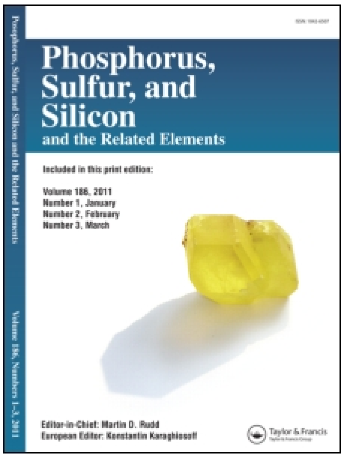

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Supramolecular Assemblies of Sulfur- and Selenium- Containing Expanded Porphyrins Mediated Through Noncovalent Interactions

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Various supramolecular assemblies based on expanded porphyrins building blocks containing sulfur and/or selenium in the core, formed through multiple noncovalent hydrogen bonding interactions are highlighted. Specifically, modified expanded porphyrins such as 22 π sapphyrins, 26 π rubyrins, and 34 π octaphyrins self assemble in solid state through C—H$\cdots$O, C—H$\cdots$N, C—H$\cdots$S, C—H$\cdots$Se, C—H$\cdots\pi$, and C—H$\cdots$Cl interactions to form dimeric, oligomeric, and three dimensional networks. Furthermore, the supramolecular networks promoted by trapped solvent molecules such as nitrobenzene and bound anions such as chloride or trifluoroacetate through noncovalent interactions will be discussed.

Keywords Expanded porphyrins; inverted porphyrins; noncovalent interaction; octaphyrin; rubyrin; sapphyrin

INTRODUCTION

Expanded porphyrins are a class of conjugated-macrocyclic compounds in which pyrrole/hetero cyclic rings are linked to each other in a cyclic fashion through meso carbon bridges. Unlike porphyrins, which are 18 π electron systems, the expanded porphyrins contain more than 18 π electrons in their conjugated pathway. The different ways of expanding

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a porphyrin ring include (1) increasing the number of bridging atoms separating the heterocyclic ring by adding one carbon atom between the meso and the α-pyrrolic position as in 20 π homoporphyrin **1**, (2) increasing the number of conjugated double bonds between the four pyrrolic rings as in 22 π bis vinalogous porphyrin **2**, and (3) to add additional heterocyclic rings to the porphyrin frame work as in 22 π sapphyrin **3** (see Chart 1).

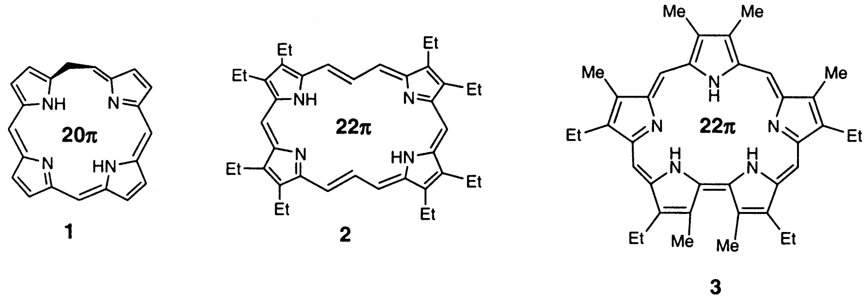


CHART 1

Studies on expanded porphyrin systems are important from several points of view. The presence of more number of heteroatoms with larger cavity size makes them useful ligands for coordination of lanthanide and actinide metals.[1,2] Unlike porphyrins, the protonated forms of expanded porphyrins are known to bind anions and in favorable cases even anion transport has also been observed.[3] Furthermore, they are useful in biomedical applications such as sensitizer for Photo Dynamic Therapy (PDT) as contrasting agents in magnetic resonance imaging (MRI) and as radiation therapy enhancers.[4] More recently, their use as nonlinear optical materials has been envisaged because of their longer wavelength absorption.[5] They also are useful to address the fundamental property of aromaticity in cyclic annulenes. On the other hand, inverted porphyrins are porphyrins isomers which have one or more of core nitorgens pointing out of the ring and the pyrrole β-CH ring protons are in the aromatic ring current region as in **4**. They also are known as N-confused porphyrins.[6,7] Inverted porphyrins act as important organometallic ligands where one or more M—C bonds can be generated inside the porphyrin core in addition to the presence of M—N bonds. They are also important ligands to stabilize unusual oxidation states of metals.[8]

