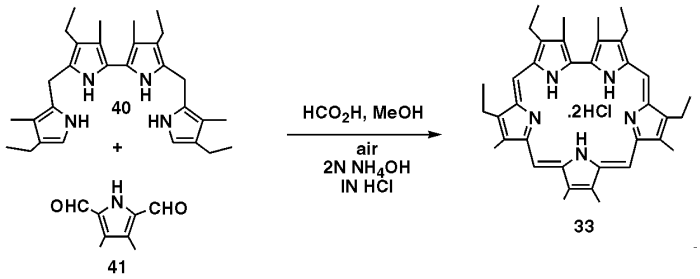
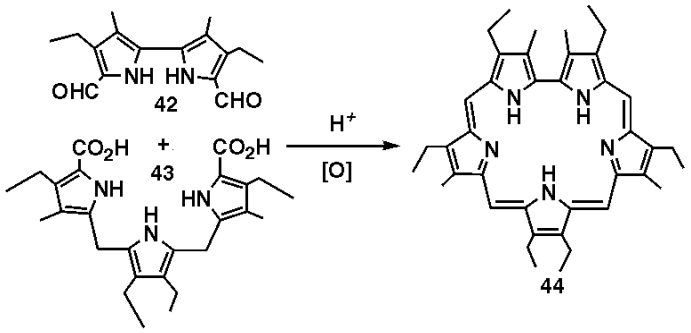


Chart 1.

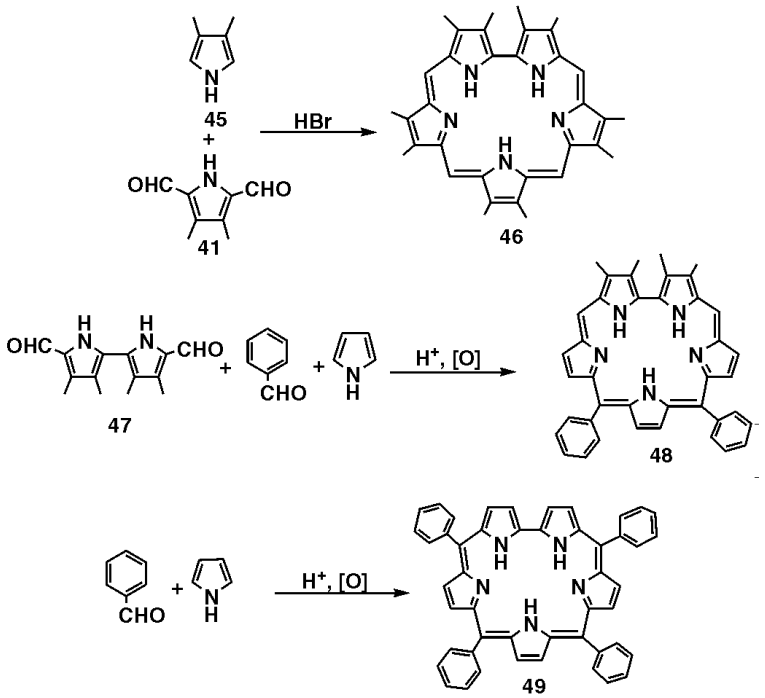


Scheme 10.

Woodward and coworkers have exploited one-pot synthesis of sapphyrins first by the reaction of 3,4-dimethyl pyrrole **45** with pyrrole dialdehyde **41** to produce sapphyrin **46** in <1% yield[8]. Later Sessler and coworkers synthesized **48** from acid catalysed reaction of pyrrole, bipyrroledialdehyde **47** and benzaldehyde in 10% yield[58]. Latos–Grazyski and coworkers reported the first *meso*-tetraphenyl sapphyrin **49** from the reaction of benzaldehyde and pyrrole in 1:3 molar ratios under oxidative acid catalysis in 1·1% yield[59]. Scheme 12 describes the above reactions. Dolphin's group reported the efficient synthesis of **48** and 4**9** by appropriately choosing 5,10-diphenyltripyrrane and bipyrrole precursors[60]. Smith and coworkers reported the formation of sapphyrin in 20% yield from biladiene and formyl pyrrole[61].



Scheme 11.

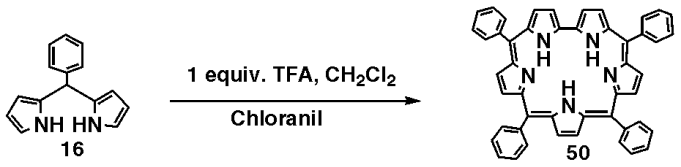


Scheme 12.

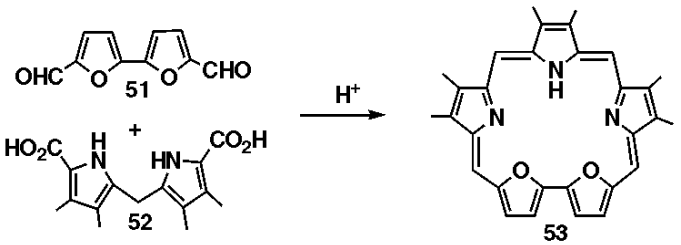
Recently Lindsey's group has improved the yield of sapphyrins and N-confused porphyrins in Rothemund type of reaction by using appropriate reaction conditions [43a]. Chandrashekar and coworkers [42] have shown that with a single precursor dipyrromethane bearing phenyl group, sapphyrin **50** is obtained with TPP and *meso*-tetraphenyl rubyrin when the acid used for catalysis is trifluoroacetic acid (TFA) as shown in scheme 13.

Substitution of one or more pyrrolic units with other heterocycles such as furan, thiophene and selenophene leads to heteroasapphyrins. Core modification leads to changes in cavity size, electronic structure. There are only limited reports on the syntheses and characterization of core modified expanded porphyrins in the literature. Johnson and coworkers developed the first example of such a system when they tried to generate heteroatom analogues of corroles starting from diformylbifuran **51** and dipyrromethane **52** synthesizing dioxa sapphyrin **53** along with the sought after dioxacorrole as shown in scheme 14 [62].

Sessler and coworkers [63] have synthesized a series of *b*-substituted sapphyrins containing one or more heteroatoms by the usual 3+2 methodology selecting appropriate precursors as explained in scheme 11. Chandrashekar and coworkers [64] have reported a series of *meso*-aryl sapphyrins **56** where O, S and Se replace two or three core nitrogens by an easy and efficient MacDonald 3+2 condensation involving tripyrromethanes **54** and diols **55** in high yield (16–63%) and the product distribution varies with the nature and concentration of acid used (scheme 15). Another method reported by the same group to synthesize core-modified sapphyrins involves an unprecedented coupling of tripyrromethane **54** resulting in the formation of diheteroatom substituted *meso*-aryl sapphyrins **57** in moderate yields along with disubstituted *meso*-aryl porphyrins and *meso*-aryl rubyrins as shown in scheme 15 [65]. During the course of this work, Latos–Grazynski and coworkers reported the formation of **57** in low yield in a Rothemund reaction of 2,5-disubstituted thiophene diol and pyrrole [63d]. The first carba sapphyrin **60** was reported by Lash and coworkers through a (4+1) MacDonald condensation between a tetrapyrrole dicarboxylic acid **58** and diformyl indene **59** as shown in scheme 16 [66].



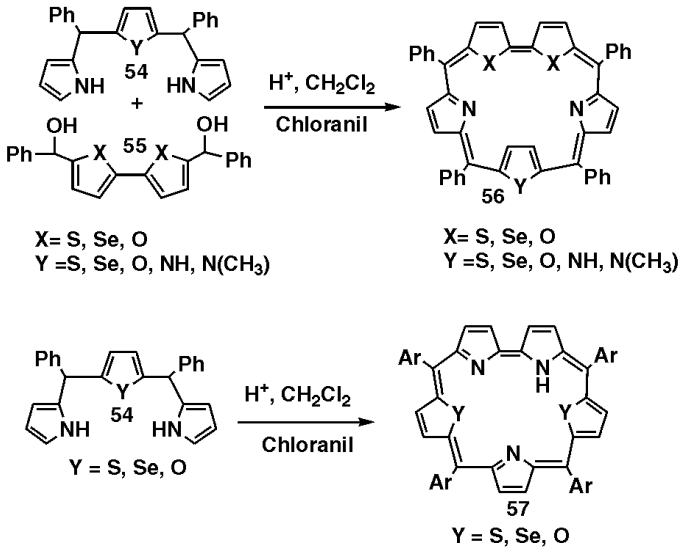
Scheme 13.



