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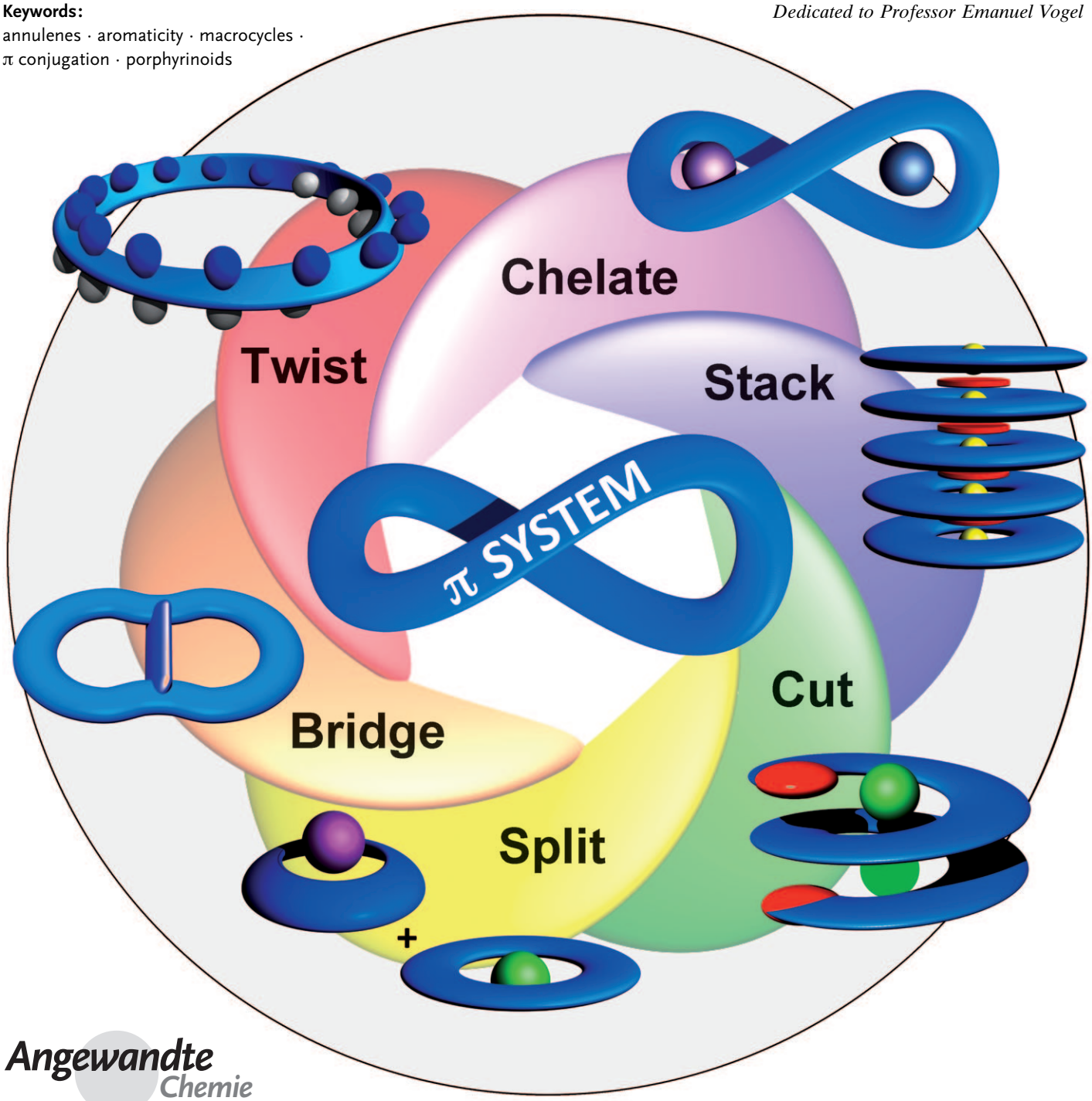
Porphyrinoids

Expanded Porphyrins: Intriguing Structures, Electronic Properties, and Reactivities

*Shohei Saito and Atsuhiro Osuka**

Keywords:
annulenes · aromaticity · macrocycles · π conjugation · porphyrinoids

Dedicated to Professor Emanuel Vogel



The chemistry of expanded porphyrins, which are higher homologues of porphyrins, has been intensively explored for the last three decades. Expanded porphyrins exhibit structures, electronic properties, coordination chemistry, and reactivities that are entirely different from those of porphyrins. Through these studies, it has become increasingly apparent that expanded porphyrins are attractive in views of aromaticity and multimetal coordination, or as functional dyes, nonlinear optical materials, ion receptors, or stable organic radicals. As such, we have continuously witnessed the emergence of expanded porphyrins that exhibit unprecedented structures and properties, as is highlighted by the facile realization of Möbius aromatic and even antiaromatic systems with twisted molecular structures. In this Review, the recent progress of the chemistry of expanded porphyrins after the seminal Review by Sessler and Seidel in 2003 is presented.

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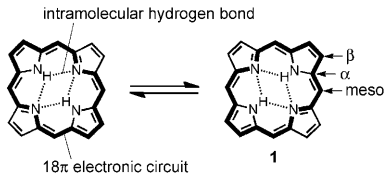
1. Introduction

1.1. Porphyrins

Porphyrins **1** are pigments that are well known because of their vital roles in natural systems. They are ubiquitous in our world and have been referred to as the "pigments of life". In fact, life relies heavily on the biological processes that are performed or catalyzed by porphyrin-containing proteins or coenzymes. Needless to say, chlorophylls are key in photosynthesis and the oxygen produced from photosynthesis is transported, stored, and reduced in diverse ways by heme-containing proteins. Therefore it is natural that porphyrins remain of fundamental interest in both basic and applied fields.[1]

Porphyrin frameworks consists of four pyrrole subunits that are connected in a coplanar fashion at their α-carbon atoms through a methine carbon bridge. In the resultant square-planar porphyrin skeleton, the effective hydrogen bonds between the pyrrolic protons and iminic pyrrolic nitrogen atoms are also structurally important (Scheme 1).



Scheme 1. Porphyrin tautomerism.

The four inward-orientated pyrrolic nitrogen atoms can serve as an effective, dianionic ligand towards various metal ions to allow for the formation of metalloporphyrins, some of which fulfill catalytic functions in key synthetic reactions. Porphyrins often undergo facile electron-transfer reactions to generate cationic or anionic radicals, thus reflecting their relatively low LUMO levels and high HOMO levels. Most porphyrins exist as a conjugated 18π-electronic aromatic circuit with rare examples of 16π- or 20π-electronic antiaromatic or non-aromatic species.[2]

1.2. Definition of Expanded Porphyrins

The simple definition of an expanded porphyrin is a "porphyrinoid larger than a porphyrin" (Figure 1).[3,4] However, this definition is not rigorous, because the term "porphyrinoid" itself is not clearly defined. In their 2003

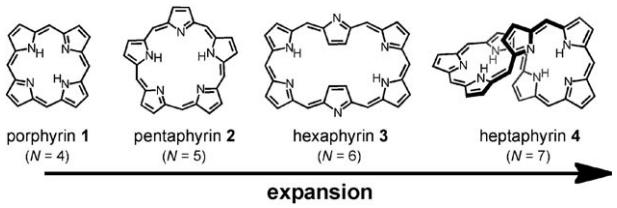


Figure 1. Porphyrin and expanded porphyrins, where *N* represents the number of pyrrole subunits.

Review, Sessler and Seidel proposed a definition of expanded porphyrins as "macrocycles that contain pyrrole, furan, thiophene, or other heterocyclic subunits linked together either directly or through one or more spacer atoms in such a manner that the internal ring pathway contains a minimum of 17 atoms".[3b] On the basis of this definition, the chemistry of

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expanded porphyrins was reviewed in order of ring size. In this Review, we take a different viewpoint by focusing on representative topics in the chemistry of expanded porphyrins; thus we describe their synthesis, structure, coordination chemistry, chemical reactivity, ion binding ability, chirality, aromaticity, and photophysical properties. For the most part, we will focus on all-pyrrole-based expanded porphyrins. Accordingly, related macrocyclic systems such as core-modified expanded porphyrins,[5] Schiff base type expanded porphyrins,[6] calixpyrroles,[7] and calix[*n*]phyrins[8] are excluded from this Review, despite the interest they have attracted in recent years.

1.3. Nomenclature

The systematic nomenclature of porphyrin analogues, as proposed by Franck and Nonn,[9] is useful for expanded porphyrins. In this nomenclature, an name of an expanded porphyrin consists of three parts: 1) a core name that indicates the number of pyrrole subunits in such a way as to use pentaphyrin **2**, hexaphyrin **3**, and heptaphyrin **4** for expanded porphyrins consisting of five, six, and seven pyrrolic subunits, respectively, 2) the number in the square-bracketed prefix indicates the number of π electrons in the effective macrocyclic conjugation, and 3) the numbers in the round-bracketed suffix indicate the numbers of bridging carbon atoms between the constitutional pyrrole groups, starting from the largest unit. According to this nomenclature, porphyrin **1** and hexaphyrin **3** are named as [18]porphyrin-(1.1.1.1) and [26]hexaphyrin(1.1.1.1.1.1), respectively. In this Review, some expanded porphyrins are named after their colors, which include sapphyrin for [22]pentaphyrin(1.1.1.1.0) **5**, amethyrin for [24]hexaphyrin(1.0.0.1.0.0) **6**,[10] and rubyrin for [26]hexaphyrin(1.1.0.1.1.0) **7** (Figure 2).[11]

1.4. Brief History

The historical background of expanded porphyrins and related systems is summarized in Figure 3. In contrast to the chemistry of porphyrins, the chemistry of expanded porphyrins still remains at rudimentary stage and started only after the serendipitous discovery of sapphyrin **5** by Woodward et al. in 1966, although the full report of the discovery was published only in 1983.[12] In the early stages (1966–1990),

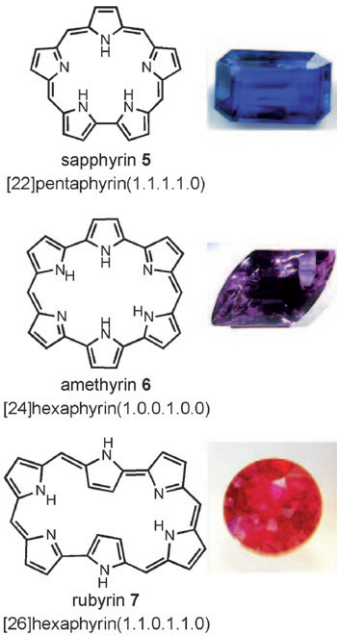


Figure 2. Color-related names and systematic names of expanded porphyrins.

the main contributions were made by Johnson and co-workers on sapphyrins,[13] LeGoff and Franck, and their respective co-workers on vinylogous porphyrins (which were also called "platyrins") such as **8**[14] and **12**,[18] Day, Marks et al. on uranyl superphthalocyanines **9**,[15] Gossauer and co-workers on pentaphyrins, hexaphyrins, and their metal complexes **10**,[16] and Vogel et al. on porphyrin isomers such as porphycene **11** and corrphycene.[17] These works were reviewed by Jasat and Dolphin in 1999.[4a] We feel that the renaissance of expanded porphyrins is largely due to Sessler and co-workers, who reported texaphyrin **13** in 1988,[19a] and on the improved synthesis of sapphyrin **14** in 1990,[20a] and demonstrated the potential of these expanded porphyrins in many fields including anion recognition, photodynamic therapy (PDT), functional dyes, aromaticity, and magnetic resonance imaging (MRI).[10,19,20] In particular, Sessler and co-workers have developed the water-soluble texaphyrin Gd^{III} complex **15**, which is referred to as motexaphin gadolinium (MGd) and is a promising anticancer reagent that allows clear MRI contrast.[19] The same research group also reported [40]decaphyrin(1.0.1.0.0.1.0.1.0.0) (turcasarin) **16**, which is the first

Shohei Saito (1982, Tokyo) studied chemistry at Kyoto University under the supervision of Prof. Dr. Osuka. After completing his PhD on the development of large expanded porphyrins as flexible π-conjugated systems in 2010, he joined the group of Prof. S. Yamaguchi of Nagoya University as an Assistant Professor.

Atsuhiro Osuka (1954, Aichi) received a PhD from Kyoto University in 1982. In 1979, he started his academic carrier at Ehime University as an Assistant Professor. In 1984, he moved to Kyoto University, where he became a Professor in 1996. He received the Japanese Photochemistry Award in 1999 and the Chemical Society of Japan Award in 2010. His research interests cover many aspects of synthetic approaches toward novel porphyrin-related compounds that have intriguing structures, properties, and functions.

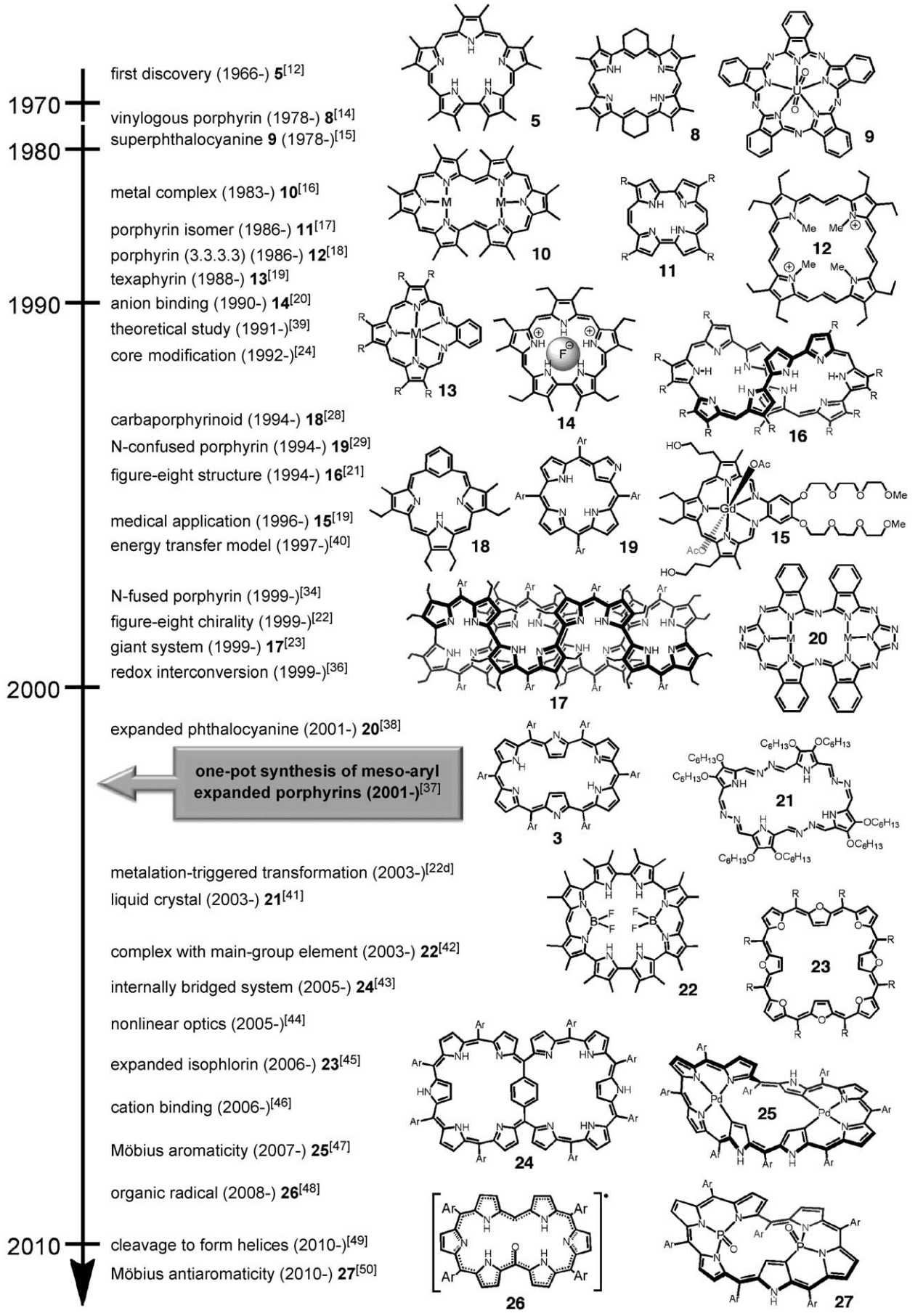


Figure 3. Historical summary of expanded porphyrins and related porphyrinoids.

"figure-eight" large decapyrrolic macrocycle that exists as two limiting helical conformations that interconvert slowly at room temperature.[21] Similar chiral helical conformations were found for octaphyrins by Vogel and co-workers; this work culminated in unprecedented metalation-induced skeletal rearrangements of large expanded porphyrins (Section 4).[22] As a remarkable example, Setsune and co-workers have characterized the highly distorted gigantic expanded porphyrins [64]hexadecaphyrin(1.0.1.0.1.0.1.0.1.0.1.0.1.0.1.0) **17** by X-ray diffraction analysis.[23]

Core-modified expanded porphyrins that contain other heterocycles such as thiophene, furan, selenophene, and tellurophene instead of pyrrole subunits have been actively developed since the early examples were reported by Ibers, Cava, and Vogel, and their respective co-workers.[24] Recent examples have been mainly contributed by the research groups of Chandrashekar,[5] Latos-Grażyński,[25] and Lee.[26]

Another important category is carbaporphyrinoids, in which one or more of pyrrole rings are replaced by carbocyclic units[25d,27] or N-confused pyrroles.[4c] Intriguingly, these molecules offer a possibility to stabilize rare higher oxidation states of metal complexes. In 1994, Berlin and Breitmaier first prepared *meta*-benziporphyrins **18**, which were extensively investigated by Lash and coworkers.[28] In the same year, N-confused porphyrins (NCPs) **19** were independently discovered by Furuta and Latos-Grażyński, and their respective co-workers.[29] Subsequently, the chemistry of carbaporphyrinoids has been actively developed by Furuta et al.,[4c,30,34] Lash et al.,[31,33] and Latos-Grażyński and co-workers.[32] Recent interesting examples are azuliporphyrins,[33] benziporphyrin analogues,[32a] and N-fused porphyrins (NFPs).[34] Expanded analogues of N-confused porphyrins and carbaporphyrins have also been actively explored.[35]

Torres and Kobayashi, and their respective co-workers have independently synthesized expanded phthalocyanines such as **20**,[38] although the intrinsic synthetic difficulties of this class of macrocycles hampered their rapid development.

In 1999, Cavaleiro and co-workers reported an important example of the isolation and characterization of meso-aryl-substituted [26]hexaphyrin **3** and [28]hexaphyrin **37**.[36] We subsequently reported the facile one-pot synthesis of the series of meso-aryl-substituted expanded porphyrins, including **3**.[37] This result allowed us to embark on a systematic investigation on the chemistry of meso-aryl expanded porphyrins.