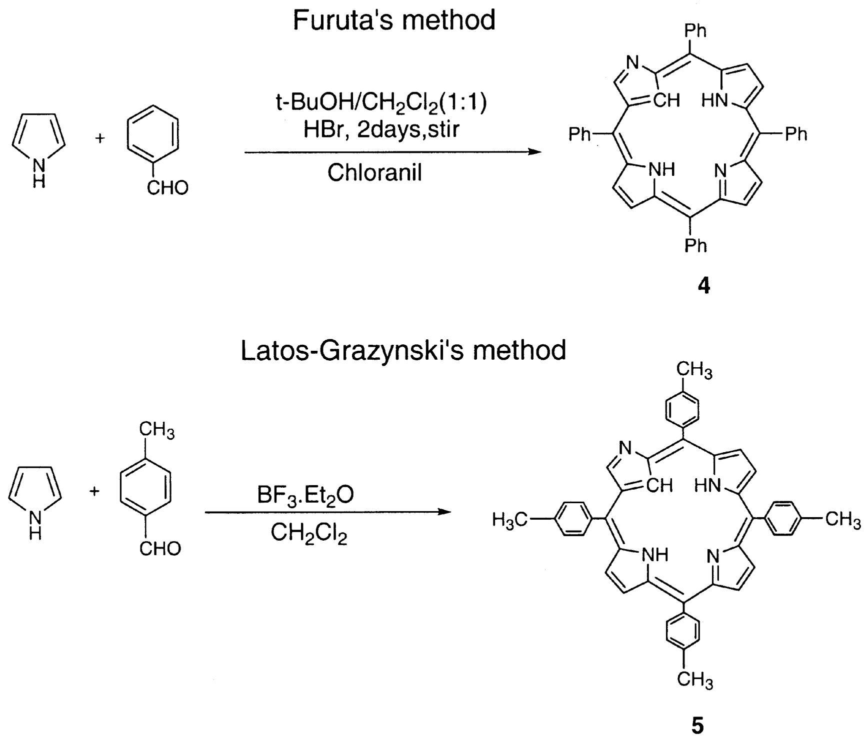
Recently, several groups significantly have contributed to the development of expanded porphyrin chemistry and inverted porphyrin with emphases on synthesis, structure, and reactivity. Acid-catalyzed condensation of appropriate precursors under mild conditions or oxidative coupling reactions where direct pyrrole-pyrrole links can be generated at the final step of the reaction have proved highly successful for the synthesis of a range of expanded porphyrins.[1,2] From a structural perspective, expanded porphyrins with *meso* aryl substituents show a rich structural diversity where one or more heterocyclic rings exhibit an unusual 180° ring flipping leading to partially inverted structures, including N-confused macrocycles.[9,10] Reactivity studies mostly have concentrated on studying the ability of these macrocycles to bind anions and cations. Expanded porphyrins in their free base form have affinity for transition metal cations[1,2] while in their protonated form they bind anions.[3] Anions are held by weak hydrogen bonding and electrostatic interactions. The purpose of this article is to highlight the synthetic routes developed for the preparation of expanded porphyrins and inverted porphyrins, understand their structural diversity, and summarize their coordinating ability towards anions. Furthermore the formation of supramolecular assemblies mediated through noncovalent interactions also are highlighted.

INVERTED PORPHYRINS

Latos-Grazynski and coworkers, and Furuta and coworkers independently reported the first syntheses of inverted porphyrin or N-confused porphyrin under different condition using Rothemund methodology (Scheme 1).[6,7] In addition to the expected tetraphenyl porphyrin, they are able to isolate the N-confused porphyrins **4**, **5** in about 5–7% yields.