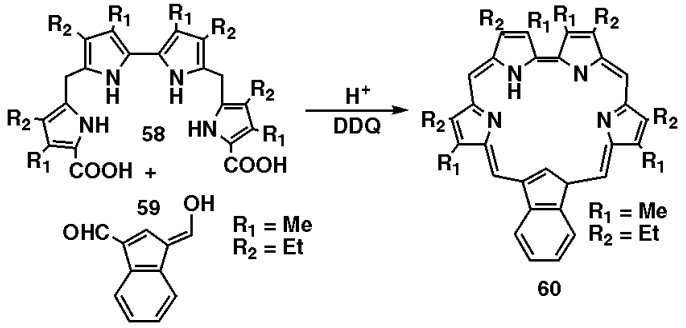
Scheme 14.

6.1b *Pentaphyrins-[22] pentaphyrin-(1.1.1.1.1):* In 1983 Gossauer and coworkers obtained pentaphyrin **34**[11,12,67] which has a Franck nomenclature [22] pentaphyrin (1.1.1.1.1) by an HBr catalysed oxidative condensation between diformyltripyrrane **61** and dipyrromethane **62** in 31% yield as shown in scheme 17. More recently *meso*-diphenyl pentaphyrin was reported by TFA catalysed 3+2 condensation by Dolphin and coworkers[60]. Pentathiapentaphyrin[68,69] and pentaselenapentaphyrin[70] were reported by Vogel's group. Very recently, Furuta and coworkers reported the formation of N-fused normal type 22***p*** electronic pentaphyrin containing a fused tripentacyclic ring from the Rothemund reaction of aldehyde and pyrrole in presence of $BF_3.Et_2O$ and DDQ[71].

6.1c *Smaragdyrins-[22] pentaphyrin-(1.1.0.1.0):* Another pentaphyrin **35** with a trivial name 'smaragdyrin or norsapphyrins' are [22] pentaphyrin (1.1.0.1.0)[8,72] that has only three *meso* carbons that bear a structural relationship with sapphyrins as corrole does to porphyrin. It was first reported as a dioxa smaragdyrin **64** from the 3+2 reaction of a



Scheme 15.

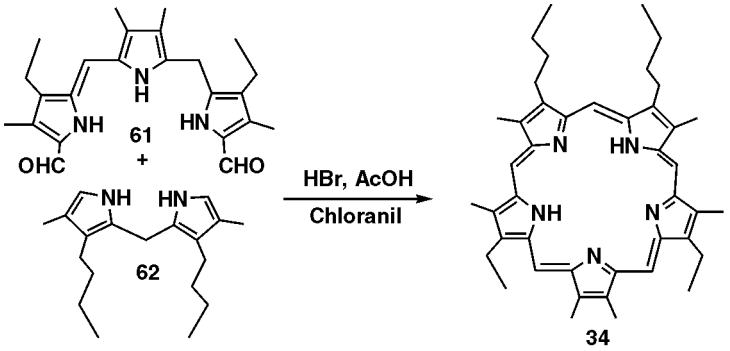


Scheme 16.

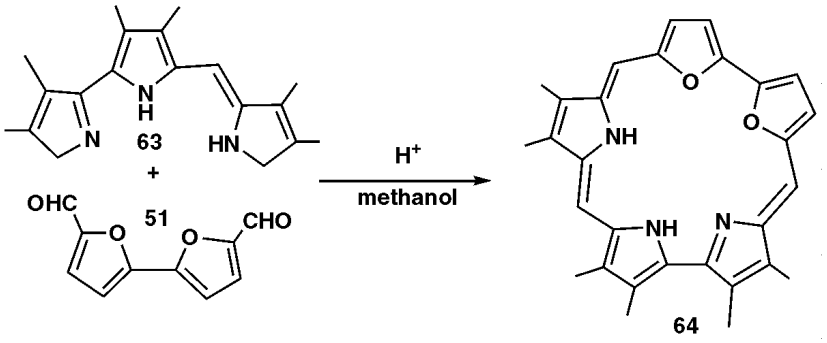
pyrrolyl bipyrrole **63** and diformyl bifuran **51** as shown in scheme 18. An all-aza analogue **35** was also synthesized but was found to be sensitive towards light and was decomposed in the silica gel column. Recently Chandrashekar and coworkers have published a facile and efficient synthesis for the formation of *meso*-aryl smaragdyrin bearing one S or O, **65** by an oxidative coupling reaction involving tripyrrane **54** and dipyrromethane **16** (scheme 19)[73].

6.1d *Isosmaragdyrins-[22] pentaphyrin-(1.1.1.0.0):* Sessler and coworkers synthesized a new contracted sapphyrin namely 'isosmaragdyrin' or [22] pentaphyrin (1.1.1.0.0) **36** via a terpyrrole dialdehyde **66** and dipyrromethane diacid 67[10]. The same group also reported the synthesis of mono oxa isosmaragdyrin **68** using a similar 3+2 methodology as shown in scheme 20.

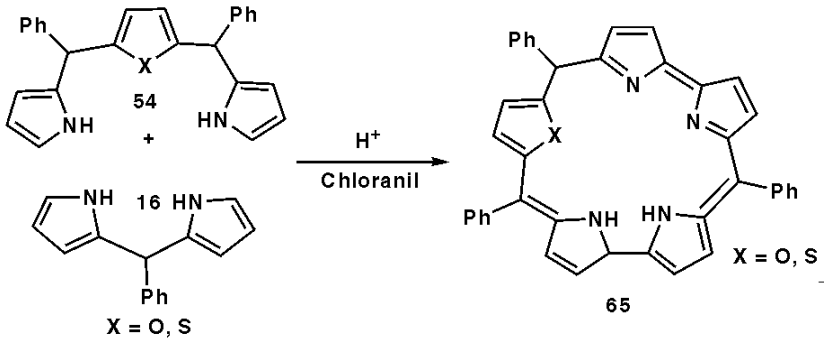
6.1e *Ozaphyrins-[22] pentaphyrin-(2.0.2.0.0):* Johnson and Ibers prepared another 22***p*** aromatic macrocycle, which is an isomer of mono oxasapphyrin that was, assigned a trivial name 'ozaphyrin' due to its Oz-like emerald green colour in solution. It is a [22] pentaphyrin-(2.0.2.0.0), **37** which was prepared by coupling the bis (pyrrolyl) furan/thiophene **69** with diformyl bipyrrole **70** under McMurry conditions as shown in



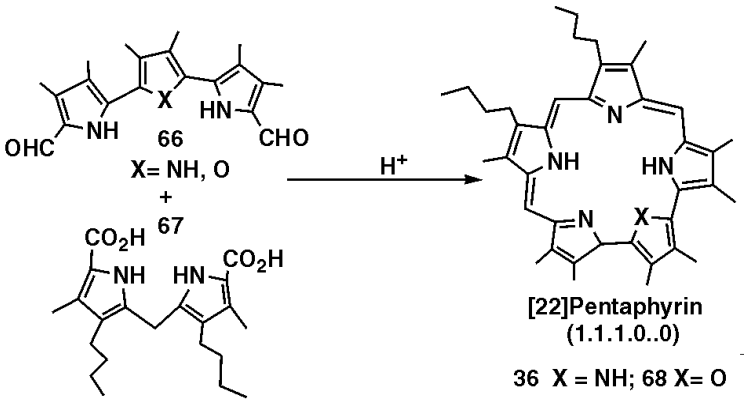
Scheme 17.