1.5. General Features

1.5.1. General Properties

Expanded porphyrins share two structural features: 1) a large and flexible annulene-like π-conjugated electronic network and 2) a regularly arranged amine–imine interconvertible pyrrole subunits that allow for variable π-electronic states of macrocycle, metal coordination, and intra- and/or intermolecular hydrogen-bonding interactions. The first feature leads to good solubility, high aromaticity, and unique photophysical properties, including absorption that leads to intense colors ($\varepsilon \approx 50\,000$ up to $380\,000\ M^{-1}\,cm^{-1}$[48a]; Figure 4),

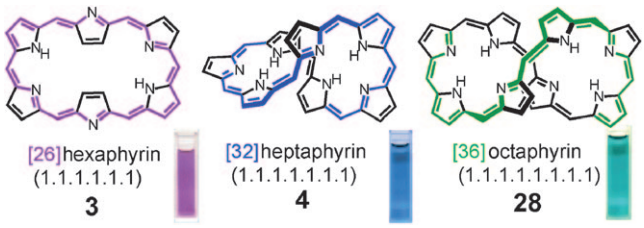
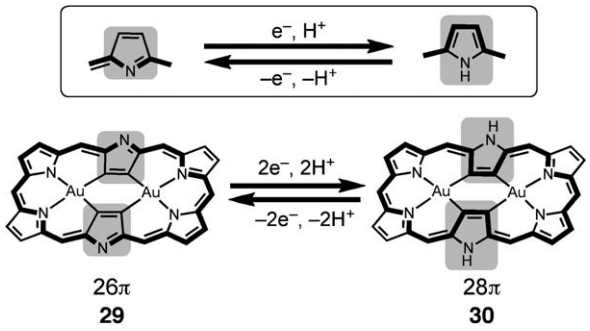


Figure 4. π Conjugation and intense solution colors of large macrocycles.

a large two-photon-absorption (TPA) cross-section ($\sigma^{(2)} \approx 1000$ up to 13000 GM),[51,52] and fluorescence in the near-infrared (NIR) region.[44,46,35g,54f,56b] The second set of features allow for facile interconversion between different neutral redox states (Scheme 2), metal complex formation, anion binding, and porphyrinlike tautomerism (Figure 5).



Scheme 2. Interconversion between stable redox states **29** and **30**.

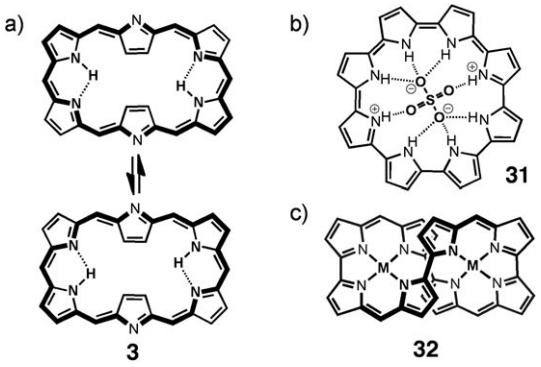


Figure 5. Functions of pyrrolic nitrogen atoms: a) Intramolecular hydrogen bonds and tautomerism, b) anion binding, and c) metal coordination.

1.5.2. Conformational Flexibility

Since the electronic, optical, and coordination properties of expanded porphyrins are dependent upon their conformations, control over their conformations is crucial. The conformations of expanded porphyrins depend on the following factors: 1) the intrinsic structural constraints that arise from the requirement to form a conjugated cyclic structure, 2) peripheral substituents at the β and/or meso positions, 3) intra/intermolecular hydrogen bonding, 4) solvent polarity,

and furthermore, hydrogen-bond-donating and accepting properties of the solvent, 5) temperature, and 6) the aromatic versus antiaromatic characters of the electronic π system. Flexible conformational changes of meso-aryl substituted sapphyrins were revealed by Latos-Grażyński and co-workers both for the neutral and protonated states.[53] With regard to conformational dependence on the aromatic versus antiaromatic characters, Möbius aromaticity has become an interesting topic, since 4nπ expanded porphyrins usually adopt twisted figure-eight conformations but prefer twisted Möbius conformations upon appropriate stimuli (Section 7).

[26]Hexaphyrins(1.1.1.1.1.1) **3** represent the most studied case of conformational dependence.[16,36,54] Thus, a detailed discussion is given for this species. Two major conformations have been identified, namely a rectangular conformation (Figure 6a) and a dumbbell-shaped conformation (Figure 6b). Through extensive studies, it has been recognized

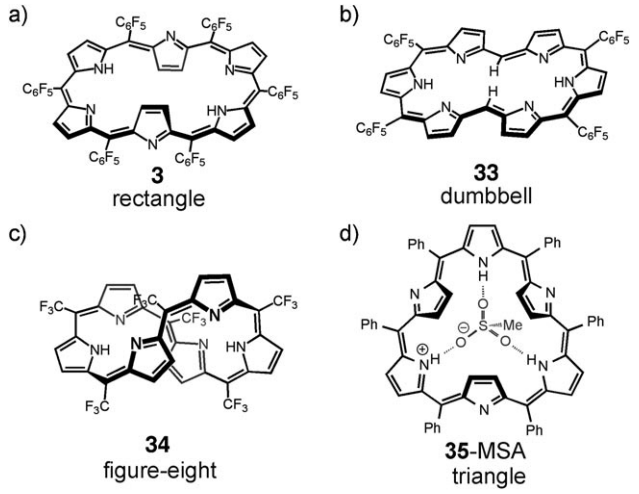
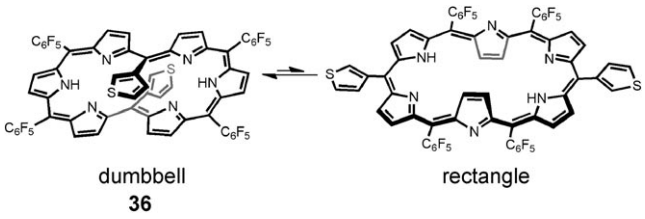


Figure 6. Various conformations of [26]hexaphyrins(1.1.1.1.1.1).

that most meso-aryl [26]hexaphyrins adopt rectangular conformations, in which two pyrrole rings in the long central side are inverted, while the remaining four pyrrole rings point inwards to adjoin the effective intramolecular hydrogen bonding. This structure is almost planar, which allows its strong 26π aromaticity, although the planarity is lower than that of porphyrins because of the steric hindrance between the inner β protons at the inverted pyrrole rings. A dumbbell-shaped conformation may be preferred over a rectangular conformation because of its four hydrogen-bonding interactions, but is disfavored because of the steric repulsion between the inward-facing meso-substituents. In the meantime, an interesting example was reported that demonstrated direct evidence of conformational interconversion between dumbbell-shaped and rectangular structures for 5,20-meso-thien-3-yl-10,15,25,30-meso-pentafluorophenyl substituted [26]hexaphyrin **36** (Scheme 3). This hexaphyrin actually exists in an equilibrium between these conformers because the steric repulsion of the meso-aryl groups that point inwards in the dumbbell conformation is mitigated with a less bulky thien-3-yl substituent.[54a] In an extreme case, the 5,10,20,25-pentafluorophenyl substituted [26]hexaphyrin **33**, which lacks



Scheme 3. Conformational equilibrium of **36**.

the repulsive meso-aryl groups, adopts a rigid dumbbell conformation (Figure 6b) with perfect planarity and effective intramolecular hydrogen bonding. As a consequence of this predominant planar conformation, this hexaphyrin exhibits a particularly sharp and intense Soret-like band ($\varepsilon = 380\,000\,\mathrm{M^{-1}cm^{-1}}$ at $\lambda = 549$ nm).[48a] The predominant planar and rectangular conformation of hexakis(pentafluorophenyl)hexaphyrin can thus be understood mostly in terms of serious steric interactions between the opposite two pentafluorophenyl substituents in a dumbbell conformation. By the same reasoning, the observed dumbbell conformation of β-alkyl-substituted hexaphyrins can be accounted for in terms of the steric hindrance of the β-alkyl substituents in the rectangular geometry.[16]

Figure-eight conformations (Figure 6c) are relatively rare for [26]hexaphyrins(1.1.1.1.1.1) but are observed for those that bear bulky substituents at the meso and/or β positions, such as meso-CF_3 substituted [26]hexaphyrin **34**.[54c] In the figure-eight structures, weak 26π aromaticity is still retained.[55] As an interesting case, a meso-phenyl-substituted [26]hexaphyrin adopts a triangular conformation upon protonation with methanesulfonic acid (MSA) to give **35**-MSA (Figure 6d and Scheme 5).[35 g]

Conformational features of [28]hexaphyrins(1.1.1.1.1.1) **37** are more complicated because the macrocycles that bear $4n\,\pi$-electronic networks prefer singly twisted Möbius conformations over planar rectangle and dumbbell (the so-called Hückel) conformations (Figure 7).[47c] This will be discussed in detail below.

In general, the conformational flexibility and complexity becomes more apparent for larger expanded porphyrins. A limited number of large expanded porphyrins have been structurally well characterized, including the helical turcasarin **16** reported by Sessler et al.,[21] the helical [64]hexade-

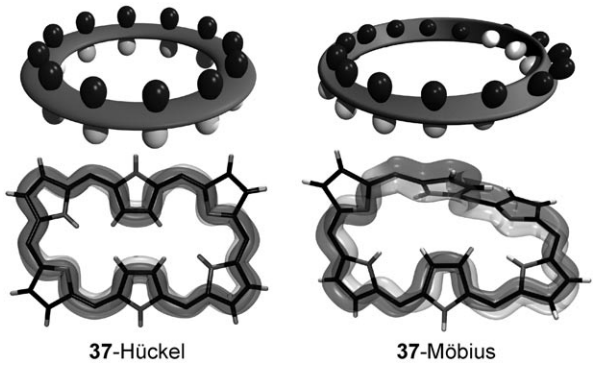


Figure 7. Major conformers of **37**. Left: Hückel rectangular conformer **37**-Hückel. Right: Möbius conformer **37**-Möbius.

caphyrin(1.0.1.0.1.0.1.0.1.0.1.0.1.0.1.0) **17** by Setsune and co-workers,[23] the planar and aromatic core-modified [34]octaphyrin by Chandrashekar and co-workers,[5c] the figure-eight [32]octaphyrin(1.0.1.0.1.0.1.0) by Vogel et al.,[22a] the crescent-shaped [44]decaphyrin(1.1.1.1.1.1.1.1.1.1) **40** by Osuka and co-workers,[57f] and the intramolecular helical [56]dodecaphyrin(1.1.1.1.1.1.1.1.1.1.1.1) **47** by Osuka and co-workers.[57g] We will not enter into the details of this topic in this Review.

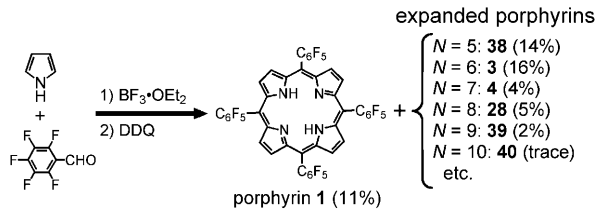
2. Synthesis and Stability

In the early stages of research, β-alkyl-substituted expanded porphyrins were mainly studied, and were synthesized by the classical acid-catalyzed condensation or chemical oxidative coupling of corresponding oligopyrrolic precursors (see Figure 3, and Sections 2.1.2. and 2.1.3.). β-Alkylated expanded porphyrins without meso-substituents are sometimes unstable under ambient conditions.[16] On the other hand, meso-aryl-substituted expanded porphyrins have been explored in various ways, and are mostly stable, as long as electron-withdrawing substituents are chosen.

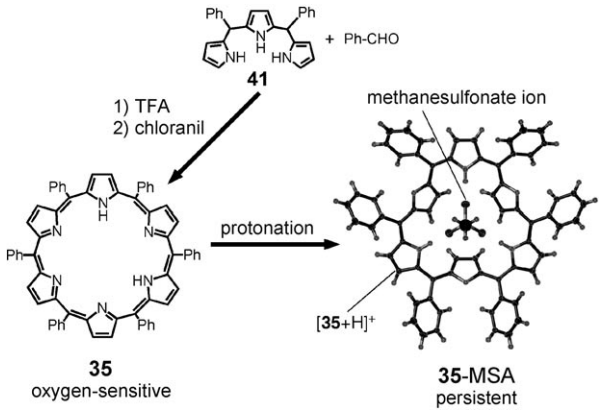
2.1. General Synthetic Methods

2.1.1. Direct Synthesis from Aldehydes and Pyrroles

In 2001, Osuka and co-workers reported the facile one-pot synthesis of a series of meso-pentafluorophenyl expanded porphyrins (Scheme 4, Figure 8).[37b] This synthesis entailed



Scheme 4. One-pot synthesis of meso-aryl expanded porphyrins by a modified Rothemund–Lindsey method, where *N* represents the number of pyrrole subunits.



Scheme 5. Synthesis of meso-phenyl hexaphyrin **35** and X-ray crystal structure of protonated form **35**-MSA.

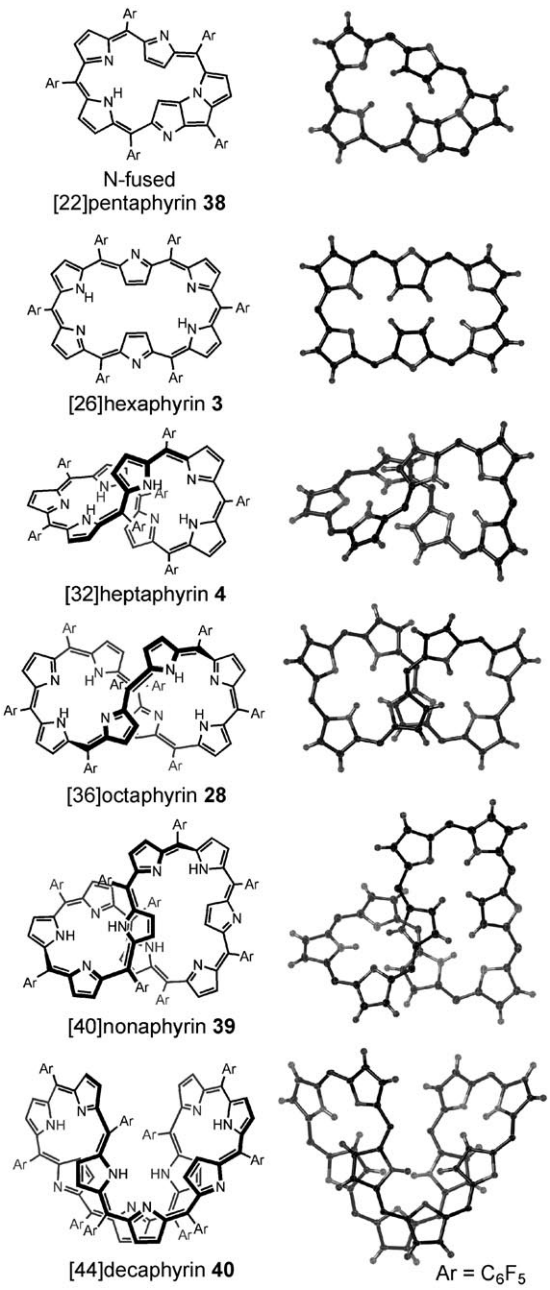
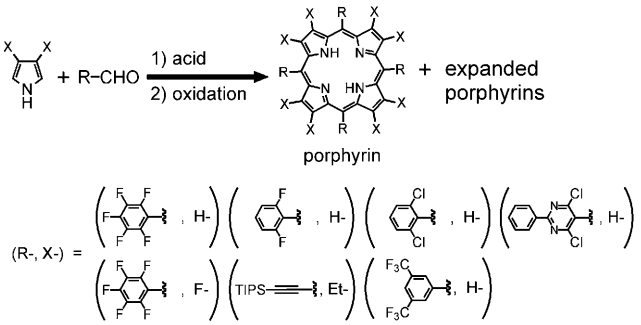


Figure 8. X-ray crystal structures of meso-C_6F_5 expanded porphyrins. Meso-C_6F_5 substituents are not shown for clarity.

the simple Rothemund–Lindsey protocol that involves the $BF_3{\cdot}OEt_2$-catalyzed condensation of pyrrole and 2,3,4,5,6-pentafluorobenzaldehyde at a concentration of 67 mM and subsequent oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The best result was obtained with pentafluorobenzaldehyde; this behavior may be mainly due to the stabilities of both intermediate expanded porphyrinogens toward acidolysis and expanded porphyrins toward oxidation. These expanded porphyrins have an advantage of simple ^{1}H NMR spectra because of the absence of signals of the meso-aryl substituents. After detailed studies, it was thought that only 2,6-disubstituted electron-deficient aryl aldehydes give expanded porphyrins and neither 2-substituted nor 2,6-

unsubstituted aryl aldehydes do not produce expanded porphyrins. As such, the formation of N-fused [22]pentaphyrin and [26]hexaphyrin was reported from the similar reaction with 4,6-dichloro-2-phenylpyrimidine-5-carbaldehyde (Scheme 6).[56a] Recently, however, Imahori and co-

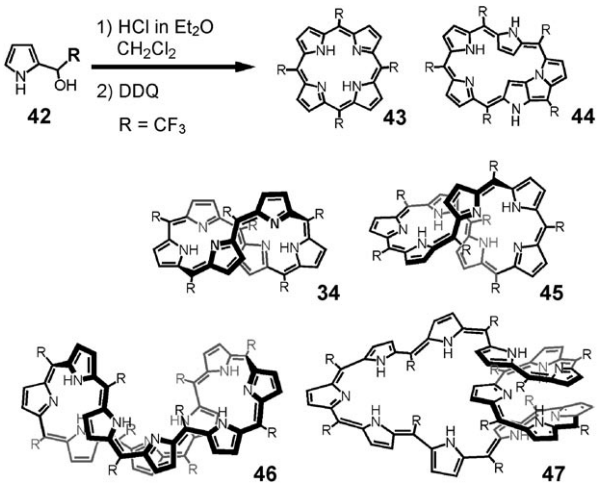


Scheme 6. Rothemund–Lindsey synthesis of expanded porphyrins. TIPS = triisopropylsilyl.

workers reported the formation of some expanded porphyrins from the trifluoroacetic acid (TFA)-catalyzed reaction of pyrrole and 3,5-bis(trifluoromethyl)benzaldehyde.[56b] Since only porphyrin was produced when $BF_3{\cdot}OEt_2$ was used as catalyst in this reaction, the trifluoroacetate ion was considered to serve as a template for the formation of expanded porphyrins (Scheme 6).

X-ray crystal structures of the meso-aryl expanded porphyrins are shown in Figure 8. Larger macrocycles tend to adopt distorted, nonplanar conformations. It is worth noting the peculiar instability of meso-phenyl hexaphyrin(1.1.1.1.1.1) **35**. In 1997, Dolphin and co-workers reported the synthesis of meso-phenyl hexaphyrin from meso-phenyl tripyrrane **41**, but full characterization was hampered by the instability toward air.[58] We recently reinvestigated the synthesis of this hexaphyrin and confirmed its instability in a neutral form in air. It was also found that this hexaphyrin could be stored under an inert gas and that its stability was remarkably improved by protonation, presumably as a consequence of the enhanced resistance to molecular oxygen. Interestingly, a triangular structure has been revealed for the protonated form **35**-MSA (Scheme 5).[35g]

Perfluorinated expanded porphyrins were prepared similarly from the condensation of 3,4-difluoropyrrole and pentafluorobenzaldehyde (Scheme 6).[56c] Meso-trifluoromethyl-substituted expanded porphyrins were also prepared by the acid-catalyzed condensation of 2-(2,2,2-trifluoro-1-hydroxyethyl)pyrrole **42** (Scheme 7).[54c] Decaphyrin **46** and dodecaphyrin **47** were shown to have highly distorted structures (Figure 9). As other examples, Krivokapic and Anderson reported the formation of meso-alkynyl-substituted pentaphyrin and hexaphyrin from the acid-catalyzed condensation of triisopropylsilylpropynal with 3,4-diethylpyrrole[56d] and a meso-5,15,25-trialkynyl-meso-10,20,30-trianthryl-substituted [28]hexaphyrin from the cross-condensation of triisopropylsilylpropynal and meso-anthryl dipyrromethane.[57c]



Scheme 7. Synthesis of meso-CF_3-substituted expanded porphyrins.