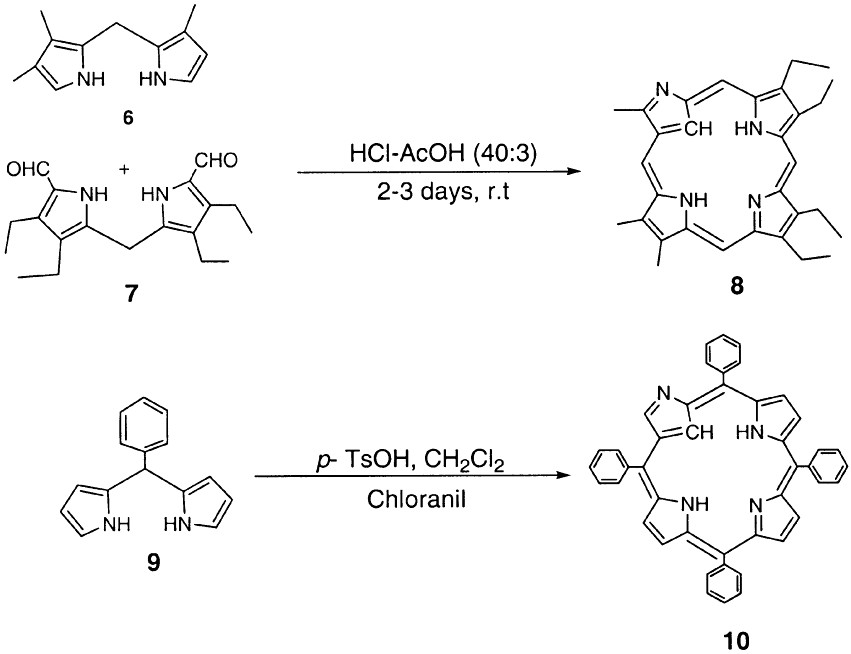
Many research groups have recently synthesised N-confused porphyrins (NCP). Dolphin and coworkers prepared periphery modified NCP **8** by the acid-catalyzed condensation of modified dipyrromethane **6** and dipyrromethanedialdehyde[11] **7** while we[12] reported the formation of *meso*-tetraaryl NCP by oxidative coupling reaction of appropriate dipyrromethane **9** in presence of 0.1 equiv. p- TsOH (Scheme 2). Recently Lindsey and coworkers[13,14] reported the formation of NCP **10** as one of the products (Scheme 2) in a one-flask synthesis of a acid-catalyzed reaction of pyrrole and aldehyde and this reaction is similar to that described earlier in Scheme 1. Lash and coworkers reported the syntheses of hexa- and heptaalkyl-substituted inverted porphyrins by a 3 + 1 condensation involving tripyrranedicarboxylic acid and pyrrole-2,4-dicarboxaldehyde.[15]

The remarkable ability to act as tetra coordinate ligands to form transition metal complexes involving a metal-carbon bond inside the porphyrin cavity has resulted in the formation of divalent simple and organometallic Ni(II) and Ni(III) complexes,[16,17] rare organo Cu(II)



SCHEME 1

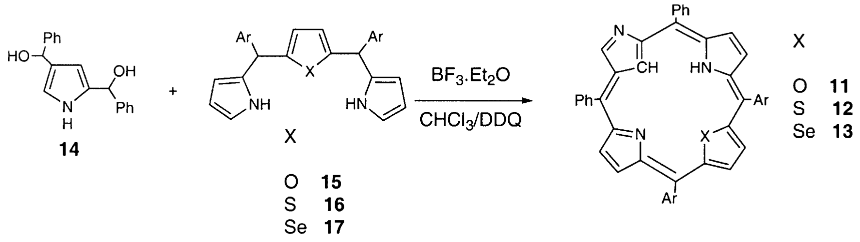
complexes, and Ag(III) complexes with metal-carbon bonds.[18,19] Recently Furuta and coworkers have reported the formation of three types of Pd (II) complexes,[20] one involving inner coordination sites and the other two involving both inner and outer N-coordination sites resulting in the formation of double-decker complexes. In the reaction of N-confused tetratolyl porphyrin and $Pd(OAc)_2$ the formation of products was found to be solvent dependent. Macrocycle **4** also was found to complex Sb(V) and the resulting metal complex was found to be a potential candidate for molecular wire component.[21] The surprising ease of the formation of metal-carbon bonds is attributed to the presence of an Arduengo-type aromatic carbene-like structure,[22] which makes the β-carbon inside the porphyrin cavity *exotic* since it stabilizes a variety of oxidation states for transition metal-like Nickel used for complexation which otherwise is difficult to obtain with parent tetraphenyl porphyrin. Thus owing to the inner-core carbon and outward-pointing nitrogen, the coordination chemistry involved with **4** differs greatly from