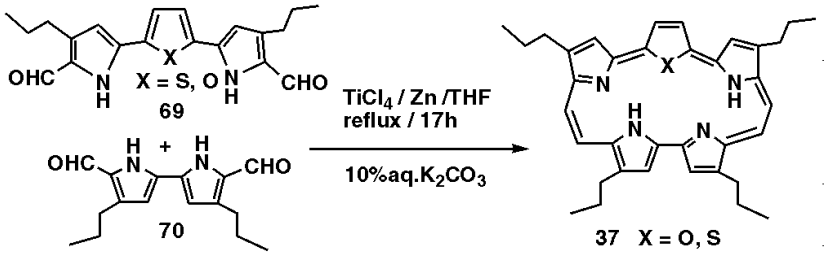
Scheme 18.



Scheme 19.



Scheme 20.



Scheme 21.

scheme 21 [19,21]. In addition to the expected ozaphyrin, the respective porphycene **2** and bronzaphyrin, which is a six membered expanded porphyrin, were formed.

6.1f *Dehydropentaphyrin-(2.1.0.0.1) and [22] pentaphyrin-(2.1.0.0.1):* [22] Pentaphyrin (2.1.0.0.1) **38** was synthesized by condensing terpyrrole **71** with an alkyne bridged bipyrrole **72** under standard MacDonald conditions giving rise to 22***p*** aromatic macrocycle dehydropentaphyrin **73**. This on treatment with poisoned Lindlar catalyst gave rise to the expected compound **38** as shown in scheme 22 [74].

6.2 *Conjugated nonaromatic systems*

6.2a *Orangarin-[20] pentaphyrin-(1.0.1.0.0):* The smallest pentapyrrolic system synthesized to date is 'orangarin' **39**, which is a [20] pentaphyrin-(1.0.1.0.0). This compound was prepared by acid-catalysed condensation between terpyrrole **71** and bipyrrole dialdehyde **47** as shown in scheme 23 [13].

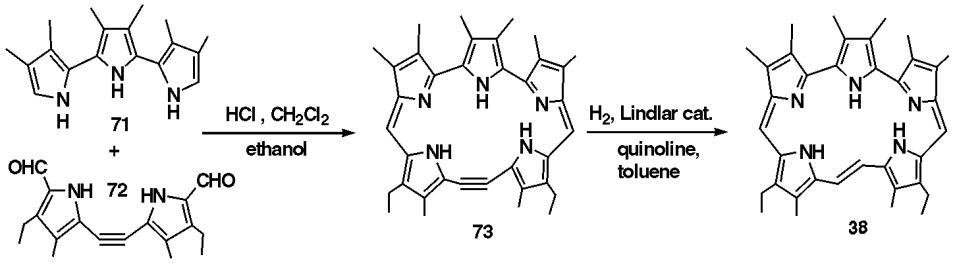
6.2b *Other systems:* Other aromatic systems having pentapyrrolic systems include pentaoxa and pentathia [30] pentaphyrin-(2.2.2.2.2) where each furan/thiophene heterocycle has been bridged by two *meso* carbons [75–77]. Another macrocycle pentaphyrin-(5.5.5.5.5) was also reported which can be treated as decavinylogously enlarged pentaphyrin [78].

7. Hexapyrrolic systems

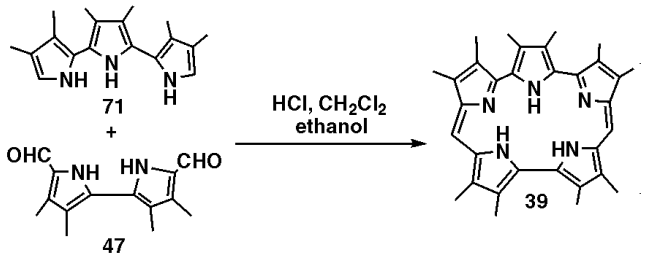
Hexapyrrolic macrocycles are expanded porphyrins with six pyrrolic/heterocyclic units connected by bridging carbon atoms. The number of *meso* carbons can be four or can be increased and decreased. Some of the nonaromatic and aromatic hexaphyrins are shown in chart 2.

7.1 *Aromatic systems*

7.1a *Rubyrins – [26] hexaphyrin-(1.1.0.1.1.0):* This expanded porphyrin **74** which is a [26] hexaphyrin-(1.1.0.1.1.0) was reported by Sessler *et al* in 1991 by condensing tetrapyrrolic precursor **81** with diformyl bipyrrole **82** under acid catalysis and subsequent air oxidation as shown in scheme 24 [18]. The resulting macrocycle was assigned the trivial name 'rubyrin' due to its dark orange-red colour in dichloromethane. The hexathiarubyrin



Scheme 22.



Scheme 23.

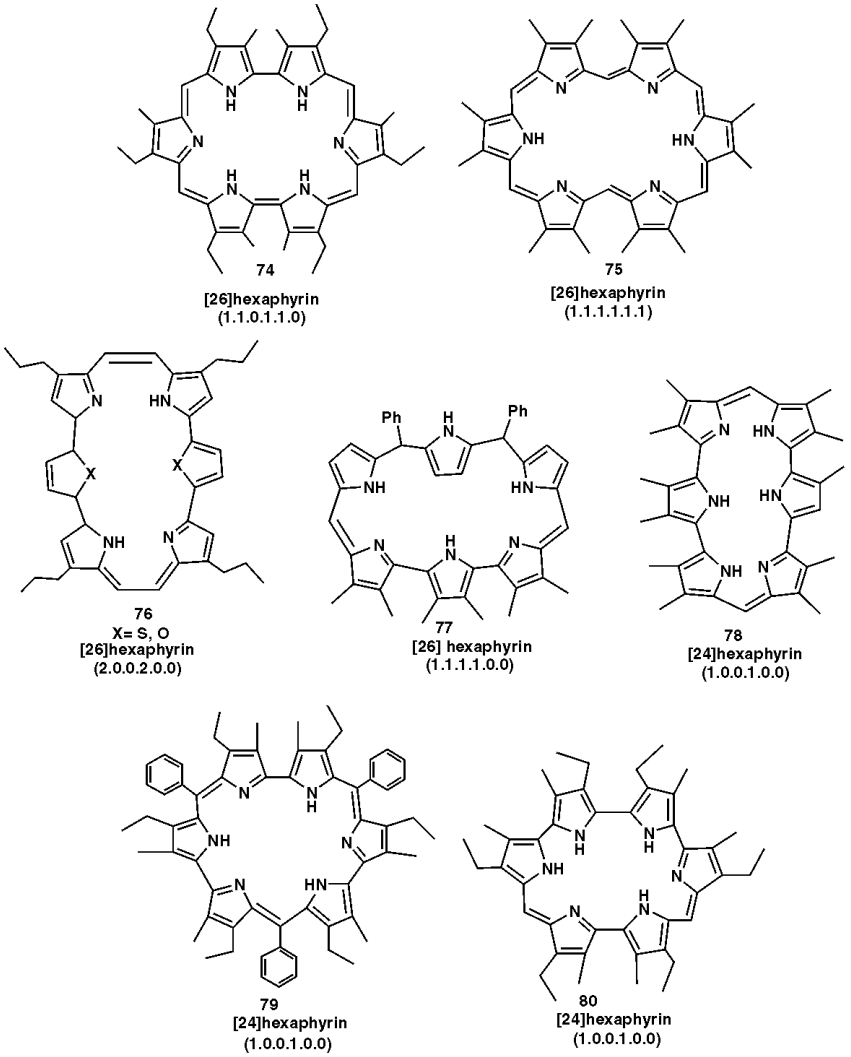
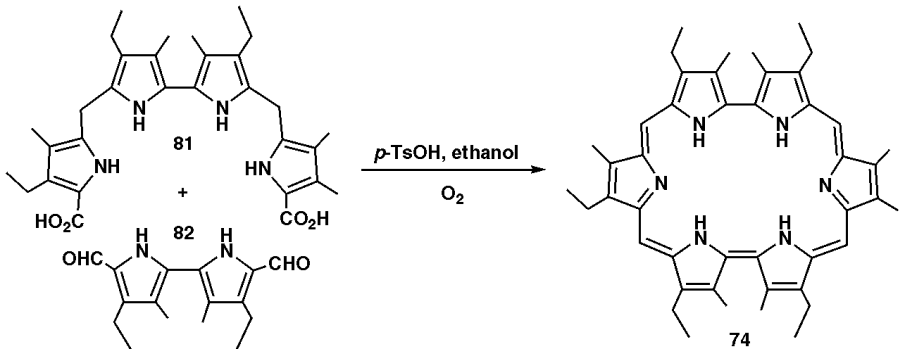


Chart 2.