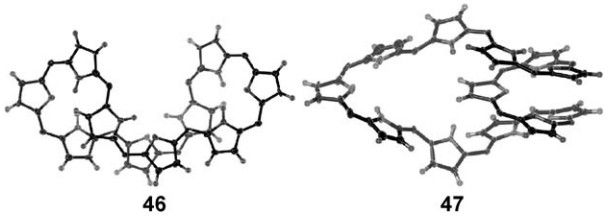
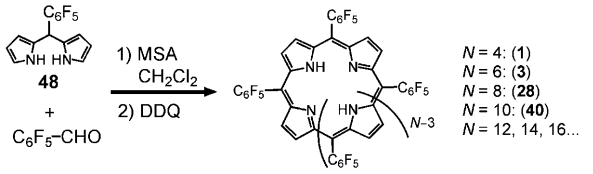


Figure 9. X-ray crystal structures of meso-CF_3 [46]decaphyrin **46** and [56]dodecaphyrin **47**. Meso-CF_3 substituents are not shown.

2.1.2. *Size-Selective Synthesis from Aldehydes and Dipyrromethanes*

The size-selective synthesis of expanded porphyrins can be made possible by employing a dipyrromethane or a tripyrrane as a building block. The acid-catalyzed condensation reaction of dipyrromethane **48** with pentafluorobenzaldehyde afforded expanded porphyrins with even numbers of pyrrole subunits (Scheme 8).[57a,f] This protocol has advantages of better yields, size-selective synthesis, easier separation, and applicability to the synthesis of expanded porphyrins that bear two different meso-aryl substituents.[57] The effective synthesis of meso-aryl-substituted dipyrromethanes has



c [mM]	T [°C]	N = 4 [%]	N = 6 [%]	N = 8 [%]	N = 10 [%]	N = 12 [%]	N = 14 [%]	N = 16 [%]	N = 18 [%]
33.3	20	9.8	15.9	7.6	2.8	0.1	0.6	trace	-
100	20	3.1	10.4	7.8	4.8	0.7	1.2	0.6	0.1
200	20	1.5	10.0	5.6	3.4	0.6	1.0	0.2	0.2
100	–10	0.6	4.1	6.3	3.2	0.9	0.6	0.4	0.1
100	0	1.1	8.6	10.2	5.5	1.1	1.5	1.2	0.8

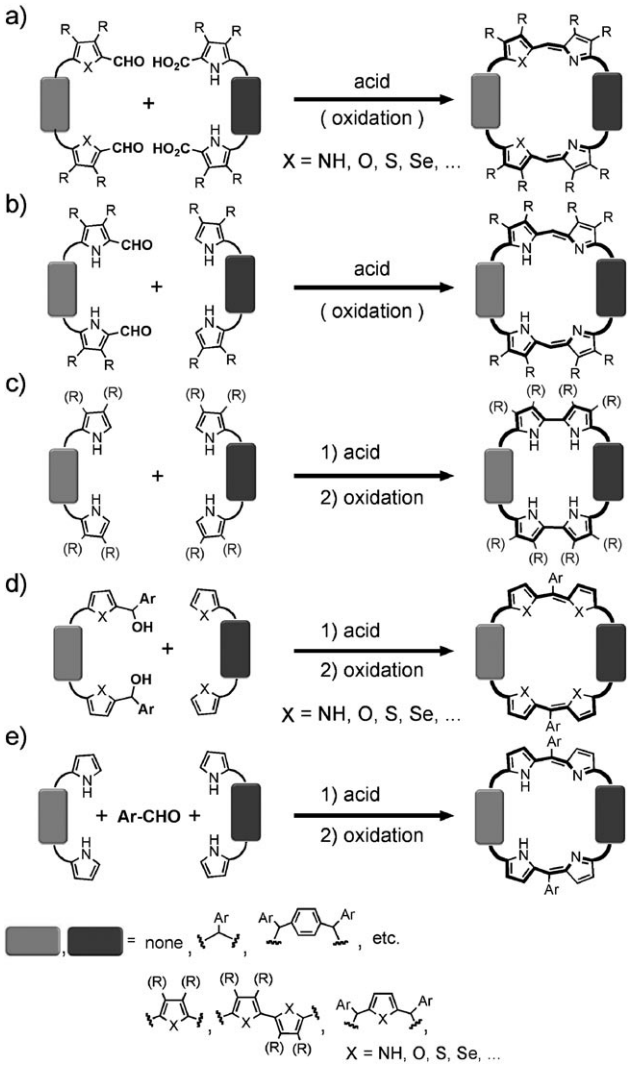
Scheme 8. Size-selective synthesis of meso-C_6F_5 expanded porphyrins.

thus been continuously pursued, and now a large-scale synthesis has been accomplished with a sufficiently high yield (ca. 90%).[59] Similar size-selective synthesis with tripyrrane was reported to produce nonaphyrin **39** in 15% yield.[57e]

The optimized reaction conditions in the size-selective synthesis using **48** were examined to produce larger expanded porphyrins (Scheme 8).[57f] Under these reaction conditions, it is possible to obtain hexaphyrin and octaphyrin on a gram scale in a one-pot reaction.

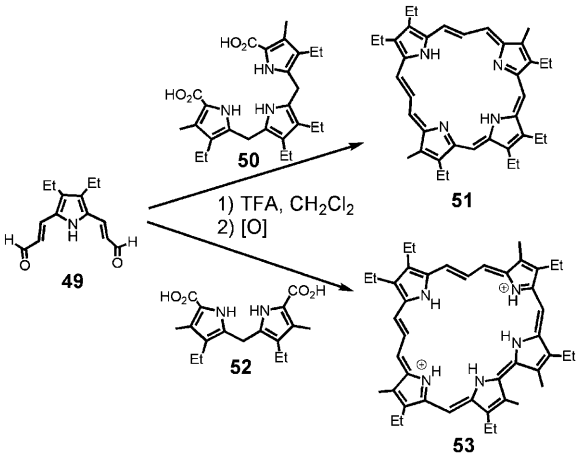
2.1.3. *Stepwise Synthesis*

Expanded porphyrins with β-alkyl substituents are usually obtained by acid-catalyzed condensation of appropriately α-substituted and α-unsubstituted oligopyrroles (MacDonald synthesis).[3–5] The representative reactions are listed in Scheme 9, and include combinations of following substrates: a) α-formyl and α-carboxyl-substituted oligopyrrolic precursors, b) α-formyl and α-unsubstituted oligopyrrolic precursors, c) both α-unsubstituted oligopyrrolic precursors to provide macrocycles that bear direct pyrrole–pyrrole linkages, d) α-(1-arylcarbinol)-substituted and α-unsubstituted oligopyrrolic precursors, and e) cross-condensation of two α-unsubstituted oligopyrrolic precursors and an aryl aldehyde. In these reactions, the substrates contain various structural motifs such as pyrrole(s), other five-membered heterocycle(s), benzene, azulene, and so on. β-Alkyl-substituted expanded porphyrins were mainly prepared by protocol (a), (b), or (c), while meso-aryl substituted macrocycles were synthesized by protocol (c), (d), or (e).[1–5] In these syntheses, the choice of the acid, oxidizing agent, and solvent is very important to achieve high yields of expanded porphyrins. Frequently employed acids are trifluoroacetic acid (TFA), *para*-toluenesulfonic acid (*p*-TSA), hydrogen chloride in alcohol, and BF_3OEt_2, while DDQ, *para*-chloranil, $FeCl_3$,[66] and $Na_2Cr_2O_7$[60] are used as an oxidizing agent.



Scheme 9. Stepwise approach for expanded porphyrins.

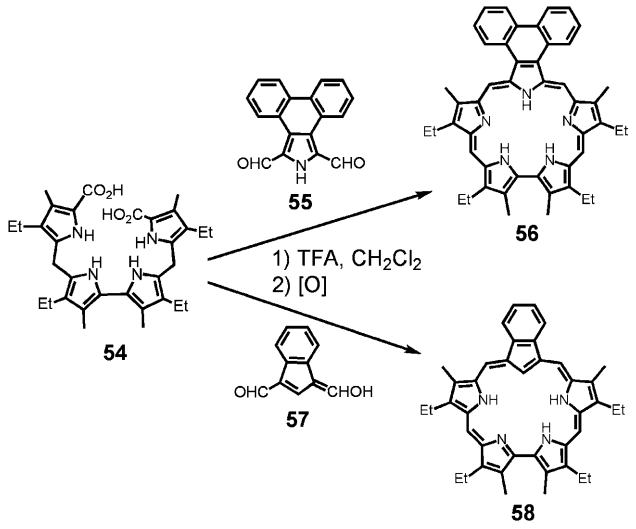
Lash and co-workers employed a "3+1" strategy for the synthesis of [22]porphyrin(3.3.1.1) **51**.[61a] Acid-treated tripyrrole **50** was condensed with pyrrole bisacrylaldehyde **49** to afford **51** as a green fraction in 32% yield. Under similar conditions, the acid-catalyzed reaction of **49** with dipyrromethane **52** in a 1:2 ratio followed by oxidative ring closure gave [26]pentaphyrin(3.3.1.0.1) **53** as a diprotonated form in 22% yield (Scheme 10).[61b]



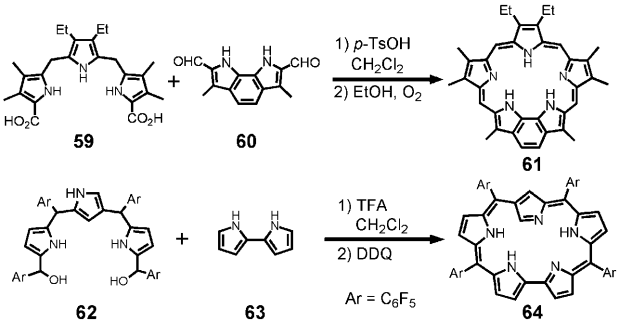
Scheme 10. Synthesis of vinylogous porphyrins.

Similarly, the "4+1" condensation of tetrapyrrole **54** with fused pyrrole dialdehyde **55** or 1,3-diformylindene **57** furnished the phenanthrene-fused sapphyrin **56** or benzocarbasapphyrin **58** in 33 and 38% yields, respectively (Scheme 11).[62] The benzosapphyrin **61** was also prepared by a stepwise route from **59** and **60** (Scheme 12).[63] The N-confused sapphyrin **64** was prepared by the oxidative ring-closure reaction of the pentapyrrole compound or the "3+2" condensation reaction of **62** and **63** (Scheme 12).[64]

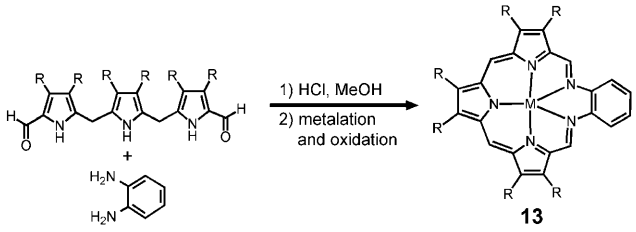
As a different but quite effective protocol, Sessler and coworkers employed a reversible imine-forming reaction to fulfill the final cyclization reaction of Schiff base macrocycles such as texaphyrin **13** (Scheme 13).[19] Since the imine moieties allow metal coordination, texaphyrin and other macrocycles that contain nonconjugated systems exhibit rich coordination chemistry.[6b,65]



Scheme 11. Synthesis of fused sapphyrins by a "4+1" approach.



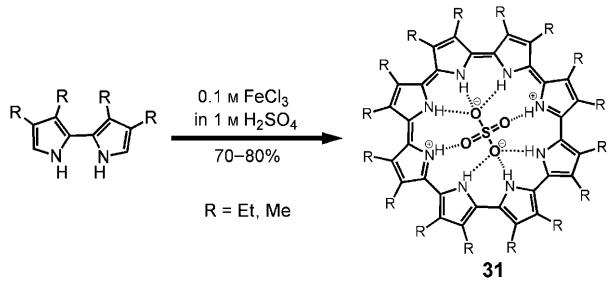
Scheme 12. Synthesis of novel sapphyrins by a "3+2" approach. Ts = 4-toluenesulfonyl.



Scheme 13. Synthesis of a Schiff base macrocycle by imine formation.

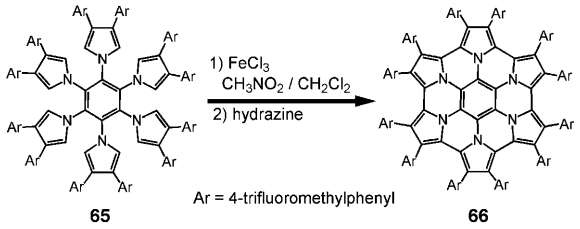
2.1.4. Template Synthesis

Encouraged by the template synthesis of superphthalocyanine with the uranyl cation (**9**),[15] many trials have been attempted for template synthesis of expanded porphyrins but mostly failed, except a remarkable example of cyclo[8]pyrrole (**31**; Scheme 14).[66] It was discovered that a $FeCl_3$-induced oxidative coupling of α,α′-bipyrrole gave cyclo[*n*]pyrroles in good yields under biphasic conditions. In this protocol, cyclo[8]pyrrole was selectively prepared in an excellent yield (up to 79%) in the presence of sulfate ions in the aqueous phase. Replacement of dihydrogen sulfate with hydrogen chloride resulted in loss of the size selectivity to give cyclo[6]pyrrole, cyclo[7]pyrrole, and cyclo[8]pyrrole in 15%, 5%, and 25% yield, respectively.



Scheme 14. Synthesis of cyclo[8]pyrrole **31** using the sulfate ion as a template.

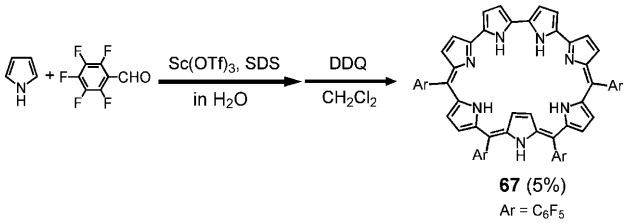
In an entirely different approach, Müllen and co-workers synthesized circularly fused hexapyrrolohexaazacoronenes (HPHAC) **66** by oxidation of the hexapyrrolyl benzene **65** (Scheme 15). Interestingly, HPHAC can be regarded as a fully benzene-fused hexaphyrin(0.0.0.0.0.0), and the dication appears to possess full aromaticity.[67]



Scheme 15. Synthesis of hexapyrrolohexaazacoronenes **66**.

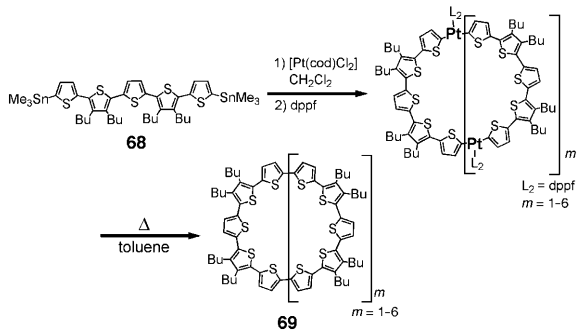
2.2. Other Synthetic Methods

In 2006, Bucher, Sessler, and co-workers reported that the electrochemical oxidative coupling of α,α′-bipyrrole is quite effective for the synthesis of cyclo[8]pyrrole **31**.[66e] Hiroto et al. have demonstrated that the acid-catalyzed condensation is possible in an aqueous micellar environment in spite of its dehydrative nature, giving unprecedented heptaphyrin **67** (Scheme 16).[68]



Scheme 16. Synthesis of heptaphyrin **67** in the aqueous phase.

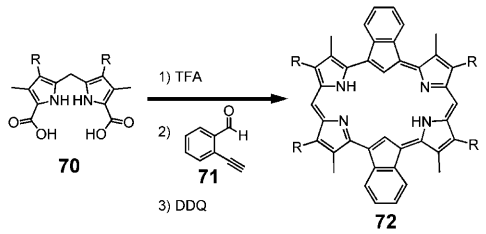
Although the Wittig reaction did not work efficiently in the final cyclization step in the synthesis of expanded porphyrins, the McMurry coupling was sometimes effective in cyclization to form expanded porphyrins and cyclic oligothiophenes.[69] Bäuerle and co-workers have explored a platinum(II)-mediated coupling of oligothiophenes **68** to



Scheme 17. Synthesis of cyclo[*n*]thiophenes **69** by platinum(II)-mediated coupling. cod = cyclooctadiene, dppf = diphenylphosphinoferrocene.

effectively provide a series of giant cyclo[*n*]thiophenes **69** (Scheme 17).[70]

Very recently, Peterson and Bampos have reported the one-pot synthesis of aromatic indene-incorporated hexaphyrin **72** as a result of an unexpected in situ annulation during a "2+2" aldehyde–dipyrromethane condensation of **70** and **71** (Scheme 18).[71] Macrocycle **72** can be formulated as a [22]dibenzodicarbahexaphyrin(1.0.0.1.0.0) species. The availability of this facile route to edge-aryl moieties in expanded porphyrins creates new possibilities in porphyrinoid design.



Scheme 18. Synthesis of indene-incorporated hexaphyrin **72**.

3. Metal Complexes

Expanded porphyrins can form a variety of metal complexes, and can often accommodate more than two metal ions to produce multimetal complexes. Different metalation conditions are required, depending upon the ligand structure and metal ion. Importantly, metal coordination requires a particular coordination structure around the metal ion, thus resulting in significant structural changes to the expanded porphyrin. In metalated expanded porphyrins,[4d,e] metal ions are bound to 1) pyrrolic nitrogen atoms (or Schiff base type imine groups), 2) pyrrolic β-carbon atoms through C–H bond activation, 3) counteranions, 4) coordinative solvents, or 5) intramolecular oxygen atoms inserted during metal complex formation. Cases (3)–(5) are represented by "L" in this section. Weaker metal–π interaction and metal–C–H bond agostic interactions are also observed.[72] At the present stage, the metalation behavior of expanded porphyrins is rather difficult to predict, but are synthetically useful for the production of unprecedented metal complexes with novel structures and electronic properties (see also Section 4) and even for triggering irreversible chemical transformations. The coordination substructures of reported metal complexes (Figure 10) include 1) a porphyrinlike tetrapyrrotrimethene, 2) a tetrapyrrodimethene, 3) a tripyrrodimethene and one or two extra ligand(s), 4) a tripyrrodimethene with an additional ligand in a square-planar geometry, 5) an NCP-type tetrapyrrolic NNNC ligand, 6) an NNCC ligand with two metal–carbon bonds, 7) a dipyrromethene with two extra ligands, and 8) a dipyrromethene with two carbonyl ligands in a square-planar geometry.

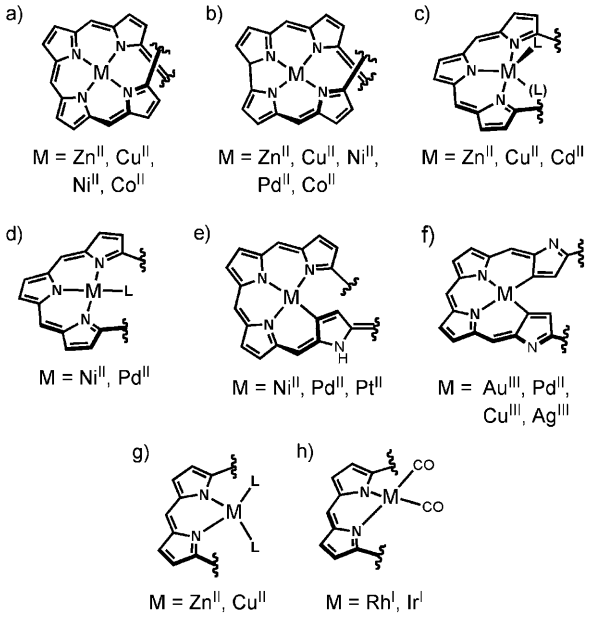


Figure 10. Representative coordination modes of expanded porphyrin metal complexes.