SCHEME 2

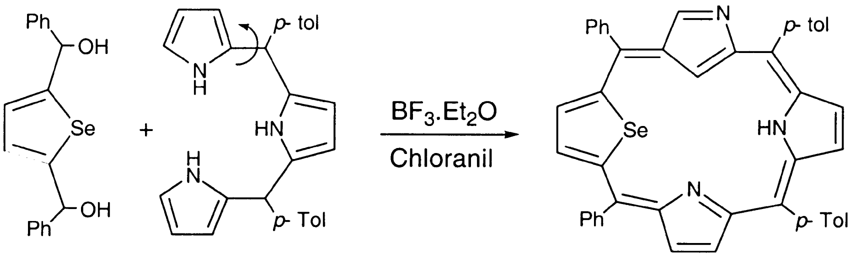
that of normal porphyrins. This characteristic, multivalent nature of NCP is explained by the stabilization of polarized metal-carbon bond by the deprotonation of the outward pointing NH in the confused pyrrole. NCP can act both as a divalent (NCP^{2-}) and trivalent (NCP^{3-}) ligand with d^8 metals like Ni^{2+} and Ag^{3+}. On the other hand, Pd^{2+} coordinates to N-confused porphyrin in a different fashion. In this case Pd^{2+} coordinates both inside carbon and the periphery nitrogen of the N-confused ring.

Recently we[12] and Lee and co-workers[23] reported the synthesis of core-modified inverted porphyrin by $3+1$ methodology (Scheme 3).



SCHEME 3

Very recently Latos-Grazynski and coworkers[24] reported a pyrrole-inverted isomer of 5,10,15,20-teraaryl-21-selena porphyrin *i.e.*, 5, 10, 15, 20-tetraaryl-22-selenaporphyrin **18** in 1% yield where the selenophene ring is *cis* with respect to the inverted pyrrole ring (Scheme 4) from the precursor diol **19** and tripyrrin **20**.



19 **20** **18**

SCHEME 4

The single crystal X-ray structure of the thia N-confused porphyrin **12** confirmed the proposed structure[12] (Figure 1). A close look at the packing diagram (Figure 2) reveals another interesting aspect of the structure. There are two molecules in the unit cell and these molecules are linked to each other through a noncovalent weak N—H---N and C—H---N intermolecular hydrogen bonds involving the pyrrole-NH, the nitrogen atom of the N-confused ring, and the carbon atom of pyrrole ring. Four such interactions produce a cyclophane-like dimeric structure where the two N-confused ring are almost one above the other. The N—H· · ·N distance of 3.14 Å,[5] bond angle 117.2° and C—H---N distances of 3.24 Å, and bond angle 128.25° are in the range expected for N—H---N and C—H---N hydrogen bonds reported in literature. Also, there are two intramolecular N—H---S hydrogen bonds and one C—H---S hydrogen bond in each molecule between pyrrole N1-H, N3-H, pyrrole C-13, and thiophene sulphur with an average distance of 2.74 Å and 3.45 Å for N—H---S and C—H---S hydrogen bonds, respectively.

EXPANDED PORPHYRINS

22 π Meso Aryl Sapphyrins

Sapphyrins are a class of expanded porphyrins in which five pyrrole/heterocyclic rings are linked to four meso carbon bridges with one direct pyrrole-pyrrole link. They contain 22 π electrons in the conjugated