Scheme 24.

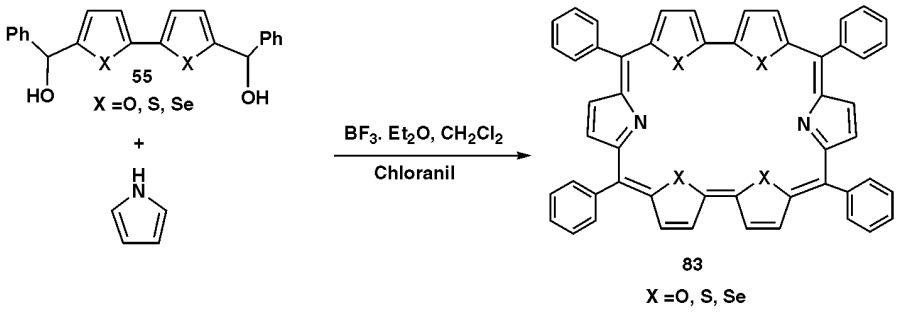
was synthesized by Vogel and coworkers in about 20% yield by the acid catalyzsed condensation between dithiophene dialcohol and 3,4-diethyl thiophene [7b].

Chandrashekar and coworkers reported an easy efficient methodology for first tetrathia/tetraselena/tetraoxa *meso*-tetraphenylrubyrins **83**, by the 2+1 condensation of 5,5′-*bis*(phenyl hydroxy methyl) 2,2′-bithiophene/biselenophene/bifuran diol **55** and pyrrole under Lindsey conditions followed by oxidation with chloranil as shown in scheme 25 in 19–28% yield [79,80]. The same group reported the formation of rubyrins containing three heteroatoms by acid catalyzed 4+2 condensation of tetrapyrrane **84** and corresponding diol **55** under TFA catalysis yielding 20–28% yield of expected rubyrins **85** and **86** as shown in scheme 26 [80].

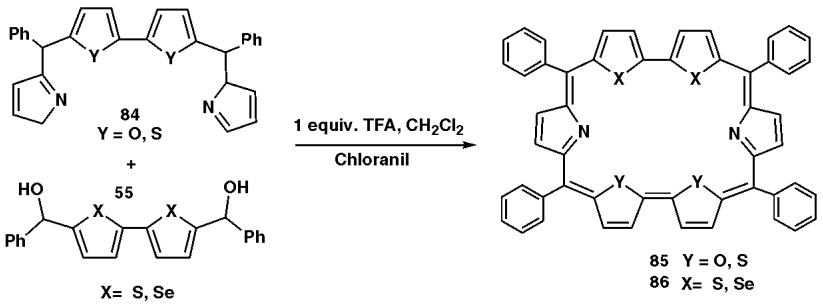
Another report from the same group describes an unprecedented coupling of tripyrranes **54** in presence of protic acid yielding rubyrins **86** as one of the products along with sapphyrins and porphyrins. The mixed coupling of tripyrranes **54** yielded rubyrins **87** bearing three heteroatoms. The reaction scheme is shown in scheme 27 [65,81].

7.1b *Hexaphyrin-[26] hexaphyrin-(1.1.1.1.1.1):* Hexaphyrin **75** was first reported by Gossauer and coworkers [12,67]. It was synthesized by the acid-catalysed 3+3 condensation of α-free tripyrranes **88** and tripyrrane dialdehyde **89** as shown in the scheme 28.

First *meso*-aryl hexaphyrin was reported by Dolphin and coworkers through Lindsey type condensation between 5,10-diphenyl tripyrrane and benzaldehyde, and was found unstable [60]. Cavaleiro and coworkers, through the Rothemund type synthesis involving pentafluorobenzaldehyde and pyrrole reported the first stable *meso*-aryl hexaphyrin [82].



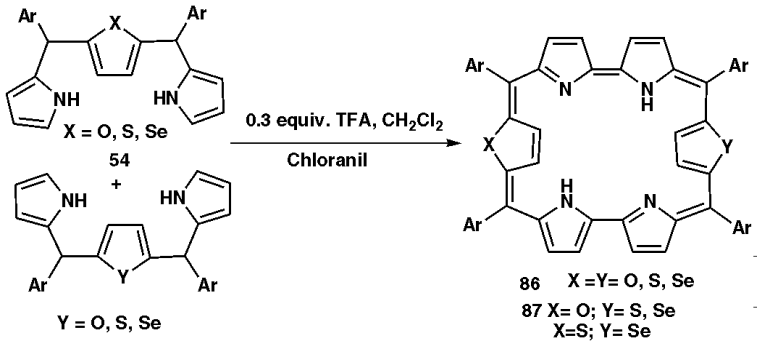
Scheme 25.



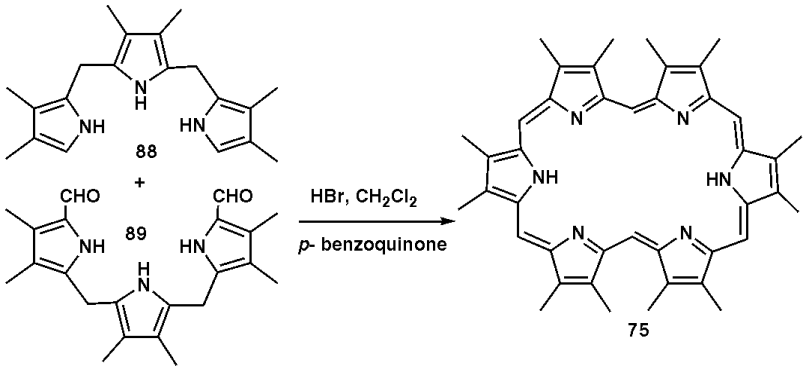
Scheme 26.

7.1c *Bronzaphyrin – [26] hexaphyrin-(2.0.0.2.0.0):* This class of macrocycle owes its existence to the synthetic efforts of Johnson and Ibers [20,21], Cava and coworkers [83–85] and the groups of Merz and Neilden [86]. Heteroatom containing [26] hexaphyrin-(2.0.0.2.0.0), **76** was synthesized by a McMurry coupling involving monooxaterpyrrole or monothiaterpyrrole precursor **69** (scheme 29).

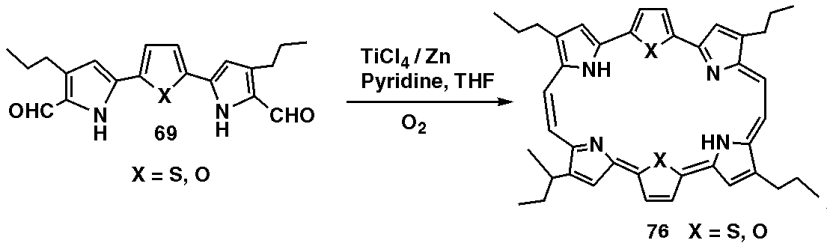
7.1d *[26] Hexaphyrin-(1.1.1.1.0.0):* Sessler and coworkers very recently reported an all-aza isomer of rubyrin with an inverted pyrrole ring **77**, where the pyrrolic units are



Scheme 27.



Scheme 28.



Scheme 29.

connected in a 1.1.1.1.0.0 fashion. This macrocycle was obtained in 46% yield from an acid-catalysed condensation reaction of a 1:1 mixture of diphenyltripyrrane **54** with the diformyl hexamethylterpyrrole **90** as shown in scheme 30 [87].