3.1. Group 12 Metals (Zn, Cd, and Hg)

Of the Group 12 metals, Zn^{II} ions have been most studied in metalation reactions of expanded porphyrins. In the cases of (a) and (b) in Figure 10, the macrocycle adopts a twisted conformation as seen for figure-eight octaphyrins (Figure 11a, **73**),[73a,b] while coordination modes of type (c) and (g) are observed for "gable"-shaped or planar hexaphyrins (Figure 11b, **74**).[73c,d] No examples of expanded porphyrins that bear a C–Zn bond (i.e., an organometallic species) have been reported to date.[74] Cd^{II} and Hg^{II} complexes have only been reported for meso-aryl hexaphyrin(1.1.1.1.1.1).[73c]

3.2. Group 11 Metals (Cu, Ag, and Au)

Many attractive metal complexes have been prepared with Group 11 metal ions. Interesting examples are multi-Cu^{II} hexaphyrin complexes that exhibit versatile magnetic interactions,[75] a T-shaped three-coordinate Cu^{II} heptaphyrin complex,[75d] a bis-Ag^{I} complex that is formed by allosteric metalation,[76a] and a hexaphyrin Au^{III} complex featuring C–Au bonds.[51]

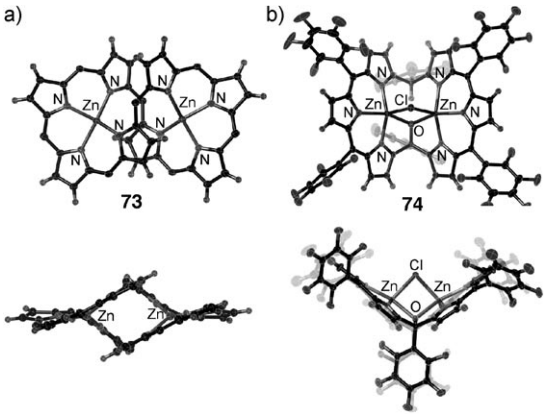


Figure 11. a) Figure-eight octaphyrin Zn^{II} complex **73** (meso-C_6F_5 substituents not shown) and b) gable hexaphyrin Zn^{II} complex **74**.

3.2.1. *Normal Coordination Modes*

Of the Group 11 metals, Cu^{II} complexes are the most studied. For cases of (a), (b), (c), and (g) in Figure 10, the nitrogen atom arrangements are essentially the same as those of Zn^{II} complexes.[75] The Au^{III} ion is unique, and allows the formation of mono- and bis-Au^{III} metal complexes **75** and **29**, which are both approximately planar (Figure 12).[51] The

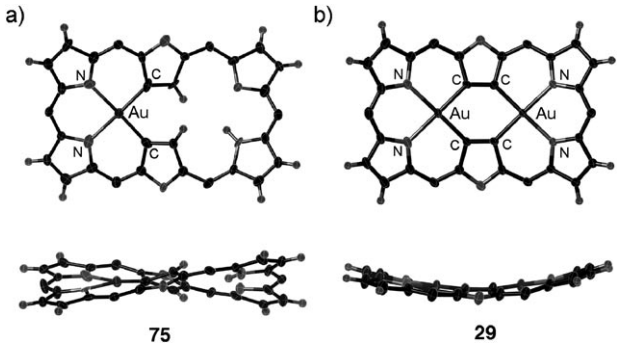


Figure 12. a) [26]Hexaphyrin mono-Au^{III} complex **75** and b) bis-Au^{III} complex **29**. Meso-aryl substituents are not shown.

rather robust nature of these complexes allowed them to be used for the evaluation of aromaticity versus antiaromaticity effect (see Section 7.3.). As a rare case, a Cu^{III} or Ag^{III} ion was accommodated in the remaining NNCC pocket of the mono-Au^{III} hexaphyrin **75** (Figure 10 f) to produce Au^{III}–Cu^{III} and Au^{III}–Ag^{III} hybrid metal complexes.[80b]

3.2.2. *Magnetic Interactions*

Since the Cu^{II} ion has a d^9 electronic configuration, Cu^{II} complexes have open-shell electronic systems. Magnetic interactions between these spins have been studied for several bis-Cu^{II} or tris-Cu^{II} complexes, mainly by ESR and SQUID measurements. A list of reported bis-Cu^{II} complexes **77**–**81** and the mixed-valence complex **82** and *J* values that represent the extent of the magnetic interaction are given in

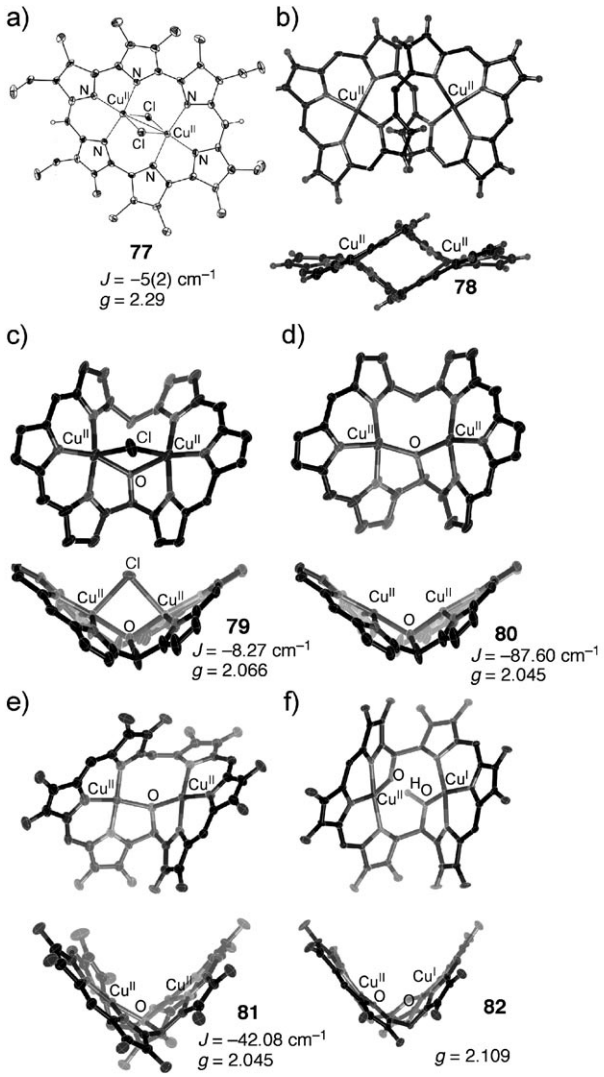


Figure 13. Bis-Cu^{II} complexes of expanded porphyrins with exchange coupling constants. Meso-aryl substituents are not shown in (b)–(f).

(Figure 13).[75] In all these complexes, antiferromagnetic coupling between two Cu^{II} ions is commonly observed with *J* values that depend on the bridging ligand and macrocyclic conformation.

In 2007, a tris-Cu^{II} complex of calix[3]dipyrrin **83** was reported as a spin-frustrating system (Figure 14), where the

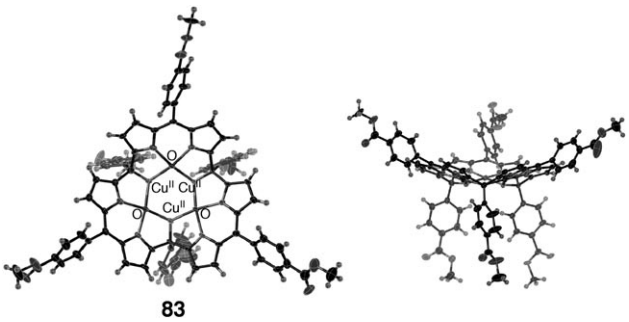


Figure 14. Calix[3]dipyrrin tris-Cu^{II} complex **83**. Left: View of the Cu_3 plane; right: side view.

analysis of variable-temperature magnetic susceptibility gave a J value of $-44.1\ cm^{-1}$ for the intramolecular interaction and a θ value of -0.99 K ($\theta k_B = 0.69\ cm^{-1}$) for the intermolecular interaction in a triangular model.[75e]

3.2.3. Mixed-Valence Cu^{II}–Cu^{I} Complexes

After showing that a Schiff base expanded porphyrin can serve as an effective ligand for Ni^{II}, Zn^{II}, and Cu^{II} ions, Sessler et al. demonstrated that the bis-Cu^{I} complex **84** could be prepared by the reaction with the mesitylene (Mes) Cu^{I} reagent Cu_5Mes_5 and oxidized with air to give the bis-Cu^{II} complex **85**, with a concurrent structural change in the coordination mode (Figure 15).[75f]

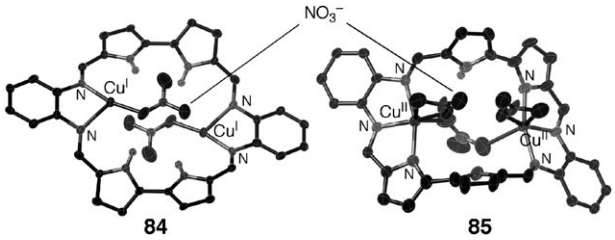


Figure 15. Schiff base expanded porphyrin bis-Cu^{I} complex **84** and bis-Cu^{II} complex **85**. β-alkyl substituents are not shown.

The Cu^{II}–Cu^{I} mixed-valence complex **86** was also prepared, and comprises an indene-bridged hexaphyrin platform where both Cu^{I} and Cu^{II} ions have a T-shaped three-coordination with a closely located *trans*-vinylene moiety as a forth coordinating site (Figure 16).[43b]

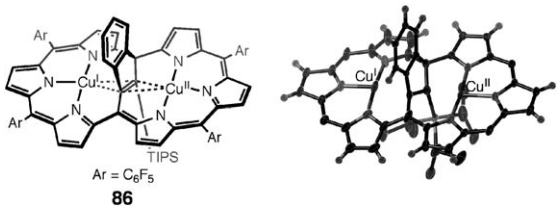
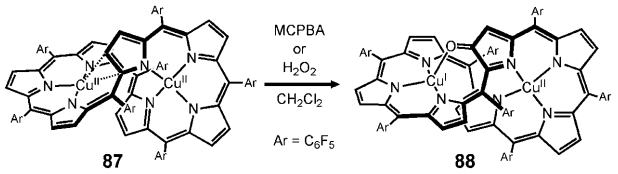


Figure 16. Molecular structure and X-ray crystal structure of indene-bridged hexaphyrin Cu^{I}–Cu^{II} hybrid complex **86**.

3.2.4. Rare Coordination Modes

As shown in Scheme 19, the heptaphyrin bis-Cu^{II} complex **87** contains two Cu^{II} ions at a hemiporphyrin-like tetrapyrrolic site and a T-shaped tripyrrodimethene site.[75d,77a,b] The copper(II)–arene interaction was suggested to supplement the coordinatively unsaturated Cu^{II} complex in the T-shaped site.[77c,d] Interestingly, the reaction with peroxides resulted in selective oxygenation at the β position that interacts with the Cu^{II} ion and gave **88**. The resulting carbonyl group occupies the fourth coordination site of the Cu^{I} ion (Scheme 19). This behavior is similar to those of three-coordinate copper proteins.[77e]



Scheme 19. Peripheral oxygenation of heptaphyrin bis-Cu^{II} complex **87**. MCPBA = *m*-chloroperoxybenzoic acid.

A T-shaped three-coordinate Cu^{II} complex **89**, which exists without any supplementary interactions, has been prepared by using a more rigid quadruply N-fused heptaphyrin ligand (Figure 17).[75d] Since the T-shaped Cu^{II} ion is highly shielded by the fused pentacyclic segments, it is remarkable that this complex is sufficiently stable to be fully characterized. The complex **89** shows high reduction potentials, which are consistent with studies of three-coordinate copper proteins.[77e]

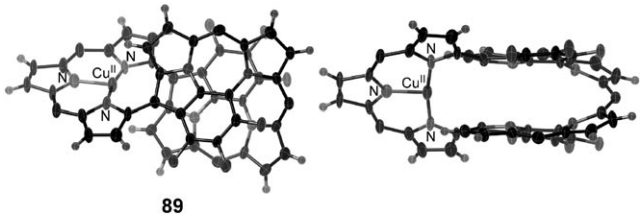


Figure 17. T-shaped three-coordinate Cu^{II} complex of quadruply N-fused heptaphyrin **89**. Nonfused meso-C_6F_5 substituents are not shown.

3.2.5. Positive Allosteric Binding

Sessler et al. have reported positive allosteric Ag^{I} insertion into a Schiff base expanded porphyrin. The bis-Ag^{I} complex **90** was directly obtained from the free-base ligand without producing the mono-Ag^{I} complex.[76a] The X-ray crystal structure of the bis-Ag^{I} complex suggests that first Ag^{I} ion complexation and concurrent hydrogen-bonding interactions induces a conformation change of the ligand that is favorable for the second Ag^{I} ion coordination (Figure 18).

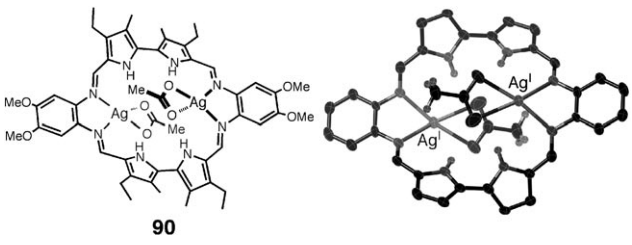


Figure 18. Molecular structure and X-ray crystal structure of Schiff base expanded porphyrin bis-Ag^{I} complex **90**. Alkyl and methoxy substituents are not shown.

3.3. Group 10 Metals (Ni, Pd, and Pt)

The coordination modes of Pd^{II} are diverse, and include type (b),[22c,73b] (d),[54e,42c] (e),[47a] and (f)[47a,57e] in Figure 10 (Section 3). In all cases, the Pd^{II} ions prefers a square-planar coordination geometry.

The $Cu^{II}Pd^{II}Pd^{II}$ complex of nonaphyrin (**91**) was reported as the first trinuclear metalated expanded porphyrins.[57d] The crystal structure reveals that one Pd^{II} ion adopts coordination type (d), and the other Pd^{II} ion adopts a T-shaped coordination with a closely located pyrrolic β-C–H bond (Figure 19). This β proton can be distinguished by its signal in the ^1H NMR spectrum and the observed particular geometrical proximity has been interpreted in terms of a C–H–Pd^{II} agostic interaction.[72]

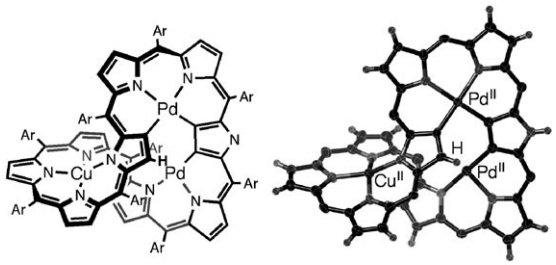
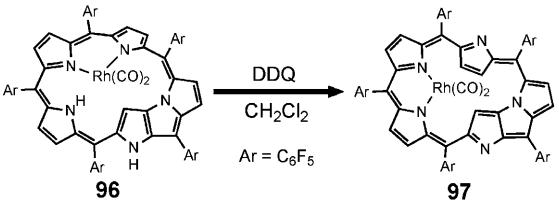


Figure 19. Nonaphyrin Cu^{II}–Pd^{II}–Pd^{II} hybrid complex **91**. Meso-aryl substituents are not shown.

Other important examples are Möbius twisted mono-Ni^{II}, mono-Pd^{II}, mono-Pt^{II} hexaphyrins **92**–**94**, mono-Pd^{II} heptaphyrin **95** and bis-Pd^{II} octaphyrin **25**, which are discussed in detail in Section 7 (Figures 40 and 41).[47a]

3.4. Group 9 Metals (Co, Rh, and Ir)

Rh^I and Ir^I complexes of expanded porphyrins were formed upon addition of $[\{RhCl(CO)_2\}_2]$ and $[\{IrCl(CO)_3\}_n]$, respectively, so that a dipyrromethene unit coordinates with rhodium(I) dicarbonyl or iridium(I) dicarbonyl (Figure 10h).[80] Two interesting examples have been reported: one is an oxidation-induced rhodium rearrangement from **96** to **97** on a N-fused pentaphyrin platform (Scheme 20),[80a] and the other is a conversion of $Au^{III}Rh^I(CO)_2$ hexaphyrin complex **98** into the $Au^{III}Rh^{III}$ complex **99**; during the conversion, the coordination features around the Rh center



Scheme 20. Oxidation-induced Rh^I rearrangement in N-fused pentaphyrin **96**.

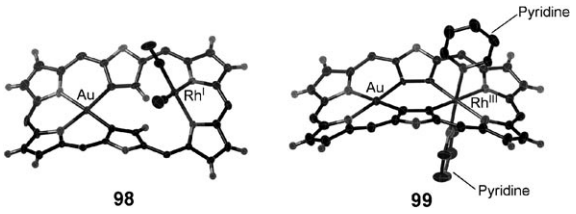


Figure 20. Hexaphyrin Au^{III}–$Rh^I(CO)_2$ hybrid complex **98** and Au^{III}–Rh^{III} hybrid complex **99**. Meso-aryl substituents are not shown.

are drastically changed from a η^2-Rh^I to a square-planar Rh^{III} ion (Figure 20).[80b]

3.5. Other Metals (Ln, Y, In, Mn, Fe, U, Np, Pu, and V)

The rich coordination chemistry of texaphyrins has been explored by Sessler et al., and includes lanthanide complexes **100** such as Gd^{III} and Lu^{III}, and other metal complexes such as Y^{III}, In^{III}, Cd^{II}, Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, and Fe^{III} (Figure 21a).[19e] Actinide complexes of hexaphyrin(1.0.1.0.0.0) such as UO_2^{2+}, NpO_2^+, and PuO_2^+ complexes **101** (Figure 21b) have also been reported.[81a]

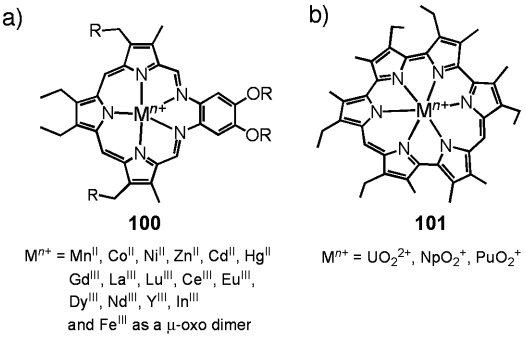


Figure 21. a) Texaphyrin metal complexes **100** and b) hexaphyrin(1.0.1.0.0.0) metal complexes **101**.

Schiff base expanded porphyrin VO_2^+ complex **102** was prepared; the V center sits in a highly distorted trigonal bipyramidal environment and, more interestingly, the Schiff base moiety undergoes an intriguing imine–enamine tautomerism so as to maximize interactions with the VO_2 center by a bimodal binding including coordinative interactions and noncovalent hydrogen bonding (Figure 22).[81b]

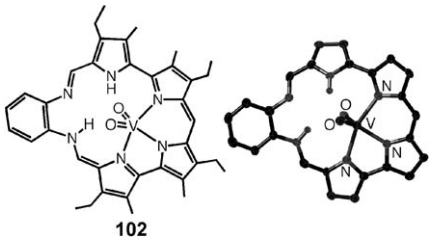


Figure 22. Molecular structure and X-ray crystal structure of Schiff base expanded porphyrin VO_2 complex **102**.