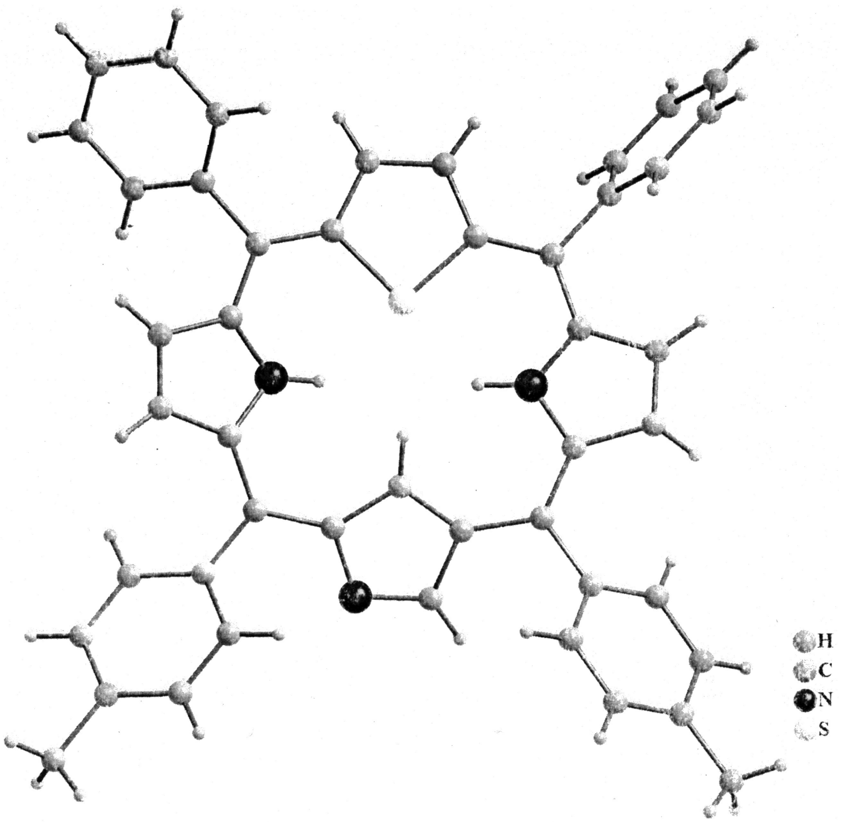


FIGURE 1 Single crystal X-ray structure of **12** (plane view).

pathway and exhibit aromatic behavior following [4n + 2] Hückel rule. Sapphyrin, **3** was discovered serendipitously by R. B. Woodward and co-workers[25] and later Sessler and co-workers developed efficient methods to synthesize them in smaller number of steps in affordable quantities[1,2] (Scheme 5). The name sapphyrin arises from its blue color in solid state and intense green color in organic solvents.

Two different types of sapphyrins are known in literature depending on the location of the substituents; β-substituted sapphyrin **3** and **21** contain alkyl substituents on the β-pyrrole positions and no substituents on meso carbons. On the other hand, in the meso aryl sapphyrin, the meso carbons contain phenyl substituents and β-pyrrole positions are free as in **24**.

Latos-Grazynski and coworkers were the first to report the synthesis of meso aryl sapphyrin by Rothemund reaction.[26] They isolated

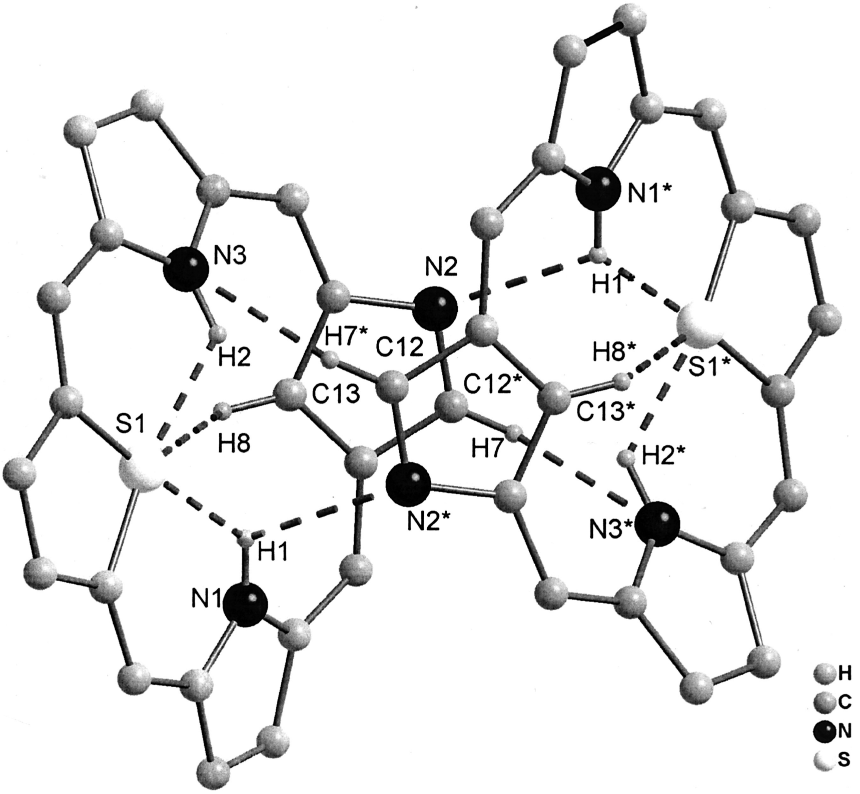
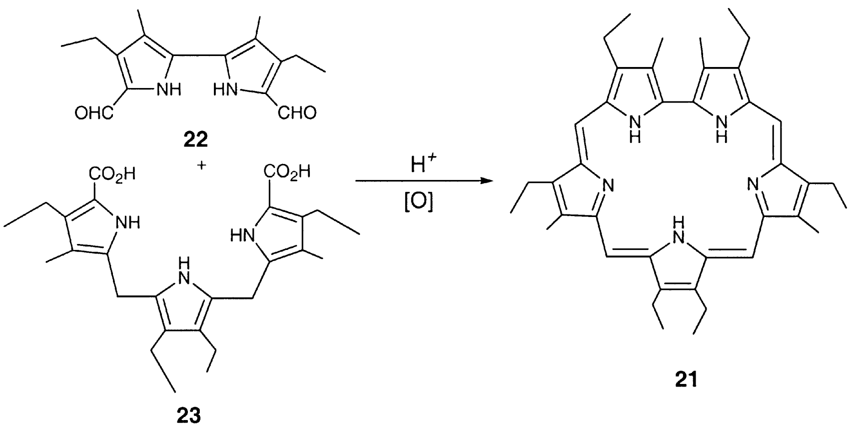
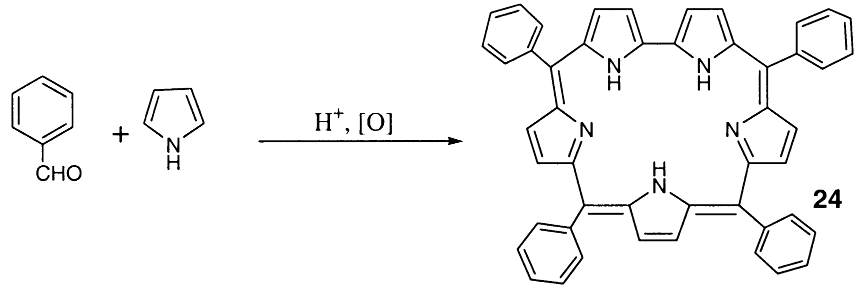