7.2 *Other aromatic systems*

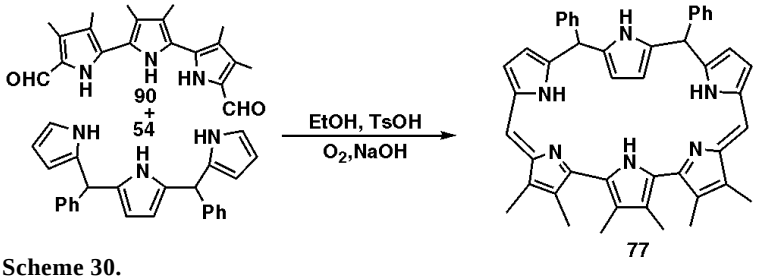
Other aromatic hexaphyrinic systems reported are hexathia [34] hexaphyrin- (2.2.2.2.2.2) where each thiophene units are connected by two bridging carbon atoms [7b].

7.3 *Hexapyrrolic nonaromatic systems*

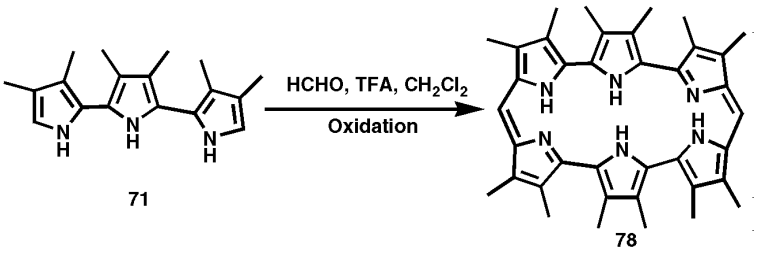
This class of hexaphyrins includes the conjugated but nonaromatic hexaphyrins reported so far. They are amethyrins, rosarins and other aromatic systems like hexaphyrins having 30 and 36π electrons associated with them.

7.3a *Amethyrin – [24] hexaphyrin-(1.0.0.1.0.0):* Amethyrin **78** is the smallest hexapyrrolic macrocyclic system synthesized to date and it is a [24] hexaphyrin-(1.0.0.1.0.0). Sessler and coworkers were the first to report it in 1995 and the trivial name 'amethyrin' owes its origin to the amethyst colour of the parent material in dilute solutions [13]. It was synthesised from acid-catalysed condensation of terpyrrole **71** and formaldehyde followed by oxidation with DDQ or *p*-chloranil as shown in scheme 31.

7.3b *Rosarin – [24] hexaphyrin (1.0.1.0.1.0):* Another nonaromatic hexapyrrolic macrocycle reported is [24] hexaphyrin-(1.0.1.0.1.0). It was assigned the trivial name 'rosarin' due to the pink-red colour it displays in its protonated form in organic solvents. Sessler and coworkers [17] reported synthesising rosarin **79** via acid catalysed condensations involving bipyrrole **91** and aromatic aldehyde as shown in scheme 32.



Scheme 30.



Scheme 31.

7.3c *[24] Hexaphyrin-(1.0.1.0.0.0):* Sessler and coworkers have very recently reported [24] hexaphyrin- (1.0.1.0.0.0), **80** choosing appropriate hexapyrrolic precursors (scheme 33)[88]. This is an isomer of amethyrin and is the smallest molecule containing a quarter pyrrole fragment.

7.4 *Other hexaphyrinoid systems*

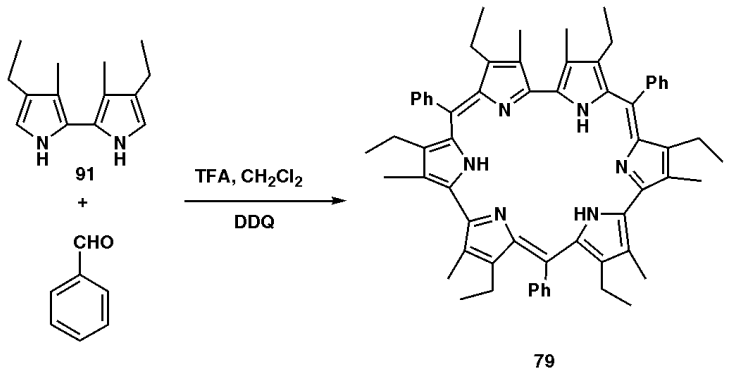
Other nonaromatic hexapyrrolic macrocycles reported are hexathia [30] hexaphyrin-(2.0.2.0.2.0)[86], hexaoxa and hexathia [36] hexaphyrin-(2.2.2.2.2.2) by McMurry type reductive coupling of respective precursors[77].

7.5 *Heptapyrrolic systems*

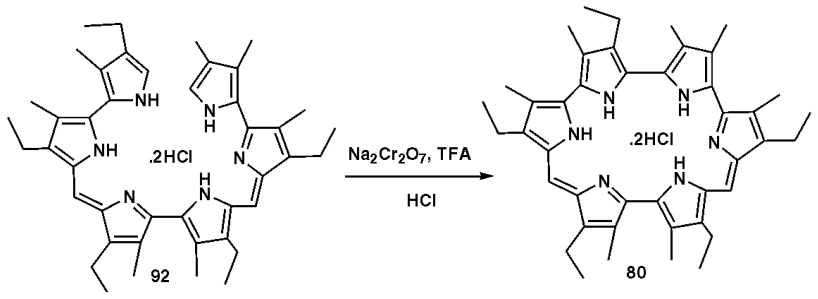
There are only very few reports on expanded porphyrins containing seven pyrrolic units till date. Seven pyrrolic units reported so far are shown in chart 3. They can also be classified as nonaromatic and aromatic systems. Heptaphyrin **92** is nonaromatic[22] while **93** and **94** are aromatic[89].

7.6 *Higher order systems*

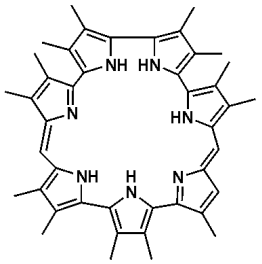
Larger macrocycles containing eight, ten, twelve and sixteen have been reported pyrrolic units. 2+2+2+2-Condensation product of 1,2-(dipyrrolyl) ethane with a bipyrrole



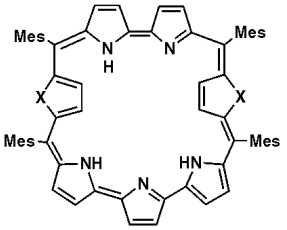
Scheme 32.



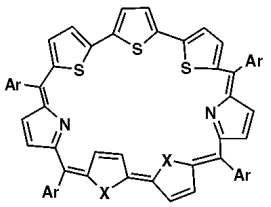
Scheme 33.



92: [28]heptaphyrin-(1.0.0.1.0.0.0)



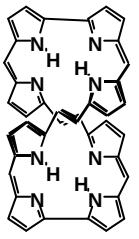
93: [30]heptaphyrin-(1.1.0.1.1.0.0), X = S, Se



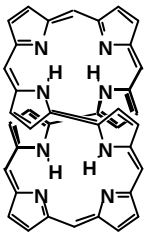
94: [30]heptaphyrin-(1.1.0.1.1.0.0), X = S, Se, O

Chart 3.