3.6. Main-Group Elements (B, P, and Si)

In 1993, Sessler and co-workers reported the synthesis of complexes **103** and **22** by insertion of B^{III} into hexaphyrin(1.0.0.1.0.0) and octaphyrin(1.0.0.0.1.0.0.0), respectively, where a dipyrromethene unit binds a BF_2 cation as in BODIPY dyes (Figure 23a).[42a] Later, Brothers and co-

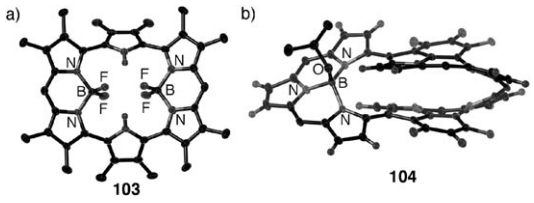
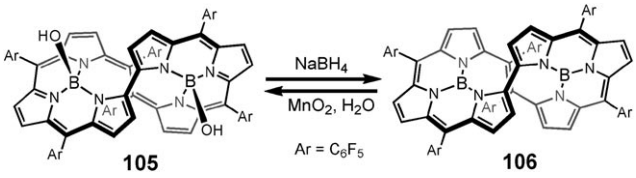


Figure 23. X-ray crystal structures of a) amethyrin B^{III} complex **103** and b) quadruply N-fused heptaphyrin B^{III} complex **104**. Nonfused meso-C_6F_5 substituents are not shown.

workers reported a variety of boron-coordinated porphyrinoids.[2e] A different coordination mode of the B^{III} ion was found for a heptaphyrin(1.1.1.1.1.1.1). Complex **104** shows a subporphyrin-like trigonal coordination geometry within a tripyrrodimethene pocket with an axial hydroxy or alkoxy ligand (Figure 23b).[42b] The axial ligand is exchangeable, in a similar manner to subporphyrins.[4f,82] As a unique case, a reversible interconversion was found between tetragonal complex **105** and trigonal complex **106** that can be triggered by the two-electron redox reaction of a hexaphyrin(2.1.1.0.1.1) between 28π versus 30π electronic systems (Scheme 21, see also Section 7.3.2.).[42c] For B^{III}-insertion-triggered transformations, see Section 4.2.6. and 4.2.7.[83]



Scheme 21. Redox-triggered interconversion between hexaphyrin(2.1.1.0.1.1) B^{III} complexes **105** and **106**.

Recently, octaphyrin mono-P^V complex and bis-P^V complex **107** were synthesized by using PCl_3 or $POCl_3$ as a phosphorylation reagent. Phosphorylation takes place initially to form a trigonal bipyramidal P^V complex at the NCC site together with axial NN ligands and secondly at the remaining NNC site to form a phosphamide group (Figure 24).[45c] Importantly, these two coordinated P^V moieties stabilize the highly reduced 40π-conjugation system for octaphyrin(1.1.1.1.1.1.1.1) that corresponds to so-called "expanded isophlorin".[45]

Silicon complexes of expanded porphyrins have not been reported to date, although Vaid and Latos-Grażyński, and their respective co-workers have confirmed that complex-

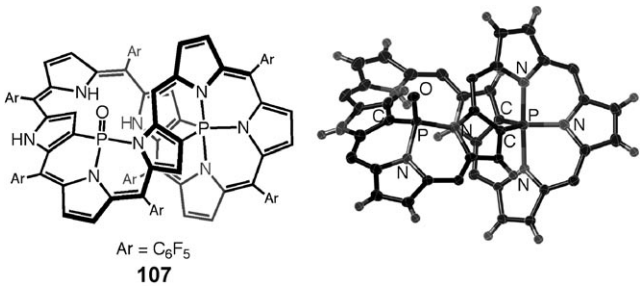


Figure 24. Molecular structure and X-ray crystal structure of octaphyrin bis-P^V complex **107**.

ation of porphyrins and N-confused porphyrins with Si^{IV} is successful for stabilizing isophlorin-like electronic states.[2a,42d]

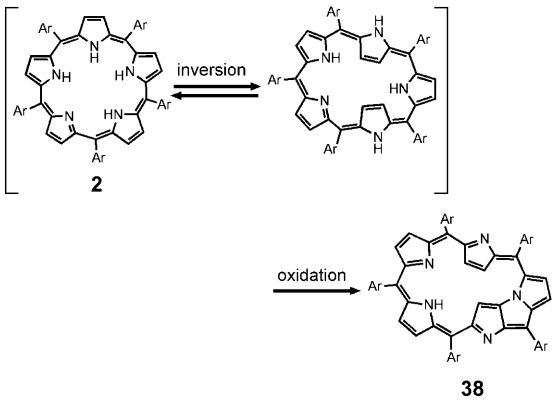
4. Chemical Reactivities

4.1. Spontaneous Reactions

Some expanded porphyrins undergo irreversible chemical reactions during synthesis and subsequent separation. These reactions are troublesome for isolation of expanded porphyrins but sometimes beneficial for creation of novel structures.

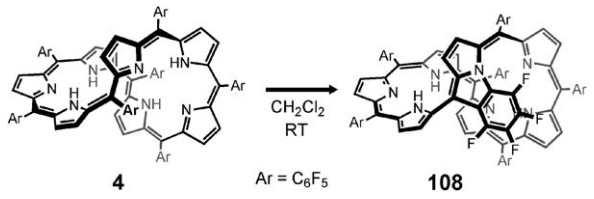
4.1.1. N-Fusion Reactions

Meso-aryl-substituted pentaphyrins **2** are always obtained as a N-fused form **38** probably because of the intrinsic strain of a nonfused structure of **2** (Scheme 22). N-Fused [22]pentaphyrins **38** have an inverted pyrrole that is fused at the β position with the neighboring pyrrolic nitrogen atom.[37a] N-fused [22]- and [24]pentaphyrins have been obtained and characterized.



Scheme 22. N-Fusion reaction of meso-aryl pentaphyrin(1.1.1.1.1) **2**.

On the other hand, meso-(*ortho*-halogenated)-aryl-substituted expanded porphyrins sometimes undergo another N-fusion reaction that proceeds by aromatic nucleophilic substitution of the *ortho*-halogen atom by the neighboring pyrrole ring. For example, meso-pentafluorophenyl [32]heptaphyrin **4** undergoes a facile N-fusion reaction at room

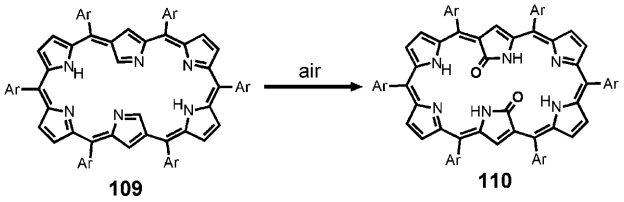


Scheme 23. N-Fusion reaction of meso-C_6F_5 heptaphyrin(1.1.1.1.1.1.1) **4**.

temperature to give **108** (Scheme 23). The N-fusion reaction of **4** can be repeated to provide quadruply N-fused heptaphyrin **144** (Figure 30).[42b]

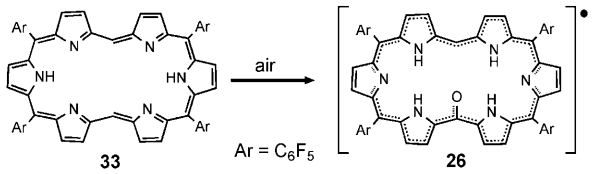
4.1.2. *Oxygen Insertion*

Furuta and co-workers have reported that N-confused expanded porphyrins undergo oxygenation reactions at the α-positions of the inverted pyrrole rings, as shown for the conversion from **109** to **110** (Scheme 24).[35d] Both the carbonyl and NH groups of the resulting amide moieties serve as a metal-coordinating ligand or a hydrogen-bonding motif.[35g] A similar oxygenation reaction was reported by Latos-Grażyński and co-workers for N-confused benzihexaphyrin.[35b]



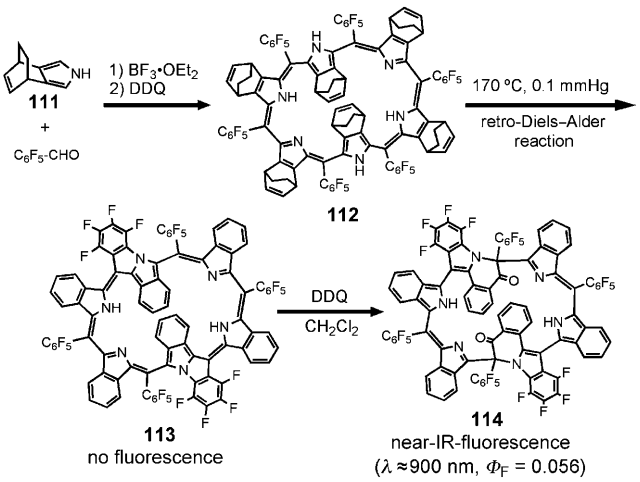
Scheme 24. Facile oxygenation of N-confused hexaphyrin **109**.

Meso-free hexaphyrin **33**, which was synthesized by the acid-catalyzed condensation of tripyrrane and trimethyl orthoformate, showed a high oxygenation reactivity and underwent oxygenation smoothly under air to give meso-oxygenated hexaphyrin **26** (Scheme 25). This compound turned out to be an extremely stable organic radical with spin density delocalized over the macrocycle (see Section 8).[48a]



Scheme 25. Facile oxygenation of meso-free hexaphyrin **33**.

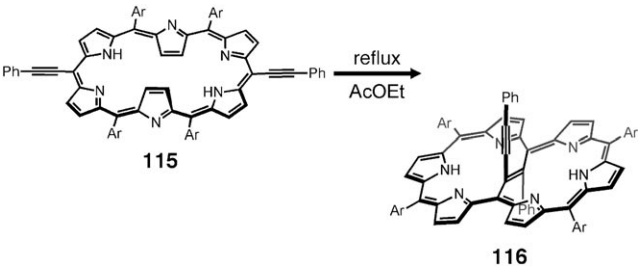
Another interesting example is doubly N-fused [28]hexaphyrin **113**. Acid-catalyzed condensation of 4,7-dihydro-4,7-ethano-2H-isoindole **111** and pentafluorobenzaldehyde produced hexaphyrin **112**, which, upon heating under low pressure, underwent the retro-Diels–Alder reaction to provide **113**. Treatment of hexaphyrin **113** with DDQ in CH_2Cl_2 slowly gave the rearranged and oxygenated product **114** that exhibits NIR fluorescence (Scheme 26).[54f]



Scheme 26. Doubly N-fused hexaphyrin **113** and its rearranged product **114**.

4.1.3. *Transannular Bridging Reactions*

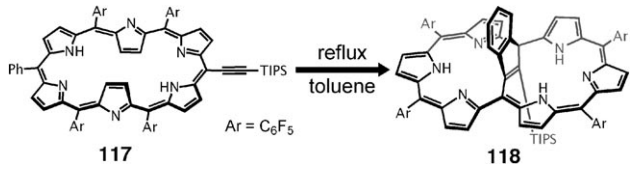
As noted in Section 1.5.2., some meso-substituted [26]hexaphyrins(1.1.1.1.1.1) exist in a conformational equilibrium between rectangular and dumbbell structures. Simple heating of 5,20-diethynyl-substituted [26]hexaphyrins **115** produced vinylene-bridged hexaphyrins **116** in good yields (Scheme 27). The predominant conformation of hexaphyrin



Scheme 27. Transannular reaction of 5,20-diethynyl-substituted hexaphyrin **115**.

115 adopts a rectangular structure with ethynyl substituents on the two opposite shorter sides. Thus, the formation of **116** was suggested to proceed via an unfavorable dumbbell conformation that was accessible only at high temperatures. The resultant cross-vinylene-bridged framework is attractive in view of its structural analogy to [4*n*]annuleno[4*n*]annulenes.[43b]

A similar transannular cross-bridging reaction has also been shown to occur for **117**, which bears an ethynyl group and a phenyl group on the shorter sides. Heating of **117** caused the conversion to indene-bridged hexaphyrins **118** (Scheme 28).[43c]



Scheme 28. Transannular reaction of 5-ethynyl-20-phenyl-substituted hexaphyrin **117**.

4.2. Metalation-Triggered Transformations

Metalation reactions of expanded porphyrins trigger various transformations, some of which are quite unexpected. In this section, we will describe meso-oxygenation reactions, hydrolytic pyrrole cleavage, pyrrolic confusion, oxidative cleavage to form linear oligopyrromethenes, transannular reactions, ring-splitting reactions, and meso-aryl group transposition. Metalation often enforces a more tightly strained figure-eight conformation, which brings two crossing oligopyrrolic π systems spatially closer and hence increases the electronic interaction between such sites in order to trigger transannular reactions.

4.2.1. Meso-Oxygenation Reactions

Meso-oxygenation has been found to be a rather common process in the metalation of [26]hexaphyrin(1.1.1.1.1.1) **3**. Gable-shaped mono-meso-oxygenated complexes **79**, **74**, and **119** are formed upon metalation with Cu^{II}, Zn^{II}, and Cd^{II} ions, respectively.[73c,75b] Experiments using $H_2{}^{18}O$ showed that water is the source of the oxygen atoms. While metalation of 5,20-meso-free meso-tetraaryl hexaphyrin(1.1.1.1.1.1) **33** with Cu^{II} or Zn^{II} ions resulted in planar complexes **120** (Figure 25),[73d] metalation with $[Ni(acac)_2]$ (acac = acetylacetonate) under similar conditions gave the double-meso-oxygenated complex **121**.[48] In all these complexes, the incorporated oxygen atoms serve to bind metal ions. Macrocyclic π conjugation is disrupted in **79**, **74** and **119**, but is preserved in **120** and **121**.

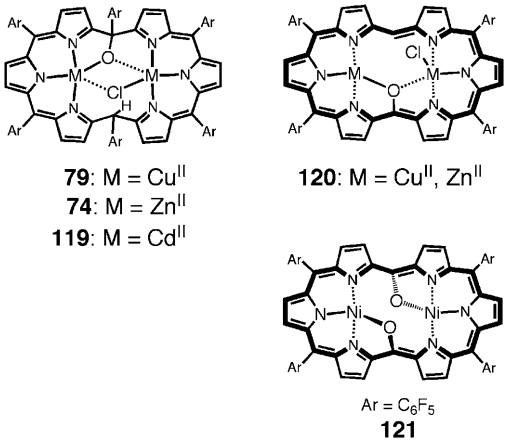
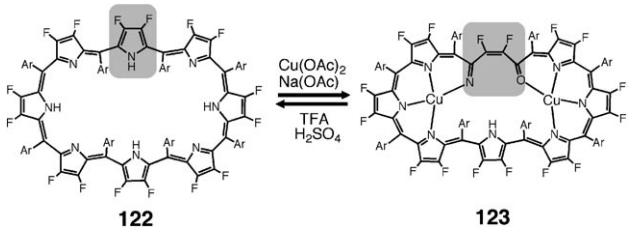


Figure 25. Meso-oxygenated hexaphyrin bis-metal complexes.

4.2.2. Pyrrole Cleavage and Recyclization

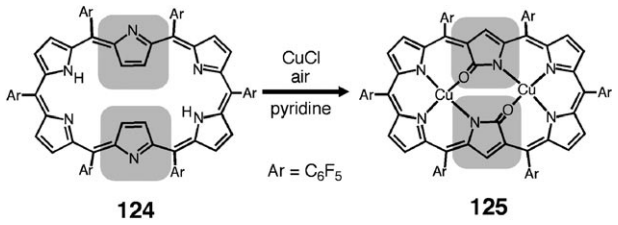
Hydrolytic cleavage of one of the pyrrole rings of perfluorinated octaphyrin **122** occurred upon metalation with Cu^{II} ions (Scheme 29). The resulting bis-Cu^{II} complex **123** adopts a saddle-shaped structure, in which the cleaved imine and carbonyl moieties serve as a coordination group for Cu^{II} ions. Interestingly, treatment of **123** with TFA and sulfuric acid effected the quantitative regeneration of **122** with recyclization of the keto–imine unit to a pyrrole ring.[76b]



Scheme 29. Hydrolytic pyrrole cleavage of perfluorinated octaphyrin **122**. Ar = C_6F_5.

4.2.3. Pyrrolic Confusion

A pyrrolic confusion reaction was unexpectedly effected upon metalation of **124** with CuCl under aerobic conditions. After treatment of **124** with CuCl in the presence of pyridine for 3 h at room temperature, the doubly N-confused [26]hexaphyrin bis-Cu^{II} complex **125** was isolated in 24% yield (Scheme 30).[54d] This macrocycle, which has been shown to be

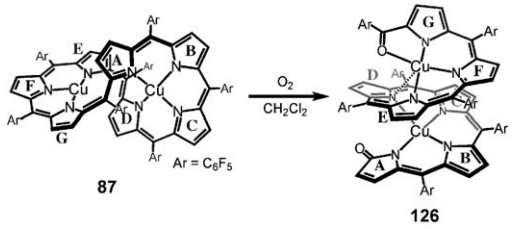


Scheme 30. Pyrrolic confusion of **124** triggered by metalation with Cu^{I} ions.

an effective ligand for various metal ions,[54d,g] was previously prepared by a multistep synthesis in a low overall yield.[35d] Thus, the reaction to form **125** is synthetically useful. The mechanism still remains unclear but similar pyrrole confusion during the synthesis of di-*para*-benzihexaphyrin **153** from *para*-phenylene linked tripyrrane analogues with bulky meso-substituents was recently reported by Latos-Grażyński and co-workers.[35b]

4.2.4. Oxidative Cleavage

The photooxidative cleavage of porphyrinoids has been studied in relation to the metabolism of chlorophylls to generate oligopyrroles that play an important role as natural products such as bile pigments. The oxidative cleavage of



Scheme 31. Oxidative cleavage of heptaphyrin bis-Cu^{II} complex **87**.

heptaphyrin **4** and octaphyrin **28** were recently reported.[49] The heptaphyrin bis-Cu^{II} complex **87** was gradually cleaved under aerobic conditions to produce the helical heptapyrrolic Cu^{II} complex **126**. Interestingly, the cleavage occurred selectively at the C(meso)–C(α) bond next to pyrrole A that interacts with the Cu^{II} ion, which has a T-shaped geometry (Scheme 31).[75d] The oxygen source has been confirmed to be molecular oxygen, as in the case of porphyrin cleavage. The obtained complex **126** is quite rare in that it exhibits an intense absorption band in the NIR region ($\varepsilon = 11\,000\,M^{-1}cm^{-1}$ at $\lambda = 1262$ nm) and highly delocalized spin density, thus reflecting the effective π conjugation along the helical backbone (Figure 26).

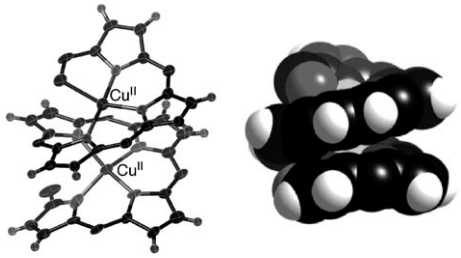


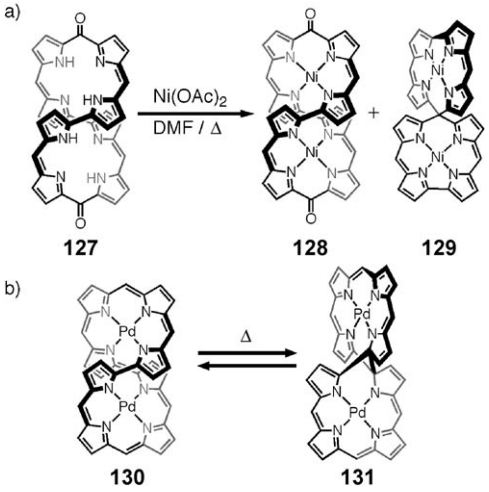
Figure 26. X-ray crystal structure of **126**. Meso-aryl substituents are not shown.