FIGURE 2 Molecular packing diagram of **12** showing cyclophane-like dimeric structure (noninteracting atoms are omitted for clarity).

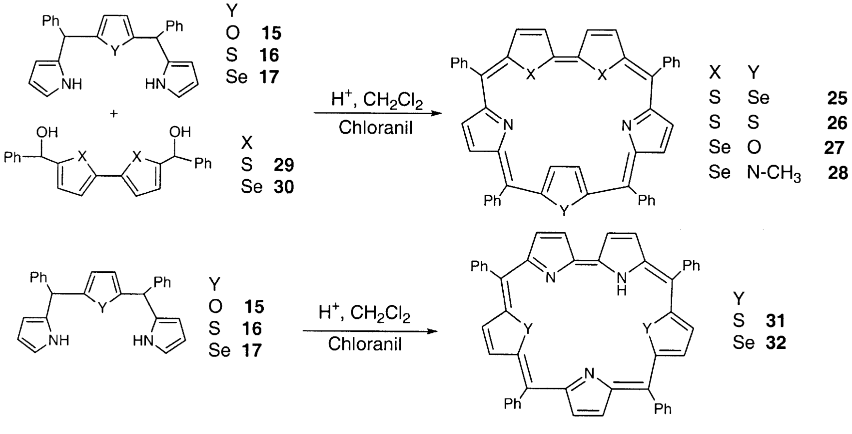


SCHEME 5



SCHEME 6

sapphyrin as a biproduct (Scheme 6). Several meso aryl core-modified sapphyrins also are known in which one or more pyrrole rings have been replaced by other hetero rings such as N-methyl pyrrole, furan, thiophene, and selenophene **25–28**, **31**, and **32**. We have reported a series of core-modified sapphyrin either through acid-catalyzed MacDonald condensation reaction or through oxidative coupling reactions using appropriate precursors[27–31] (Scheme 7).



SCHEME 7

In general, the meso aryl sapphyrins show two different types of structures depending on the nature of the hetero atom. They are normal structure in which all the five heteroatoms of the heterocyclic rings are pointing towards the ring current of the macrocycle as in **31** and **32** while in the inverted structure as in **25–28**, the heterocyclic ring opposite to bipyrrole/bithiophene/biselena/bifuran unit has undergone a 180° ring flipping such that the β-CH protons of the inverted ring are in the ring current region and the hetero atom is pointing outwards. A single, crystal X-ray structure confirms the inversion of the ring in the solid state and the ^{1}H NMR chemical shifts of the inverted ring protons confirm the inversion in the solution state.