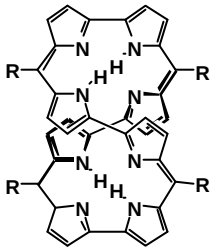
dialdehyde gave rise to the first octapyrrolic condensation product tetrahydrooctaphyrin-(2.1.0.1.2.1.0.1), which on dehydrogenation afforded fully conjugated nonaromatic [36] octaphyrin-(2.1.0.1.2.1.0.1) **95**[14]. Acid-catalysed condensation and subsequent dehydrogenation of tetraethyl substituted dipyromethane diacid with tetraethyl bipyrrole yielded a 2+2+2+2-product [34] octaphyrin-(1.1.1.0.1.1.1.0) **96**[15]. Another octapyrrolic system [32] octaphyrin-(1.0.1.0.1.0.1.0), **97** was synthesized from 4+4 condensation of tetrapyrrole with the related dialdehyde in presence of TFA [15]. All the octaphyrins **95–97** were reported by Vogel's group and they were found to exist in chiral figure eight conformations; the possibility exists that these might be separated into individual enantiomers. Compound **96** in spite of having 34***p*** aromatic pathways, revealed no



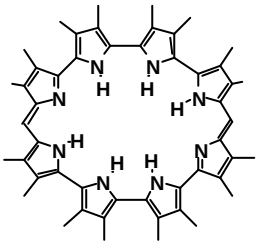
95
[36]Octaphyrin
(2.1.0.1.2.1.0.1)



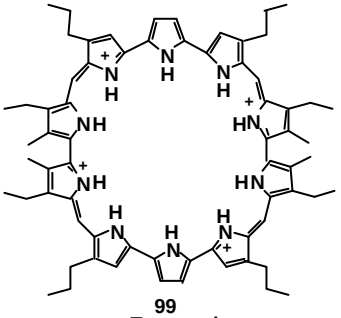
96
[34] Octaphyrin
(1.1.1.0.1.1.1.0)



97 R = H, Ar
[32]Octaphyrin
(1.0.1.0.1.0.1.0)

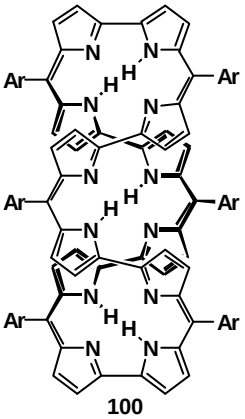


98
[32] octaphyrin
(1.0.0.0.1.0.0.0)



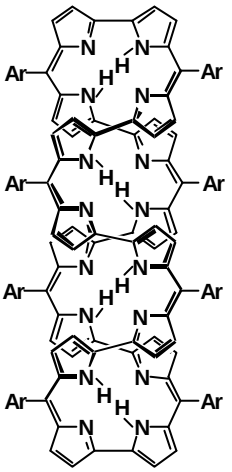
99
Turcasarin
[40] decaphyrin
(1.0.1.0.0.1.0.1.0.0)

diamagnetic ring current and planarity associated with aromatic character in solution and solid state. This may be interpreted as the lack of overall aromaticity arising from nonplanarity, ring size and self-cancelling magnetic moments within each half of the macrocycle. Another [32]octaphyrin-(1.0.0.0.1.0.0.0) **98** was reported by Sessler *et al* by oxidative coupling of tetrapyrrole[22]. This compound was also nonaromatic and nonplanar but it does not take up a figure eight conformation unlike other octaphyrins reported. Another expanded porphyrin having ten pyrrolic units, turcasarin **99**, named for its bright turquoise colour in organic solvent, was synthesized by Sessler and coworkers by co-condensation of terpyrrole and bipyrrole dialdehyde[23]. **98** has 40π electrons in its conjugative pathway and has the scientific name [40] decaphyrin (1.0.1.0.0.1.0.1.0.0). Setsune and coworkers reported an easy and efficient methodology for the syntheses of rosarin, octa, dodeca, and hexadecacyclopyrroles by utilising the age-old Rothemund synthetic procedure involving tetraethyl bipyrrole with benzaldehyde in presence of 0·25 eq. TFA followed by oxidation with DDQ. The macrocycles obtained were namely rosarin, [32] octaphyrin, [48] dodecaphyrin (1.0.1.0.1.0.1.0.1.0.1.0) **100** and [64] hexadecaphyrin (1.0.1.0.1.0.1.0.1.0.1.0.1.0.1.0) **101**[24]. Very recently Setsune *et al*[90] have succeeded in synthesizing [80]icosapphyrin and [96]tetracosapphyrin.



100

[48] dodecaphyrin-
(1.0.1.0.1.0.1.0.1.0.1.0)

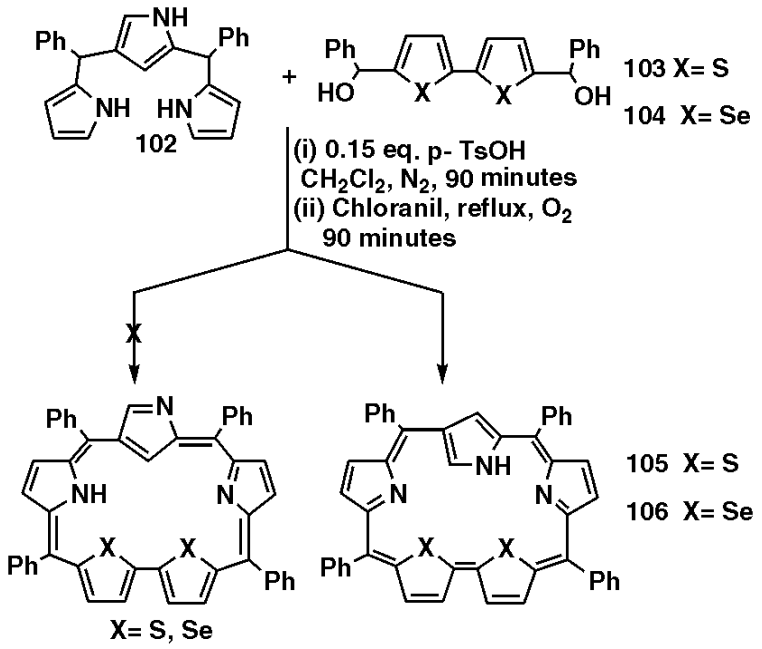


101

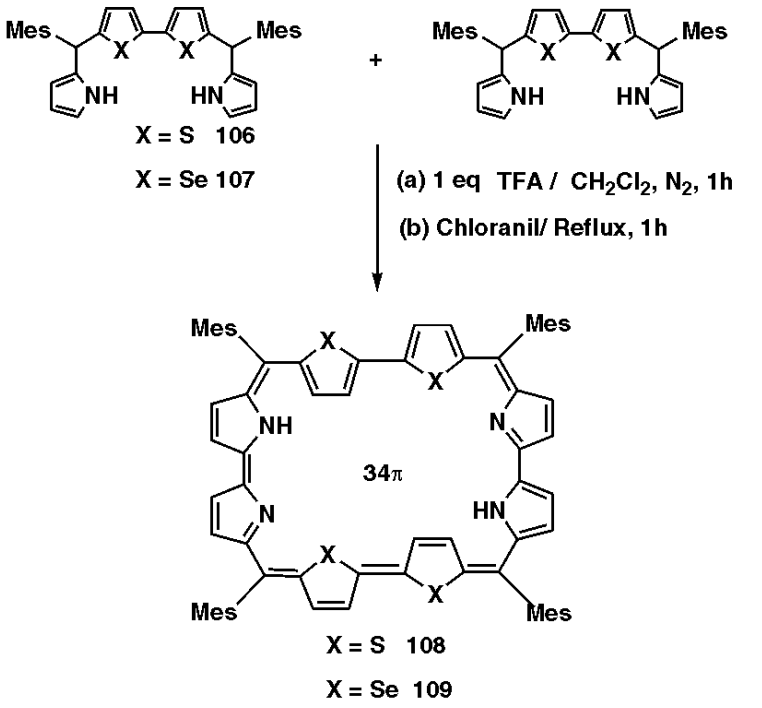
[64] hexadecaphyrin-
(1.0.1.0.1.0.1.0.1.0.1.0.1.0.1.0

7.7 *Aromatic N-confused sapphyrin*

Very recently Chandrashekar and coworkers[91] have succeeded in synthesizing first example of modified sapphyrin with inverted N-confused pyrrole ring (scheme 34). The single crystal structure of **105** shows inverted structure where the N-confused pyrrole opposite the bithiophene unit is inverted and makes a dihedral angle of 25·17° with respect to the mean plane containing four *meso* carbons. The aromatic nature of **105** was evident from Cα–Cβ being greater than Cα–Cβ distances (1·46 vs 1.35 for one pyrrole ring).