4.2.5. *Transannular Reactions*

In 2003, Vogel et al. reported metalation-triggered skeletal rearrangements of figure-eight macrocycles. Metalation of 5,24-dioxo-octaphyrin(1.1.1.0.1.1.1.0) **127** with $Ni(OAc)_2$ gave **128** together with the spirodicorrole bis-Ni^{II} complex **129**, which was formed by the extrusion of a carbon dioxide molecule (Scheme 32a).[22d] The interesting equilibrium between bis-Pd^{II} complex **130** and bis-spirodiporphyrin skeleton **131** through C(α)–C(α) bond formation was also reported (Scheme 32b).[22d] These transformations are apparently initiated by transannular electronic interactions at the hinge positions.

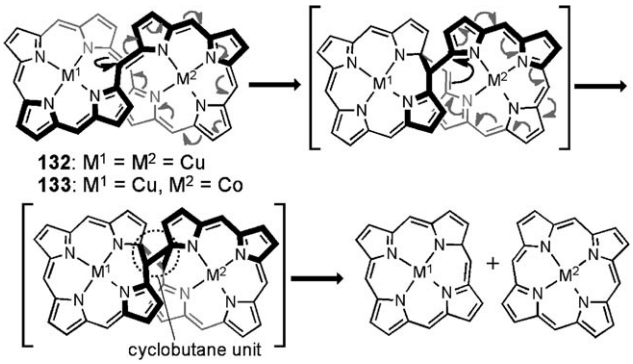
4.2.6. *Splitting Reactions*

[36]Octaphyrin **28** is a non-aromatic macrocycle in terms of its 36π electronic network, a figure-eight conformation, and distinct bond-length alteration. Metalation of this octaphyrin with Cu^{II} ions proceeded in a stepwise manner.



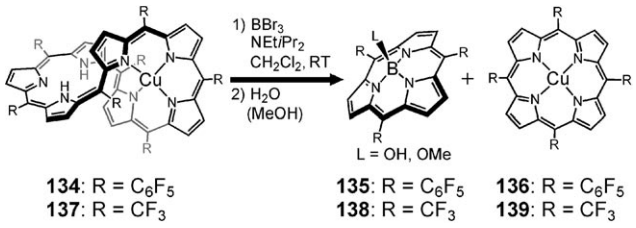
Scheme 32. a) Metalation of **127** with Ni^{II} ions and b) equilibrium between **130** and **131**, where β-alkyl substituents are not shown.

Surprisingly, upon heating, [36]octaphyrin (1.1.1.1.1.1.1.1) bis-Cu^{II} complex **132** was quantitatively split into two Cu^{II} [18]porphyrins in an unprecedented topological process.[75c] The same splitting reaction also proceeded quantitatively for the octaphyrin $Cu^{II}Co^{II}$ hybrid complex **133**. On the basis of theoretical calculations, the reaction mechanism was proposed to be a formal metathesis-like process that proceeds by cycloreversion of spirocyclobutane intermediate as shown in Scheme 33.[73a] The theoretical analysis also indicates that the transannular interaction that is enhanced upon metalation initiates the splitting reaction.



Scheme 33. Possible mechanism for the splitting reaction of octaphyrin bismetal complexes, where meso-aryl substituents are not shown.

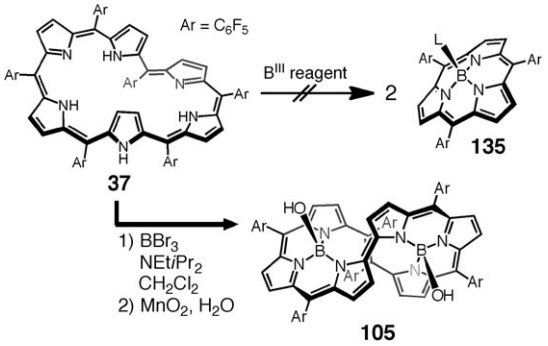
Treatment of meso-pentafluorophenyl [32]heptaphyrin mono-Cu^{II} complex **134** with BBr_3 in the presence of diisopropylethylamine led to the extrusion of B^{III} [14]subporphyrin **135** in 36% yield along with the formation of Cu^{II} porphyrin **136** in 13% yield (Scheme 34).[83a] This reaction is synthetically useful, since the subporphyrin **135** cannot be prepared by the usual synthetic protocols.[4f,82] The same splitting strategy was applied to meso-trifluoromethyl [32]heptaphyrin **137**, which provided subporphyrin **138** and Cu^{II} porphyrin **139**.[83b]



Scheme 34. Splitting reaction of heptaphyrin Cu^{II} complexes to produce subporphyrins.

4.2.7. *Transposition of C(meso)Ar Groups*

The results described in Section 4.2.6. led us to envision a similar splitting reaction of [28]hexaphyrin(1.1.1.1.1.1) **37** to produce two molecules of [14]subporphyrin **135** (Scheme 33). To test this hypothesis, the hexaphyrin **37** was treated with BBr_3. Unexpectedly, [28]hexaphyrin(2.1.1.0.1.1) bis-B^{III} complex **105** was obtained as a consequence of formal transposition of the meso-Ar substituents over the pyrrole units (Scheme 35).[42c] Although the rearrangement mechanism still remains unclear, it is apparent that this transposition of the meso-aryl substituent requires the formation of C(α)–C(α) and C(meso)–C(meso) bonds and the concurrent (or successive) cleavage of two C(meso)–C(α) bonds. Free-base [26]hexaphyrin(2.1.1.0.1.1) was prepared by demetalation of **105** with an excess of MnO_2.



Scheme 35. C(meso)-aryl group transposition reaction of **37**.

5. Ion Binding

Since the first demonstration of the anion binding property of sapphyrins in 1990, Sessler et al. have pioneered many related functions including nucleotide transportation,[84] noncovalent energy transfer,[40] and anion extraction from aqueous media.[66h] An impressive example is the very effective binding of an sulfate ion by cyclo[8]pyrrole **31** through multiple hydrogen bonds (Figure 27).[55] In contrast, highly selective cation binding ability of expanded porphyrins, which is distinguished from metal complexation, was first reported by Wong et al. in 2006.[46]

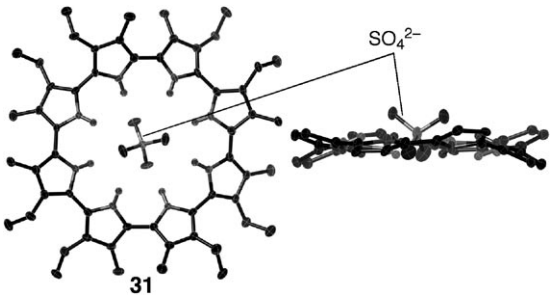
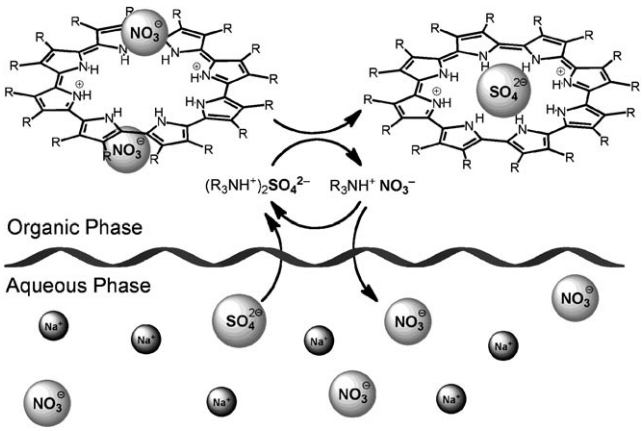


Figure 27. X-ray structure of **31**/SO_4^{2-} ion complex.

5.1. Anion Binding

5.1.1. *Selective Anion Extraction*

Sessler, Moyer et al. have focused on the strong binding affinity between protonated cyclo[8]pyrrole and a sulfate anion. Highly sulfate-selective extraction has been shown to occur from aqueous media by using **31** and Aliquat 336 nitrate (A336N), a commercially available phase-transfer catalyst consisting of a mixture of tri(C_8,C_{10}-*n*-alkyl)methylammonium nitrates (Scheme 36).[66h]



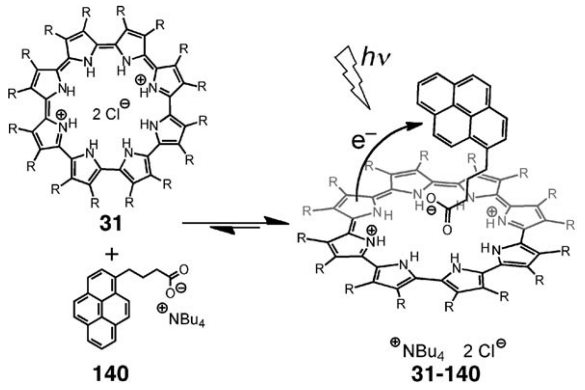
Scheme 36. Sulfate ion extraction with cyclo[8]pyrrole **31**.

5.1.2. *Photoinduced Electron Transfer in an Anion-Bound Complex*

In 2008, Sessler, Kadish, Fukuzumi et al. reported the formation of an anion-bound supramolecular complex of cyclo[8]pyrrole **31** and 1-pyrenebutyrate **140** (Scheme 37), in which photoinduced electron transfer was reported to proceed in an uncommon direction to form $\mathbf{31}^{\cdot+}$–$\mathbf{140}^{\cdot-}$, which is a high-energy charge-separated state, rather than the alternative putative state, $\mathbf{31}^{\cdot-}$–$\mathbf{140}^{\cdot+}$. Furthermore, the charge-separated state was reported to have a lifetime of 300 μs because of the Marcus inverted effect.[66i]

5.2. Cation Binding

Wong and co-workers have reported that hexaphyrin (1.1.1.1.1.0) **141** functions as a chemodosimeter for Hg^{2+} ions



Scheme 37. "Umpolung" photoinduced charge separation in the complex **31**–**140**.

by NIR fluorescence sensing. The fluorescence quenching induced by the addition of Hg^{2+} ions in methanol is sensitive enough to detect Hg^{2+} ion concentrations as low as 10^{-7} M, where high selectivity is also confirmed even in the presence of other cations (Figure 28).[46a] This strong affinity was

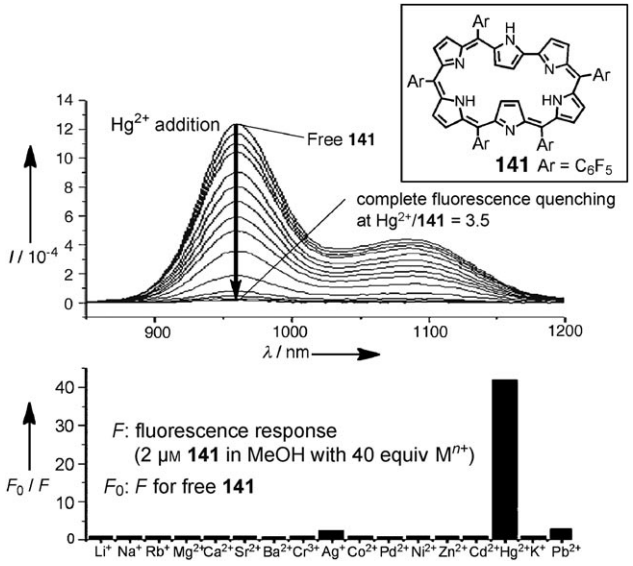


Figure 28. Hg^{2+}-selective sensing by NIR fluorescence of hexaphyrin(1.1.1.1.1.0) **141**.

suggested to originate from the interaction between the heavy atom and the electron-rich aromatic ring. Similarly, the sensing ability of meso-C_6F_5 hexaphyrin(1.1.1.1.1.1) **3** for Ag^+ ions has also been discussed.[46b] Soon after this report, Shen, You, Rurack, and co-workers described the sensitivity of phenanthrene-fused core-modified rubyrin toward Hg^{2+} ions.[46c]

6. Chiral Figure-Eight Structures

The figure-eight motif began to attract interest after the report on a highly twisted X-ray crystal structure of the β-alkyl-substituted [40]decaphyrin(1.0.1.0.0.1.0.1.0.0) (turcasarin) **16** by Sessler et al. in 1994.[10] In general, larger expanded porphyrins often adopt figure-eight conformations probably because of structural strains and effective intramolecular hydrogen-bonding interactions. These figure-eight conformations are intrinsically chiral but interconvert rapidly between two enantiomeric forms. In 1999, Vogel and coworkers succeeded in the optical resolution of β-alkyl octaphyrins **142** and bis-Pd^{II} complex **143** with figure-eight conformations, and the CD spectra of free-base **142** were also assigned on the basis of X-ray diffraction analysis of one enantiomer of the Pd complex **143**-(*P*,*P*) (Figure 29),[22c] although the assignment is disputable by comparison with theoretical results.[22e] The inversion barrier was also estimated to be greater than 85 kJ mol^{-1} even for the free-base octaphyrin **142**.[22c]

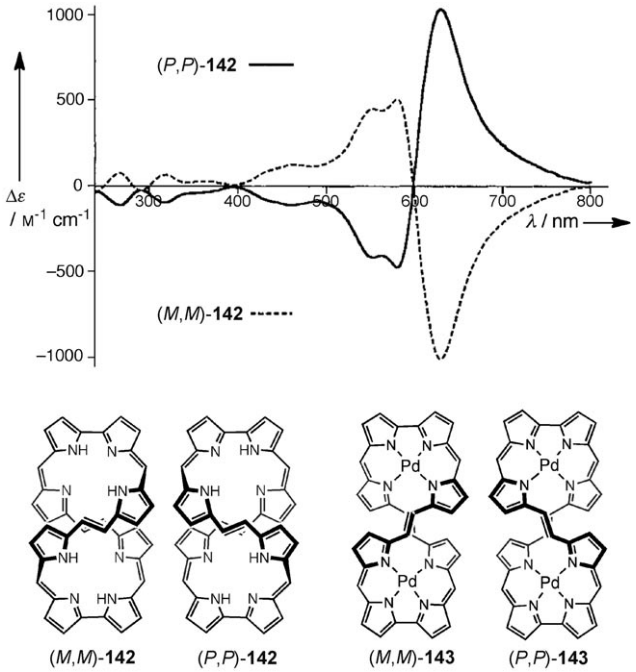


Figure 29. Figure-eight octaphyrin(1.0.1.0.1.0.1.0) **142** and its Pd^{II} complexes **143**. Upper: CD spectra of **142** (Rzepa's revised assignment). β-Ethyl substituents are not shown.

6.1. Optical Resolution

The figure-eight structure of quadruply N-fused meso-aryl-substituted [34]heptaphyrin **144** is rigid enough to allow the optical resolution of the two enantiomers. The resulting CD spectra show a prominent Cotton effect around 755 nm (Figure 30).[42c]

6.2. Chiral Sensing and Induction with Helical Molecules

Setsune and co-workers used octaphyrin(1.0.1.0.1.0.1.0) **145** as a probe for sensing the absolute configuration of carboxylic acids at low concentrations. The analysis of the

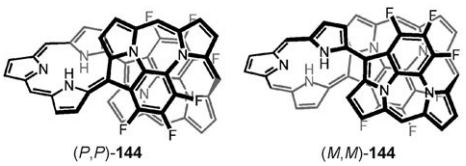
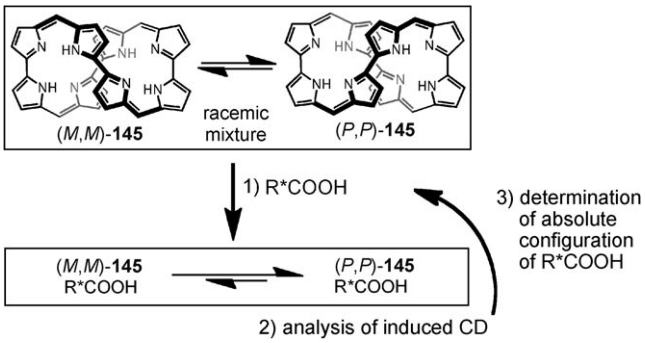


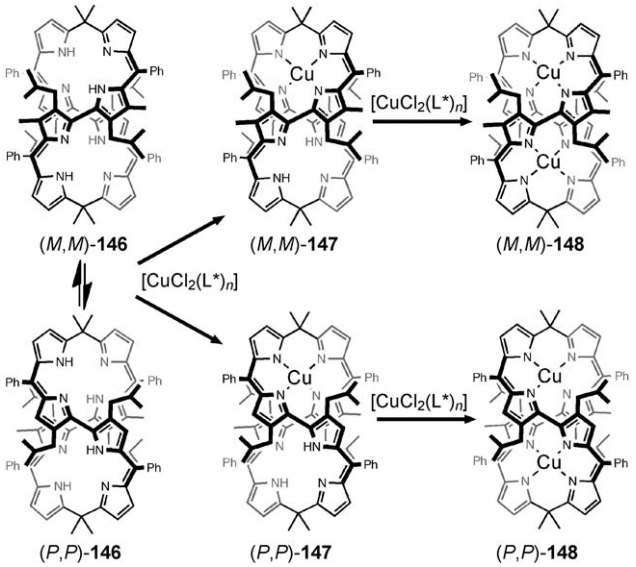
Figure 30. Quadruply N-fused heptaphyrin **144**. Nonfused meso-pentafluorophenyl substituents are not shown.

positive or negative Cotton effect that is induced in the CD spectrum of **145** upon binding chiral carboxylic acids permits the determination of the absolute configuration by comparison with data obtained from standard molecules (Scheme 38).[85a]



Scheme 38. Chiral sensing with octaphyrin(1.0.1.0.1.0.1.0) **145**. β-Ethyl and meso-phenyl substituents are not shown.

Setsune et al. have also demonstrated that enantioselective metalation of calix-type octaphyrin **146** provides helically asymmetric metal complexes with low enantioselectivity. Insertion of Cu^{II} ions into **146** in the presence of an optically active amine led to mono-Cu^{II} octaphyrin **147** with up to 19% *ee* and the second Cu^{II} metalation step of enantiomeric complexes **147**-(*M*,*M*) and **147**-(*P*,*P*) proceeded at significantly different rates to give bis-Cu^{II} complexes **148**-(*M*,*M*) and **148**-(*P*,*P*) with up to 33% *ee* (Scheme 39).[85b]



Scheme 39. Enatiomeric metalation of calix-type octaphyrin **146**. L* = (R)-(+)-1-(1-phenyl)ethylamine.

7. Topology and Aromaticity

In recent years, expanded porphyrins have been recognized as an effective platform to realize various stable Möbius aromatic systems.[47,50,86] Möbius aromaticity is the concept that predicts aromatic characters for $4n\pi$ cyclic conjugated systems based on a singly twisted Möbius topology.[86] This concept, which was predicted first by Heilbronner in 1964 and by Zimmerman in 1966,[87] is very simple and intriguing, and is hence fascinating for both synthetic and theoretical studies. However, it is not easy to reconcile two conflicting structural elements, that is, the fully conjugated cyclic electronic network and twisted topology of π systems, in a single molecule. Despite this difficulty, Herges and co-workers reported a [16]annulene that has a twisted Möbius topology and moderate aromatic character.[87d,e] The potential of expanded porphyrins to form Möbius aromatic systems was first observed by Latos-Grażyński et al., who reported solvent- and temperature-dependent conformational changes between Hückel and Möbius structures for di-*p*-benzi[28]hexaphyrin **153** (Scheme 40 in Section 7.4.2.).[35a] Soon after this report, Osuka et al. began to explore various stable Möbius aromatic systems with distinct aromatic characters.[47] In this context, it is interesting to note that Herges suggested the potential of expanded porphyrins in his Review well before the actual appearance of Möbius aromatic expanded porphyrins.[86b] Besides the Möbius topology, versatile conformations are possible for expanded porphyrins, including planar, figure-eight, and helical conformations. This interesting property arises from the expanded porphyrins' conformational flexibilities, which are useful for examining the aromatic and antiaromatic properties in various conformations. An important lesson from these studies is to recognize a determinant role of molecular topology, either Hückel or Möbius, in the electronic properties of expanded porphyrins (Figure 31).