Supramolecular Assemblies Through C–H---S and C–H---Se Interactions in Sapphyrins

The X-ray crystal structures of **31** and **32** reveal that the replacement of the pyrrole NH group by S or Se changes the π-electron delocalization.[32] The bond lengths in the macrocycle are altered compared to those of free thiophene or selenophene fragments, as previously was observed for the similar systems. In both the cases the macrocycle is almost planar (deviations from the mean plane in **31** are 0.054, 0.027, and 0.028 Å for S1, S2, and N2 and −0.014 and −0.012 Å for N1 and N3, respectively). The important feature of the structure is the presence of hydrogen-bonding interactions in the cavity between N1-H1---S1 [H1-S1 2.87^{11} Å] and N1-H1---S2 [H1-S2 2.55^{11} Å] in **31**. The corresponding distances for **32** are 2.63^{23} Å [H1-Se1] and 2.28^{23} Å [H1-Se2]. The packing diagram shown in Figure 3 reveals an interesting aspect of the structure. In **31** there are two short range C23–H23---S1 hydrogen bonding interaction [2.91^5 Å, 136.3°] between the CH proton of the meso phenyl ring of one sapphyrin molecule and the sulphur atom of the thiophene ring of the other sapphyrin molecule leading to the formation of a face-to-face dimeric structure. This dimeric structure further is extended

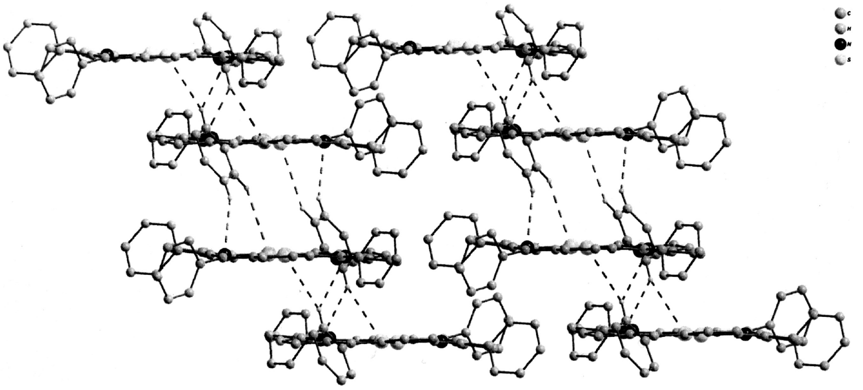


FIGURE 3 Structure of **31** showing the formation of ladder assembly. The hydrogen bonding interactions are represented by dotted lines. The solvent of crystallization and the noninteracting hydrogen atoms are omitted for clarity.

through the formation of the larger hydrogen bonding motifs involving C—H---S [3.16 Å 131.2°] and C—H---N [2.70[6,7] Å, 156.3°] thus leading to a supramolecular ladder assembly and the CH_2Cl_2 solvent molecules found inside the cavity created by three hydrogen bonding interactions (cavity is seen with the dotted lines). Thus, each sapphyrin molecule is held by four hydrogen bonding interactions of which three are C—H---S interactions and one C—H---N interaction. The thirtytwo also forms a similar assembly (Figure 4). However, here the dimeric assembly involving C—H---Se [2.94[6,7] Å, 146°] interactions are not exactly face-to-face but is slightly off set such that the meso phenyl ring of one sapphyrin molecule is situated exactly above the sapphyrin core of the other molecule, leading to a zig-zag ladder structure as shown. Here also the CH_2Cl_2 solvent is found in the cavity and the C—H---S and C—H---Se distances observed here compare well with the reported data for similar interactions.