Scheme 34.



Scheme 35.

7.8 *Aromatic 34π modified octaphyrins*

Chandrashekar and coworkers[92] reported the first example of aromatic 34π modified octaphyrins through oxidative self coupling of 5,15-dimesityl-20,21-dithio-1-norbilane (scheme 35). The crystal structure of **108** indicates a completely planar structure, where one thiophene ring is inverted in each of the bithiophene units. The dihedral angle for the inverted thiophene with respect to the mean plane defined by four *meso* carbon atoms is 4·67°. The aromatic nature of the molecule is evident from the Δδ value (17·32 ppm) and high ε value (~10^5) for the Soret absorption in electronic absorption spectra.

Acknowledgements

We thank the Department of Science & Technology and the Council of Scientific and Industrial Research, Government of India for the research grants provided.

References

1. Smith K M 1976 *Porphyrins and metalloporphyrins* (Amsterdam: Elsevier)
2. Dolphin D 1978 *The porphyrins* (New York: Academic Press) vol. 1–7
3. Battersby A R, Fookes C J R, Matcham G W J and McDonald E 1980 *Nature (London)* **17** 285
4. Latos-Grazynski L 2000 Core modified heteroanalogues of porphyrins. In *The porphyrin handbook* (eds) K M Kadish, K M Smith and R Guilard (New York: Academic Press)
5. Paolesse R 2000 Synthesis and application of corroles. In *The porpyrin handbook* (eds) K M Kadish, K M Smith and R Guilard (New York: Academic Press)
6. Sessler J L, Gebauer A and Vogel E 2000 Porphyrin isomers. In *The porphyrin handbook* (eds) K M Kadish, K M Smith and R Guilard (New York: Academic Press)
7. (a) Sessler J L and Weghorn S J 1997 *Expanded, contracted and isomeric porphyrins* (Oxford: Elsevier), and references therein; (b) Sessler J L, Gebauer A and Weghorn S J 2000 Expanded porphyrins. In *The porphyrin handbook* (eds) K M Kadish, K M Smith and R Guilard (New York: Academic Press)
8. Bauer V J, Clive D L J, Dolphin D, Paine J B, Harris F L, King M M., Loder J, Wand S W C and Woodward R B 1983 *J. Am. Chem. Soc.* **105** 6429
9. Broadhurst M J, Grigg R and Johnson A W 1972 *J. Chem. Soc., Perkin Trans. 1* 2111
10. Sessler J L, Davis J M and Lynch V 1998 *J. Org. Chem*. **63** 7062
11. Rexhausen H and Gossauer A 1983 *J. Chem. Soc., Chem. Commun*. 275
12. (a) Gossauer A 1983 *Bull. Soc. Chim. Belg.* **92** 793; (b) Gossauer A 1983 *Chimia* **37** 341
13. Sessler J L, Weghorn S J, Hiseada Y and Lynch V 1995 *Chem. Eur. J.* **1** 56
14. Vogel E *et al* 1995 *Angew. Chem., Int. Ed. Engl.* **34** 2511
15. Bröring M, Jendry J, Zander L, Schmickler H, Nendel M, Chen J, Plattner D A, Houk K N and Vogel E 1995 *Angew. Chem., Int. Ed. Engl.* **34** 2515
16. Werner A, Michels M, Zander L, Lex J and Vogel E 1999 *Angew. Chem., Int. Ed. Engl*. **38** 3650
17. Sessler J L, Weghorn S J, Morishima T, Rosingana M and Lynch V 1992 *J. Am. Chem. Soc.* **114** 8306
18. Sessler J L, Morishima T and Lynch V 1991 *Angew. Chem., Int. Ed. Engl*. **30** 977
19. Miller D C, Johnson M R, Becker J J and Ibers J A 1993 *J. Heterocycl. Chem.* **30** 1485
20. Johnson M R, Miller D C, Bush K and Becker J J 1992 *J. Org. Chem*. **57** 4414
21. Miller D C, Johnson M R and Ibers J A 1994 *J. Org. Chem*. **59** 2877
22. Sessler J L, Seidel J and Lynch V 1999 *J. Am. Chem. Soc*. **121** 11257
23. Sessler J L, Seidel D, Lynch V and Johnson M R 1994 *Angew. Chem., Int. Ed. Engl*. **33** 1509
24. Setsune J-I, Katakami Y and Iizuna N 1999 *J. Am. Chem. Soc*. **121** 8957
25. Henderson B and Dougherty T J 1992 *Photodynamic therapy: Basic principles and clinical applications* (New York: Marcel Dekker)
26. Sternberg E and Dolphin D 1996 *Current Med. Chem*. **3** 293
27. Dolphin D 1996 *Can. J. Chem*. **3** 293

28. Lauffer R B 1987 *Chem. Rev*. **87** 901
29. Tweedle M F, Brittain H G, Eckelman W C, Gaughan G T, Hagan J J, Wedeking P W and Runge V M 1998 In *Magnetic resonance imaging* 2nd edn (ed.) C L W B Partain (Philadelphia: Sanders) vol. 1, p. 793
30. (a) Anderson S, Anderson H L and Sanders J K M 1993 *Acc. Chem. Res.* **26** 469; (b) Harriman A and Sauvage J-P 1996 *Chem. Soc. Rev.* **25** 41; (c) Sauvage J-P 1998 *Acc. Chem. Res.* **31** 611
31. (a) Bonnet R 1995 *Chem. Soc. Rev.* **24** 19; (b) Milgram L R and Mac Robert S 1998 *Chem. Br.* **35** 45
32. Fabian J, Nakazumi H and Matsuoka S 1992 *Chem. Rev*. **92** 1197
33. (a) Ostovic D and Bruice T C 1992 *Acc. Chem. Res*. **25** 314; (b) Meunier B 1992 *Chem. Rev*. **92** 1411; (c) Dolphin D, Traylor T G and Xie L Y 1997 *Acc. Chem. Res*. **30** 251
34. Vogel E, Köchner M, Schmickler H and Lex J 1986 *Angew. Chem., Int. Ed. Engl*. **25** 257
35. (a) Sessler J L, Brucker E A, Weghorn S J, Kisters M, Schäfer M, Lex J and Vogel E 1994 *Angew. Chem. Int. Ed. Engl*. **33** 2308; (b) Aukauloo M A and Guilard R 1994 *New J. Chem.* **18** 1205
36. Callot H J, Rohrer A and Tschamber T 1995 *New J. Chem*. **19** 155; (b) Vogel E *et al* 1997 *Angew. Chem., Int. Ed. Engl*. **36** 1651
37. (a) Chemielewski P J, Latos-Grazynski L, Rachlewicz K and Glowiak T 1994 *Angew. Chem., Int. Ed. Engl*. **33** 779; (b) Furuta H, Asano T and Ogawa T 1994 *J. Am. Chem. Soc*. **116** 767
38. (a) Vogel E 1996 *J. Heterocycl. Chem*. **33** 1461; (b) Vogel E, Bröring M, Erben C, Demuth R, Lex J, Nendel M and Houk K N 1997 *Angew. Chem., Int. Ed. Engl*. **36** 353
39. Furuta H, Maeda H and Osuka A 2000 *J. Am. Chem. Soc*. **122** 803
40. Furuta H, Ishizuka T, Osuka A and Ogawa T 1999 *J. Am. Chem. Soc*. **121** 2045
41. Liu B Y, Bruckner C and Dolphin D 1996 *Chem. Commun*. 2141
42. Narayanan S J, Sridevi B, Srinivasan A, Chandrashekar T K and Roy R 1998 *Tetrahedron Lett*. **39** 7389
43. (a) Geier G R III and Lindsey J S 1999 *J. Org. Chem*. **64** 1596; (b) Geier G R III, Haynes D M and Lindsey J S 1999 *Org. Lett*. **1** 1455
44. Lash T D, Richter T D and Shiner C M 1999 *J. Org. Chem*. **64** 7973
45. (a) Szterenberg L and Latos-Grazynski L 1997 *Inorg. Chem*. **36** 6287; (b) Chemielewski P J, Latos-Grazynski L and Glowiak T 1996 *J. Am. Chem. Soc*. **118** 5690
46. Chmielewski P J, Latos-Grazynski L and Schmidt I 2000 *Inorg. Chem*. **39** 5475
47. Furuta H, Ogawa T, Uwatoko Y and Araki K 1999 *Inorg. Chem*. **38** 2676
48. Furuta H, Kubo N, Ishizuka T, Osuka A, Nanami H and Ogawa T 2000 *Inorg. Chem.* **39** 5424
49. Ogawa T, Furuta H, Takahashi M, Morino A and Uno H 2000 *J. Organomet. Chem.* **611** 551
50. Ghosh A 1995 *Angew. Chem., Int. Ed. Engl*. **107** 1117
51. Furuta H, Maeda H and Osuka A 2000 *J. Org. Chem*. **65** 4222
52. Chmielewski P J and Latos-Grazynski L 1995 *J. Chem. Soc., Perkin. Trans. 2* 503
53. (a) Heo P-Y, Shin K and Lee C-H 1996 *Tetrahedron Lett*. **37** 197 (b) Lee C-H and Kim H-J 1997 *Tetrahedron Lett*. **38** 3935; (c) Heo P-Y, Shin K and Lee C-H 1996 *Tetrahedron Lett*. **37** 1521; (d) Lee C-H, Kim H-J and Yoon D-W 1999 *Bull. Korean Chem. Soc*. **20** 276
54. Pacholska E, Latos-Grazynski L, Szterenberg L and Ciunik Z 2000 *J. Org. Chem*. **65** 8188
55. Sprutta N and Latos-Grazynski L 1999 *Tetrahedron Lett*. **40** 8457
56. Furuta H, Maeda H, Osuka A, Yasutaka M, Shinmyozu T and Ishikawa Y 2000 *Chem. Commun*. 1143
57. Woodward R B 1966 *Aromaticity Conference*, Sheffield, UK
58. Sessler J L, Johnson M R and Lynch V 1987 *J. Org. Chem*. **52** 4394
59. Chmielewski P J, Latos-Grazynski L and Rachlewicz K 1995 *Chem. Eur. J*. **1** 68
60. Bruckner C, Sternberg E D, Boyle R W and Dolphin D 1997 *Chem. Commun*. 1689
61. Paolesse R, Licoccia S, Spagnoli M, Boschi T, Khoury R G and Smith K M 1997 *J. Org. Chem*. **62** 5133
62. Broadhurst M J, Grigg R and Johnson A W 1969 *J. Chem. Soc., Chem. Commun*. 23
63. (a) Sessler J L, Cyr M J and Burell A K 1991 *Synlett*. 127; (b) Sessler J L, Cyr M J and Burell A K 1992 *Tetrahedron* **48** 9661; (c) Lisowski J, Sessler J L and Lynch V 1995 *Inorg. Chem.* **34** 3567; (d) Rachlewicz K, Sprutta N, Chmielewski P J and Latos-Grazynski L 1998 *J. Chem. Soc., Perkin Trans. 2* 969; (e) Sessler J L, Hoehner M C, Gebaur A, Andrievsky A and Lynch V 1997 *J. Org. Chem*. **62** 9251