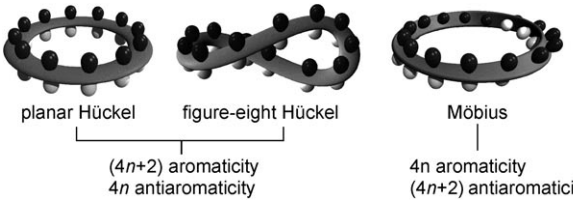


Figure 31. Relationship between topology and aromaticity.

7.1. Aromaticity of Expanded Porphyrins

In general, aromaticity is evaluated by several criteria: structural measures such as bond-length equalization and molecular planarity, energetic stabilization by resonance energy, and magnetic characters.[88] Magnetic properties such as ^{1}H NMR chemical shifts and calculated nucleus-independent chemical shifts (NICS, proposed by Schleyer et al. in 1996)[89] are known to be very sensitive to the

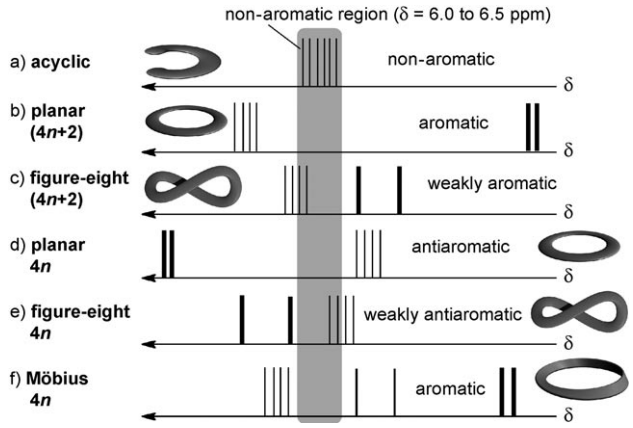


Figure 32. Typical ^{1}H NMR spectra of a) acyclic π-conjugated oligopyrrole and b–f) expanded porphyrins (each topology and number of π electrons are shown). A normal line indicates the signals of the outer pyrrolic β protons and a bold line indicates those of inner protons.

aromaticity of the system.[88–90] Representative ^{1}H NMR spectral patterns of expanded porphyrins are shown for different molecular topologies and aromaticities in Figure 32. The ^{1}H NMR chemical shifts of the peripheral pyrrolic β protons are diagnostic of their aromaticity. The spectra of non-aromatic acyclic π-conjugated oligopyrromethenes, represented by **149**[91] in Figure 33, show those signals in a narrow

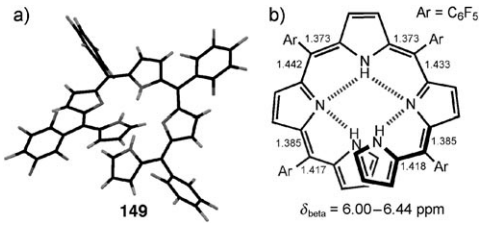


Figure 33. Oligopyrromethene **149**. a) X-ray crystal structure and b) C(meso)-C(α) bond lengths and ^{1}H NMR chemical shifts in $CDCl_3$.

range of 6.0–6.5 ppm (Figure 32a), while Hückel aromatic and antiaromatic species exhibit signals that reflect diatropic and paratropic ring currents (Figure 32b and 32d), respectively. The ^{1}H NMR spectra of Möbius aromatic species (Figure 32f) are essentially similar to those of Hückel aromatic species. Since the inner pyrrolic β protons are sensitive to the magnetic shielding or deshielding by a ring-current effect, these signals are useful for evaluating the aromatic properties of expanded porphyrins.

The electronic structure of expanded porphyrins has also been studied.[39,89] Michl and Waluk, and their respective co-workers have studied the ground-state absorption and magnetic circular dichromism (MCD) of these compounds.[39] Kim and co-workers have summarized the photophysical characteristics that are common for aromatic expanded porphyrins: 1) a sharp Soret-like absorption band in the visible region as well as distinct Q-like bands in the NIR region (Figure 34a), 2) a weak but detectable fluorescence

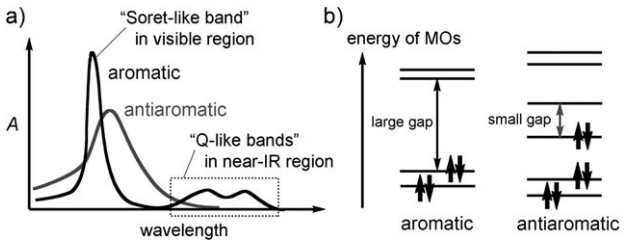


Figure 34. Typical UV/Vis/NIR absorption spectra and molecular orbital diagrams of aromatic/antiaromatic expanded porphyrins.

signal in the NIR region, 3) a relatively long excited-state lifetime, and 4) a large TPA cross-section value. Antiaromatic expanded porphyrins exhibit the opposite features: 1) a broad and ill-defined absorption spectrum without Q-like bands in the NIR region (Figure 34a), 2) no fluorescence, 3) a very short excited-state lifetime, and 4) a relatively small TPA cross-section value. These features are attributable to the characteristic electronic structures of these compounds. Aromatic expanded porphyrins have a wide HOMO–LUMO gap with almost degenerate HOMO/HOMO−1 and LUMO/LUMO+1 levels, while the antiaromatic congeners show a relatively narrow HOMO–LUMO gap without degeneracy of the HOMO/HOMO−1 or LUMO/LUMO+1 levels (Figure 34b).[44]

Fowler et al. demonstrated the induced current density of expanded porphyrins, which turned out to be very useful for visualizing a diatropic or paratropic ring current, which has not necessarily the same pathway as the conventionally expected π-conjugation circuit (Figure 35).[90a] Aihara et al.

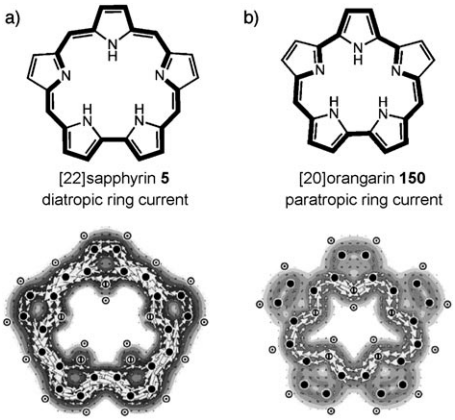


Figure 35. a) Diatropic ring current of sapphyrin **5** and b) paratropic ring current of orangarin **150**, where diamagnetic circulation is shown anticlockwise, paramagnetic clockwise.

calculated bond resonance energies for expanded porphyrins for predicting their aromatic characters and confirmed that an energetic criterion supports the aromaticity of reported porphyrinoids.[90b,c]

7.2. Hückel Aromatic Systems

7.2.1. Planar Conformations

[26]Hexaphyrin(1.1.1.1.1.1) **3** adopts a roughly planar and rectangular geometry with a small mean plane deviation of 0.54 Å,[36,54] while 5,20-meso-free [26]hexaphyrin **33** adopts a more planar conformation with an even smaller mean deviation of 0.11 Å.[48a] The bond-length equalization is apparent for **33** (Figure 36), and is distinctly different from

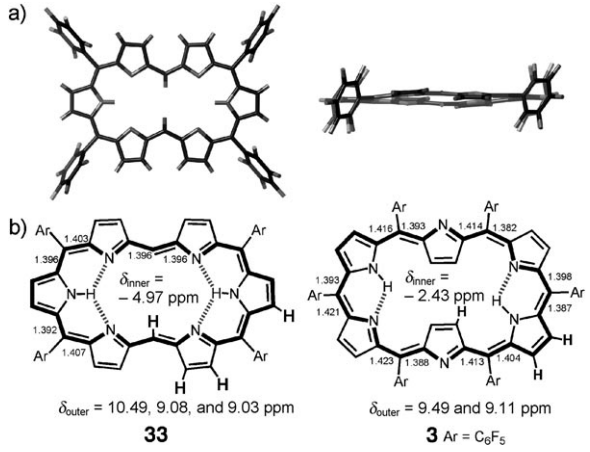


Figure 36. a) X-ray crystal structure of **33** (left: top view; right: side view) and b) the C(meso)-C(α) bond lengths and ^{1}H NMR chemical shifts of **33** and **3**.

the acyclic non-aromatic case (Figure 33). In the ^{1}H NMR spectrum of **3**, the inner and outer β protons are observed at −2.43 ppm and at 9.11 and 9.49 ppm, respectively, and the ^{1}H NMR spectrum of the hexaphyrin **33** features the inner meso protons at −4.97 ppm and the outer β protons at 10.49, 9.08, and 9.03 ppm. These data support the conclusion that both [26]hexaphyrins are strongly aromatic. The ^{1}H NMR spectrum of free base **10** with a planar dumbbell geometry shows the inner and outer meso protons at −7.3 and 12.5 ppm, respectively.[16] [22]pentaphyrins **38**,[37a] [22]sapphyrin **5**,[20] [26]rubyrin **7**,[11] diprotonated cyclo[*n*]pyrroles ($n = 6$–8),[66d] and core-modified [34]octaphyrin[5c,d] are also known as planar Hückel aromatic systems.

7.2.2. Figure-Eight Conformations

Expanded porphyrins can be aromatic when they have $(4n+2)$ conjugated π electrons in a figure-eight Hückel conformation that assures macrocyclic π conjugation. Meso-C_6F_5-substituted [34]octaphyrin(1.1.1.1.1.1.1.1) **151** is a representative case (Figure 37). Meso-CF_3-substituted [26]hexaphyrin **34**[54c,55] and [30]hexaphyrin boron complex **106**[42d] are other examples of figure-eight aromatic systems.

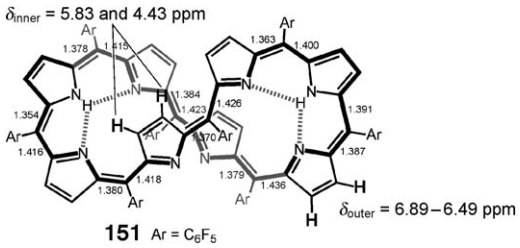


Figure 37. C(meso)-C(α) bond lengths and ^{1}H NMR chemical shifts in $CDCl_3$ at −60 °C of figure-eight [34]octaphyrin **151**.

7.3. Hückel Antiaromatic Systems

7.3.1. Planar Conformations

Hexaphyrin mono-Au^{III} and bis-Au^{III} complexes have two available oxidation states, that is, 26π- and 28π-electronic states. These states are interconvertible through two-electron redox reactions (Scheme 2). Since Au^{III} complexation forces a planar geometry, [26]hexaphyrin complexes **29** and **75** show strong aromaticity, and [28]hexaphyrin complexes **30** and **76** exhibit strong antiaromaticity, respectively (Figure 38).[51] An aromatic-to-antiaromatic change upon two-electron reduction is followed by a distinct change in the TPA value (**29**, 6100 GM; **30**, 1200 GM at $\lambda = 1200$ nm),[51b] photophysical properties, MCD pattern, and molecular orbital diagram.[51c] [24]Amethyrin **6**[10,89b] and [24]rubyrin[57g] are also known to be planar antiaromatic species.

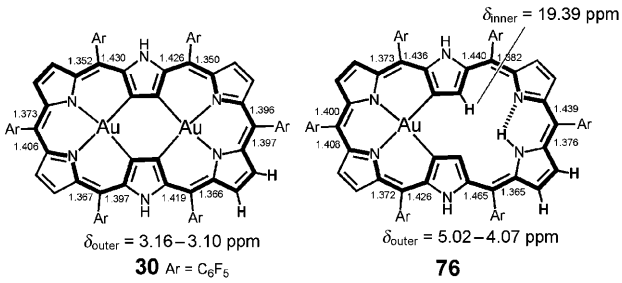


Figure 38. C(meso)-C(α) bond lengths and ^{1}H NMR chemical shifts of **30** and **76**.

7.3.2. Figure-Eight Conformations

The [36]octaphyrin bis-Pd^{II} complex **152** is an antiaromatic expanded porphyrin of a figure-eight Hückel structure, in which two Pd^{II} ions are symmetrically embedded in a NNNC pocket (Figure 39).[47a] This complex shows a paratropic ring current originating from its 36π-electronic network.

Reversible redox interconversion is possible between the 28π-electronic antiaromatic complex **105** and the 30π-electronic aromatic complex **106** in a figure-eight hexaphyrin(2.1.1.0.1.1) system (Scheme 20). Heptaphyrin **4** also exhibits a figure-eight conformation and moderate antiaromaticity in nonpolar solvents.[47e]

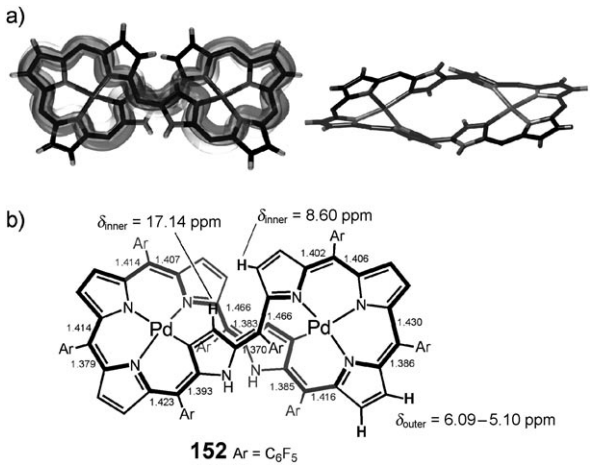


Figure 39. a) X-ray crystal structure of **152** (meso-C_6F_5 substituents; left: top view; right: side view), b) C(meso)–C(α) bond lengths and ^{1}H NMR chemical shifts of **152**.

7.4. Möbius Aromatic Systems

7.4.1. Metal Complexes

It is remarkable that $4n\pi$ expanded porphyrins tend to almost spontaneously twist their molecular structures to form Möbius aromatic systems upon the appropriate metalation reactions. This behavior has been observed for cases including bis-Pd^{II} [36]octaphyrin **25**, mono-Pd^{II} [32]heptaphyrin **95**, mono-Ni^{II} [28]hexaphyrin **92**, mono-Pd^{II} [28]hexaphyrin **93**, mono-Pt^{II} [28]hexaphyrins **94**, and mono-Rh(CO)$_2$ [24]pentaphyrin **96** (Figure 40).[47a,b] The singly twisted Möbius structures were unambiguously confirmed by X-ray crystal structure analysis and the diatropic ring currents were evident in the ^{1}H NMR spectra (Figure 41). The observed sharp ^{1}H NMR spectra indicated their rigid structures, which are different from those of the corresponding free bases. For example, ^{1}H NMR chemical shifts and C(meso)–C(α) bond lengths are shown for **25** and **93** in Figure 41. The inner

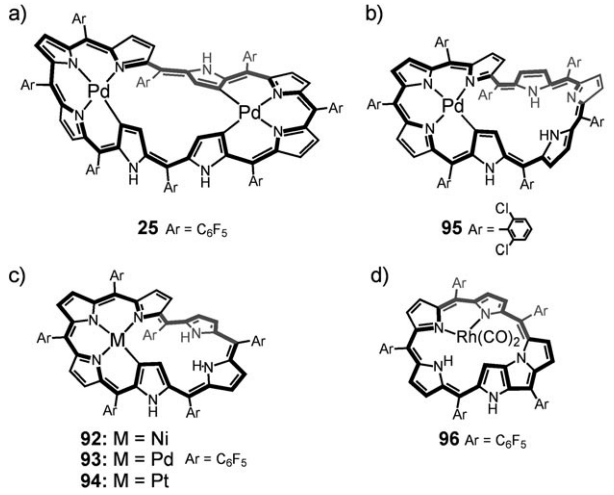


Figure 40. Möbius aromatic expanded porphyrin metal complexes. a) Bis-Pd^{II} [36]octaphyrin complex; b) mono-Pd^{II} [32]heptaphyrin complex; c) mono-Ni^{II}, Pd^{II}, and Pt^{II} [28]hexaphyrin complexes; and d) mono-Rh^{I} [24]pentaphyrin complex.

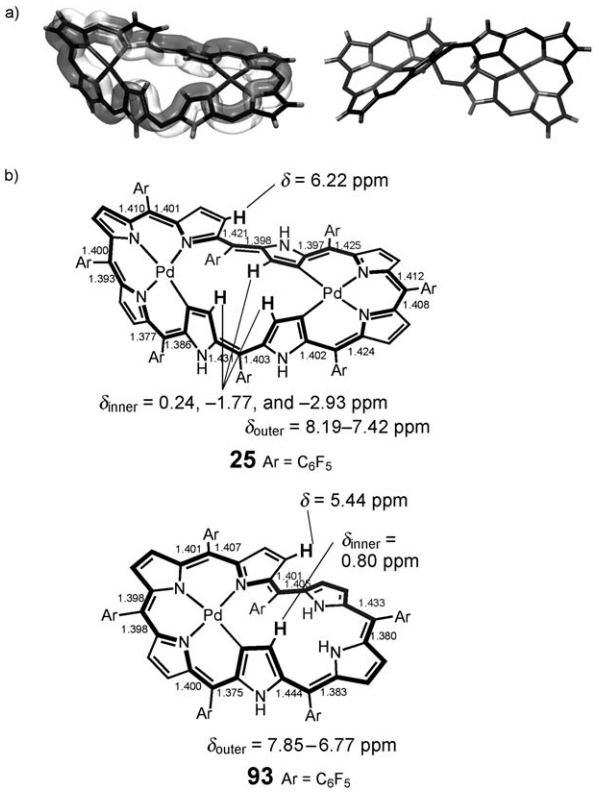
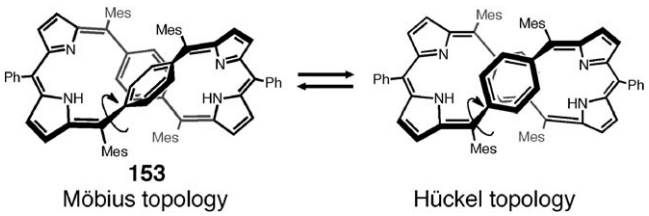


Figure 41. a) X-ray crystal structure of **25** without meso-C_6F_5 substituents and b) C(meso)–C(α) bond lengths and ^{1}H NMR chemical shifts of **25** and **93**, where the bond lengths of **25** are those of three crystallographically different structures.

β protons of the inverted pyrroles are characteristically shielded, while the outer β protons are considerably deshielded. The small bond-length alternation also supports the aromatic characters of the molecules, and the NICS values calculated inside the macrocycles are large and negative, thus supporting the evidence for the aromatic nature of the molecules.