64. (a) Srinivasan A, Anand V G, Narayanan S J, Pushpan S K, Kumar M R, Chandrashekar T K, Sugiura K-I and Sakata Y 1999 *J. Org. Chem*. **64** 8693; (b) Srinivasan A, Pushpan S K, Kumar M R, Mahajan S, Chandrashekar T K, Roy R and Ramamurthy P 1999 *J. Chem. Soc., Perkin Trans. 2* 961; (c) Srinivasan A, Mahajan S, Pushpan S K, Kumar M R and Chandrashekar T K 1998 *Tetrahedron Lett*. **39** 1961
65. (a) Narayanan S J, Sridevi B, Chandrashekar T K, Vij A and Roy R 1998 *Angew. Chem., Int. Ed. Engl*. **37** 3394; (b) Narayanan S J, Sridevi B, Chandrashekar T K, Vij A and Roy R 1999 *J. Am. Chem. Soc*. **39** 9053
66. Lash T D and Richter D T 1998 *J. Am. Chem. Soc*. **120** 9965
67. Gossauer A 1984 *Chimia* **38** 45
68. Vogel E 1996 *J. Heterocyclic Chem*. **33** 1461
69. Vogel E, Pohl M, Hermann A, Wiss T, König C, Lex J, Gross M and Gisselbrecht J P 1996 *Angew. Chem., Int. Ed. Engl*. **35** 1520
70. Vogel E, Fröde C, Breihahn A, Schmickler H and Lex J 1997 *Angew. Chem., Int. Ed. Engl*. **36** 2609
71. Shin J-Y, Furuta H and Osuka A 2001 *Angew. Chem., Int. Ed. Engl*. **40** 619
72. Broadhurst M J, Grigg R and Johnson A W 1969 *J. Chem. Soc., Chem. Commun*. 1480
73. Narayanan S J, Sridevi B, Chandrashekar T K, Englich U and Senge K R 1999 *Org. Lett*. **1** 587
74. Weghorn S J, Lynch V and Sessler J L 1995 *Tetrahedron Lett*. **36** 4713
75. Märkl G, Sauer H, Krietmeir P, Burgemeister T, Kastner F, Adolin G, Nöth H and Polborn K 1994 *Angew. Chem., Int. Ed. Engl*. **33** 1151
76. Hu Z and Cava M P 1994 *Tetrahedron Lett*. **35** 3493
77. Elix J A 1969 *Aus. J. Chem*. **22** 1951
78. Knubel G and Franck B 1988 *Angew. Chem., Int. Ed. Engl*. **27** 1170
79. Srinivasan A, Reddy V M, Narayanan S J, Sridevi B, Pushpan S K, Kumar M R and Chandrashekar T K 1997 *Angew. Chem., Int. Ed. Engl*. **36** 2598
80. Srinivasan A, Pushpan S K, Kumar M R, Chandrashekar T K and Roy R 1999 *Tetrahedron* 6671
81. Narayanan S J, Srinivasan A, Sridevi B, Chandrashekar T K, Senge M O, Sugiura K-I and Sakata Y 2000 *Eur. J. Org. Chem*. 2357
82. Neves M G P M S, Martins R M, Tomé A C, Silverstre A J D, Silva A M S, Félix V, Drew M G B and Cavaleiro J A S 1999 *Chem. Commun*. 385
83. Hu Z, Atwood J L and Cava M P 1994 *J. Org. Chem*. **59** 8071
84. Hu Z, Scordilis-Kelley C and Cava M P 1993 *Tetrahedron Lett*. **34** 1879
85. Kozaki M, Parakka J P and Cava M P 1996 *J. Org. Chem*. **61** 3657
86. Elinger F, Gieren A, Hübner T, Lex J, Merz A, Neildein R and Salbeck J 1993 *Monatsch. Chem*. **124** 931
87. Sessler J L, Seidel D, Bucher C and Lynch V 2000 *Chem. Commun*. 1473
88. Sessler J L, Seidel D, Vivian A E, Lynch V, Scott B L and Keogh D W 1994 *Angew. Chem., Int. Ed. Engl*. **33** 1509
89. Anand V G, Pushpan S K, Srinivasan A, Narayanan S J, Sridevi B, Chandrashekar T K, Roy R and Joshi B S 2000 *Org. Lett*. **2** 3829
90. Setsune J and Maeda S 2000 *J. Am. Chem. Soc*. **122** 12405
91. Pushpan S K, Srinivasan A, Anand V G, Venkatraman S, Chandrashekar T K, Joshi B S, Roy R and Furuta H 2001 *J. Am. Chem. Soc*. **123** 5138
92. Anand V G, Pushpan S K, Venkatraman S, Dey A, Chandrashekar T K, Joshi B S, Roy R, Teng W and Senge K R 2001 *J. Am. Chem. Soc*. **123** 8620