7.4.2. Conformational Equilibria

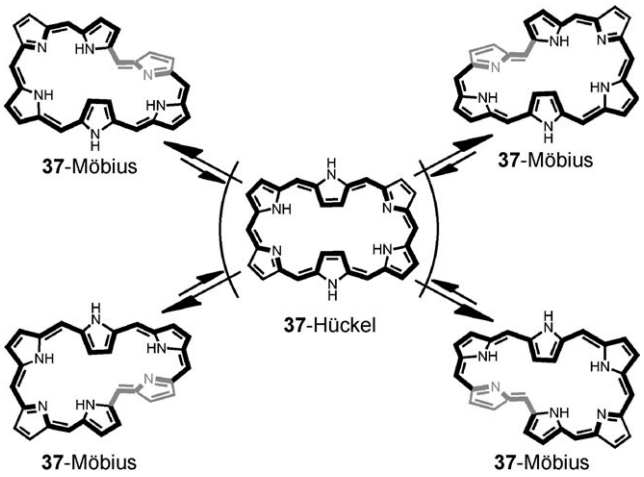
Latos-Grażyński and co-workers reported solvent- and temperature-controlled Hückel versus Möbius topological interconversion for di-*para*-benzihexaphyrin **153** in solution (Scheme 40). However, the macrocyclic ring current is weak, probably because of the localized π electrons of the benzene rings.[35a] Very recently, a three-level topological change



Scheme 40. Topological equilibrium of **153**.

(planar Hückel, Möbius, and figure-eight Hückel) of **153** was shown to occur by temperature and acid/base control.[35c]

Similar but more distinct conformational changes have been revealed for meso-aryl [28]hexaphyrin **37**, which exists in a fast equilibrium mainly between Möbius aromatic conformers and an antiaromatic planar conformer in solution at room temperature (Scheme 41). In spite of its central



Scheme 41. Equilibrium of meso-aryl [28]hexaphyrin **37**. Meso-aryl substituents are not shown.

position among expanded porphyrins, the electronic structure of **37** was a mystery since its discovery in 1999.[36] This problem arose because the simple signal pattern in the ^{1}H NMR spectra (where only three signals are seen for the β protons) suggests a highly symmetrical structure, and, in fact, several X-ray crystal structures indicate a planar, rectangular conformation **37**-Hückel with 28π conjugation, whereas the values of the ^{1}H NMR chemical shifts ($\delta = 7.71$, 7.62, and 2.63 in $CDCl_3$) and UV/Vis/NIR absorption spectra support its aromatic nature.

This problem was solved by low-temperature NMR analyses to show the frozen Möbius conformation, which is slightly energetically lower (3.7 kcal mol^{-1}) than the Hückel conformation (Scheme 41). The adoption of this conformation is strongly supported by different X-ray crystal structures of meso-2,6-difluorophenyl [28]hexaphyrin (**37**-Hückel and **37**-Möbius), which depend on the crystallization solvent (Figure 7). Therefore, the observed NMR spectra at room temperature reflect an averaged structure on the NMR timescale. Curiously, Möbius aromatic [28]hexaphyrins **37**-Möbius have been calculated to have molecular orbital diagrams that are similar to those of the corresponding Hückel aromatic [26] hexaphyrins **3**.[47c]

7.4.3. *Protonation/Neutralization Switching*

Protonation is a convenient and reversible means to switch an antiaromatic Hückel conformation of a 4*n* expanded porphyrin to an aromatic Möbius conformation. Meso-pentafluorophenyl-substituted [32]heptaphyrin **4** adopts a figure-eight conformation and is weakly antiaro-

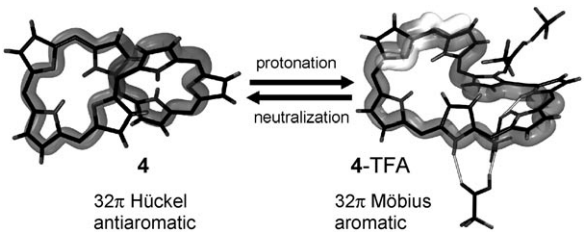


Figure 42. Switching topology between figure-eight Hückel antiaromatic conformer and Möbius aromatic conformer of **4**. Meso-aryl substituents are not shown.

matic in nonpolar solvents, in which intramolecular hydrogen bonds are formed.[47e] Upon protonation with TFA in CD_2Cl_2, the intramolecular hydrogen-bonding interactions are replaced by a intermolecular hydrogen-bond network, which results in the twisted Möbius topology of **4**-TFA with concurrent acquisition of aromatic character (Figure 42). Titration experiments revealed that the protonation proceeded in a stepwise manner to generate monoprotonated and triprotonated species, which can be differentiated by ^{1}H NMR spectra and TPA cross-section values.

Protonation-induced conformational switching is also effective for [36]octaphyrin **28** (see Figure 4). As noted above, [36]octaphyrin **28** adopts a figure-eight conformation and is non-aromatic. Upon protonation in CH_2Cl_2, the conformation of **28** changed to a twisted Möbius conformation with concurrent acquisition of aromatic character in a stepwise manner similar to that of **4**. In contrast, [38]octaphyrin is a moderately aromatic molecule in its neutral form and its aromaticity becomes more pronounced with concurrent planarization upon protonation. These protonated [36] and [38]octaphyrins **154** and **155** show similar crystal structures that have only a subtle difference in tilted angles of pyrrole subunits F and G (Figure 43), which results in their

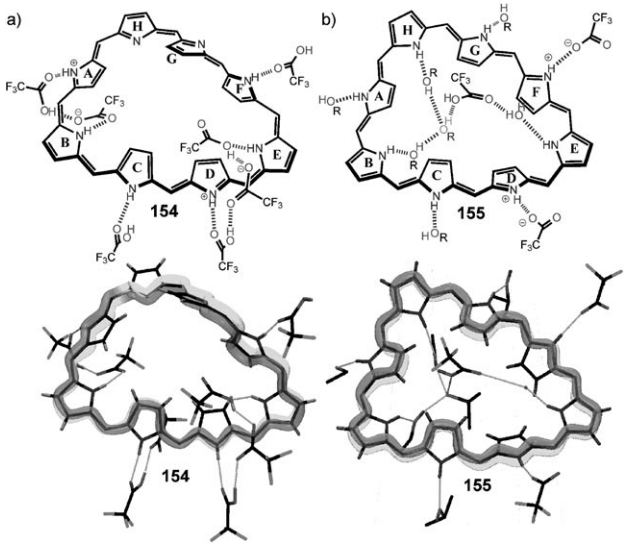
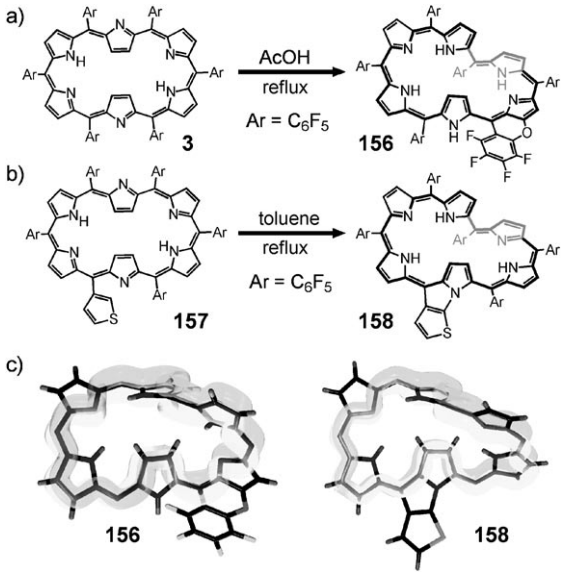


Figure 43. X-ray crystal structures of a) diprotonated [36]octaphyrin **154** and b) diprotonated [38]octaphyrin **155**. TFA was used for protonation.

different topologies. These data strongly suggest that the macrocycles control their topologies by pyrrole rotation to gain $4n\pi$ Möbius or $(4n+2)\pi$ Hückel aromatic stabilization respectively, depending on the number of π electrons.[47i]

7.4.4. Intramolecular Fusion Reactions

Heating of **3** ($Ar = C_6F_5$) in acetic acid led to the production of benzopyran-fused [28]hexaphyrin **156** (Scheme 42a)[47f] and, in a different case, heating of 3-thienyl



Scheme 42. Intramolecular fusion reaction that results in Möbius aromatic [28]hexaphyrins **156** and **158**.

substituted [26]hexaphyrin **157** in toluene resulted in the quantitative formation of thienyl-fused [28]hexaphyrin **158** (Scheme 42b).[47g] In both cases, the twisted Möbius structures were confirmed by single-crystal diffraction analysis (Scheme 42c). The fused structures lead to a decrease in conformational flexibility, thus contributing to the direct observation of the Möbius aromatic conformation without assistance of metal coordination, temperature control, or protonation.

7.4.5. Möbius Chirality

Very recently, the enantiomeric separation of [28]hexaphyrin(1.1.1.1.1.1) Ni^{II} complex **92**, Pd^{II} complex **93** and Pt^{II} complex **94** (Figure 40) has been accomplished as the first optical resolution of Möbius aromatic expanded porphyrins.[93] The X-ray crystal structure of one enantiomer was determined, which led to the unambiguous assignment of the CD spectra of the enantiomers. The activation energy for the racemization of **93** was estimated to be 127.2 kJ mol^{-1}. In addition, the first asymmetric metalation to give **93** was also accomplished with up to 23% *ee* by using a chiral Pd^{II} salt.[93]

7.5. Möbius Antiaromatic Systems

Despite the increasing number of stable $4n\pi$ Möbius aromatic molecules, $(4n+2)\pi$ Möbius antiaromatic species are quite rare. Latos-Grażyński and co-workers reported that cationic Pd^{II} vacataporphyrin **159** exhibited a weak paratropic ring current, which was ascribed to a 18π antiaromatic character based on the calculated Möbius structure (Figure 44a). Unfortunately, the chemical-shift differences were

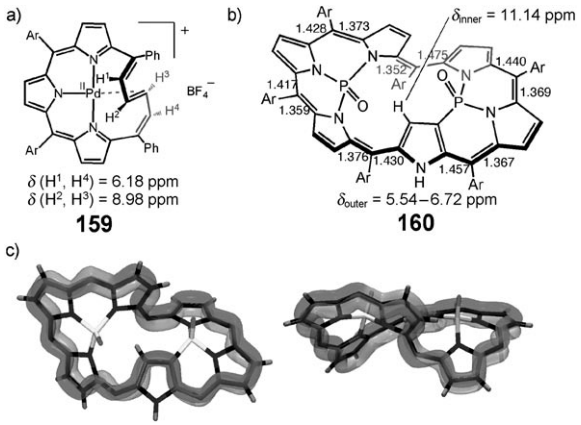


Figure 44. Möbius antiaromatic systems: a) cationic Pd^{II} vacataporphyrin **159** and b) [30]hexaphyrin bis-P^{V} complex **160** and c) top (left) and side (right) views of X-ray crystal structure. Meso-C_6F_5 substituents are not shown.

only small and the crystal structure was not solved.[50a] The [30]hexaphyrin bisphosphorus complex **160** has been identified as the first structurally characterized Möbius antiaromatic compound that is stable, neutral, and rigid.[50b] An X-ray diffraction analysis of **160** revealed the 30π macrocyclic conjugation with a twisted Möbius topology (Figure 44c). A highly reduced [30]hexaphyrin system is well-stabilized owing to the presence of two electron-withdrawing phosphamide moieties, which also confer a certain structural rigidity to the molecule. The inner pyrrolic β proton is deshielded and appears at 11.14 ppm while the outer β protons are slightly shielded (Figure 44b), thus strongly indicating a paratropic ring current despite the moderate torsional angles of the cyclic π network (up to 67°). Thus, the aromaticity reversal in the Hückel rule upon changing the number of π electrons between $(4n+2)$ and $4n$ has also been confirmed for the cyclic conjugated molecules that have a twisted Möbius topology (Figure 31).

8. Organic Radicals

Stable organic radicals have been continuously attracting considerable attention, not only for purely scientific interest in their structures and properties, but also in possible applications in organic magnets, electronic devices, organic batteries, and optical materials. To attain a high stability of organic radicals, kinetic stabilization by steric hindrance and/

or delocalization of an unpaired electron through effective conjugation is essential. Very recently, expanded porphyrins have emerged as an effective platform to produce stable radicals under ambient conditions.

8.1. Stable Monoradicals

During the synthesis of 5,20-meso-free hexaphyrin **33**, the oxygenated product **26** was isolated together with the target molecule (Scheme 25). It was found that compound **26** exhibits a typical radical character: an extremely broad and thus unassignable NMR spectrum, ESR activity, magnetic susceptibility in the solid state, and a broad and low energy UV/Vis/NIR absorption band. Thus, **26** has been assigned as a stable monoradical. Consistent with this assignment, theoretical calculations indicated a delocalized spin density over the hexaphyrin macrocycle (Figure 45). Surprisingly, the radical **26** shows remarkable stability to oxygen, moisture, and even heating in air.[48a]

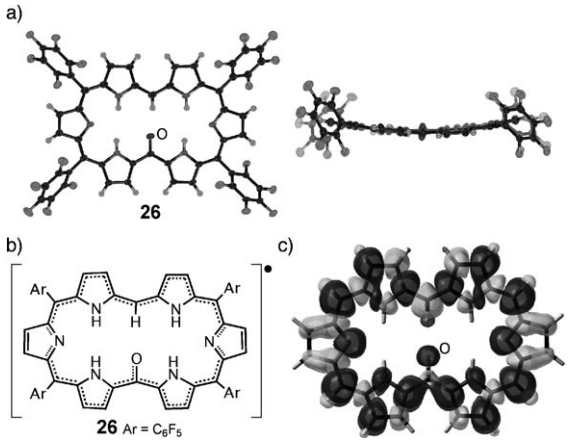


Figure 45. Meso-oxygenated hexaphyrin **26**; a) X-ray crystal structure, b) molecular structure, and c) calculated spin density distribution.

The hexaphyrin bis-Pd^{II} complex **161** has also been identified to be a stable organic radical by ESR and NMR spectroscopy and magnetic susceptibility measurements. Theoretical calculations show that the spin delocalization occurs over the entire twisted macrocyclic hexaphyrin rather than palladium ion centers. This is a rare example of a stable π radical delocalized over a distorted nonplanar system (Figure 46).[48b]

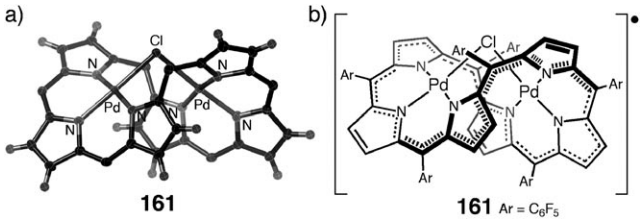
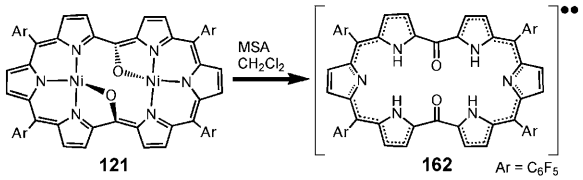


Figure 46. Hexaphyrin bis-Pd^{II} complex **161**; a) X-ray structure and b) molecular structure.

8.2. Stable Biradicaloids

The meso-dioxygenated hexaphyrin **162** has been characterized as a non-Kekulé singlet biradicaloid that was obtained by demetalation of the Ni^{II} complex **121** (Scheme 43). X-ray structural analysis of **162** shows that it has a roughly planar geometry. From the calculated SOMO orbitals and spin density distribution, two unpaired electrons are concluded to be fully delocalized over each tripyrrodimethene unit. By fitting the temperature-dependent ESR intensity data to the Bleaney–Bowers equation, the J value was estimated to be $J/k_B = -645$ K, which corresponded to an energy gap of 2.56 kcal mol^{-1} between the singlet ground state and triplet excited state.[48c]



Scheme 43. Stable singlet biradicaloid hexaphyrin **162** obtained by the demetalation of hexaphyrin nickel complex **121**.

9. Other Topics

9.1. Liquid Crystals

Sessler and co-workers employed appropriately substituted cyclo[8]pyrroles **163**–**165** for liquid-crystal applications by taking advantage of the planar structures of these compounds. Cyclo[8]pyrroles themselves do not form a mesophase but, interestingly, upon mixing with an electron-deficient aromatic small molecule, they form a columnar hexagonal phase stabilized by electron-donor/electron-acceptor interactions. The possibility of producing a material for sensing explosives was suggested, as a thin film of **165** can form a liquid-crystalline phase when contacted with trinitrobenzene vapor (Figure 47).[66f]

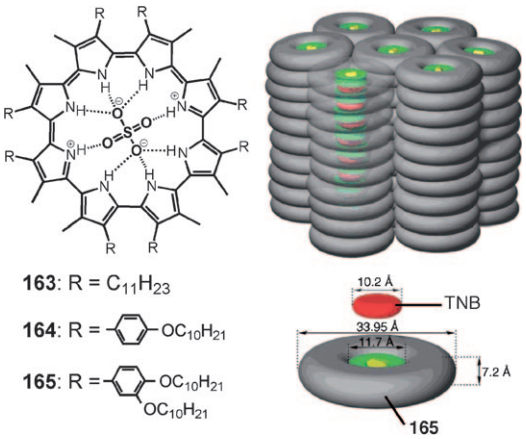
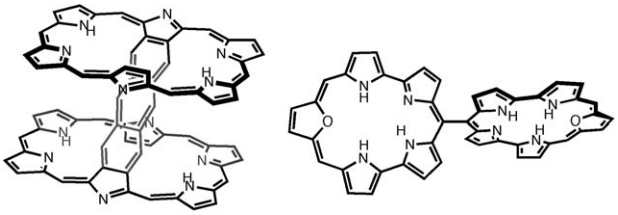


Figure 47. Cyclo[8]pyrroles **163**–**165** and model of hexagonal columnar (Col_h) liquid-crystalline phase. TNB = 1,3,5-trinitrobenzene.

9.2. Dimerization

While various covalently linked porphyrin oligomers have been developed, only a limited number of dimeric expanded porphyrins are known. Interesting examples are the anthracene-bridged double-decker hexaphyrin dimer **166** that was prepared by the regioselective Diels–Alder reaction of hexaphyrin **3** and bis-*o*-xylylene equivalents[92a] and a meso–meso linked dimer of core-modified smaragdyrin **167** (Figure 48).[92b]



166 167

Figure 48. Dimer of expanded porphyrins **166** and **167**. Meso-aryl groups are not shown.

9.3. Supramolecular Assembly

Some examples of the supramolecular assembly of expanded porphyrins have been reported. Hurley and co-workers have designed and synthesized a core-modified sapphyrin, which binds more selectively than telomestatin or porphyrin analogues to an intramolecular G-quadruplex. This stabilization may lead to inhibition of the enzyme telomerase and thus lead to applications in anticancer drugs.[94a,b] Sessler and co-workers have shown that a single-walled carbon nanotube binds strongly to a functionalized sapphyrin diol to give a water-suspendable sapphyrin–nanotube complex. The photophysical properties of the complex as donor–acceptor species for light-harvesting have also been described.[94c]

10. Summary and Outlook

Extraordinary progress has been made in the chemistry of expanded porphyrins in the past decade. A variety of structures, properties, metal complexes, reactions, and applications have been explored. In many cases, entirely unprecedented structures and reactivities have been found. Expanded porphyrins have already shown potential utility in fields of bioinspired catalysis, drug delivery, data storage, sensor, and nuclear-waste remediation. As the most important topic, expanded porphyrins have been demonstrated to serve as an effective platform to realize stable Möbius aromatic and even antiaromatic systems, which is very difficult with any other classes of macrocycles. In addition, the generation of stable radical species from expanded porphyrins has been reported. Expanded porphyrins are also quite promising because of their large TPA cross-section values. However, the chemistry of expanded porphyrins is still in its infancy and challenges still remain to explore novel structures, properties, and functions. In particular, the synthesis of new systems and the improvement of the existing synthetic methods will remain of interest. Although the field of expanded porphyrin chemistry has advanced rapidly in recent years, it is clear that much more work remains to be done.

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