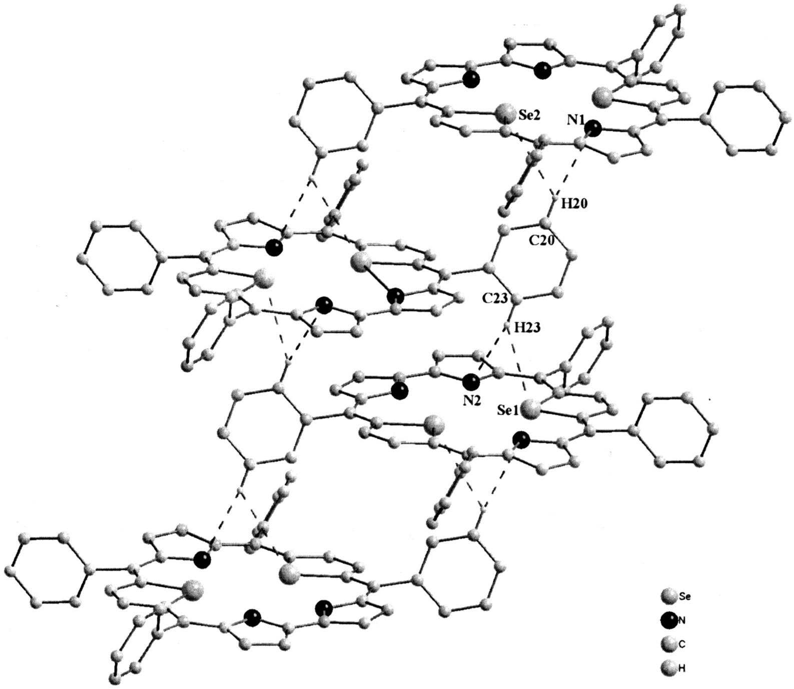


FIGURE 4 The zig-zag ladder structure formed by **32**. The various hydrogen bonding interactions are shown in dotted lines. The solvent of crystallization and the noninteracting hydrogen atoms has been removed for clarity.

Supramolecular Assemblies Through C—H---π Interactions in Sapphyrins

Unlike **31** and **32**, sapphyrin **25** exhibit an inverted structure where the selenophene ring opposite to the bithiophene unit has undergone a 180° ring flipping.[27–31] The dihedral angle between the inverted selenophene ring and the mean plane defined by 4 meso carbons of the sapphyrin is 20.56°. A careful analysis of the structure reveals each sapphyrin molecule crystallizes with a dichloromethane as a solvent of crystallization. One of the C—H protons of the solvent interacts with the sulphur atom of the thiophene ring (average distance C—H---S 2.873 Å, 161.27°). Furthermore, one of the β-CH protons of the thiophene ring is involved in an intermolecular C—H---π interaction with the pyrrole-π cloud of an adjacent molecule, thereby leading to the formation of a linear array of sapphyrin with an adjacent sapphyrin inclined at an angle of ~90° (Figure 5). The C—H---π centroid distance is 2.775 Å. **26** also shows an inverted structure where the thiophene ring opposite to the bithiophene unit has undergone a 180° ring flipping. The dihedral angle of the inverted thiophene ring with the mean sapphyrin plane is 28.28°. A detailed analysis of the structure reveals formation of a linear sapphyrin array (Figure 6) stabilized through the C—H---π interactions involving the meso phenyl rings. Specifically, each sapphyrin molecule experience four C—H---π interactions with two adjacent sapphyrins. Interestingly, the acidic CH protons of the two meso phenyl rings in each sapphyrin involve in proton donor interactions to the adjacent molecule

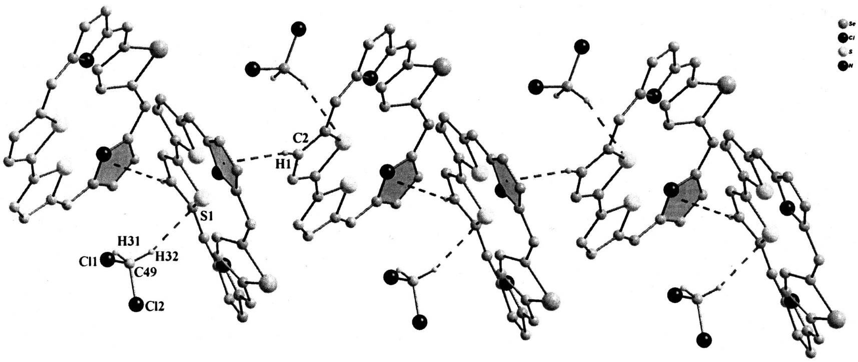


FIGURE 5 One dimensional array formed by **25** through C—H---π and C—H···S interactions. The π cloud involved is shaded for clarity. *Meso* phenyl rings and noninteracting hydrogens, which are not involved in the hydrogen bonding, are omitted for clarity.

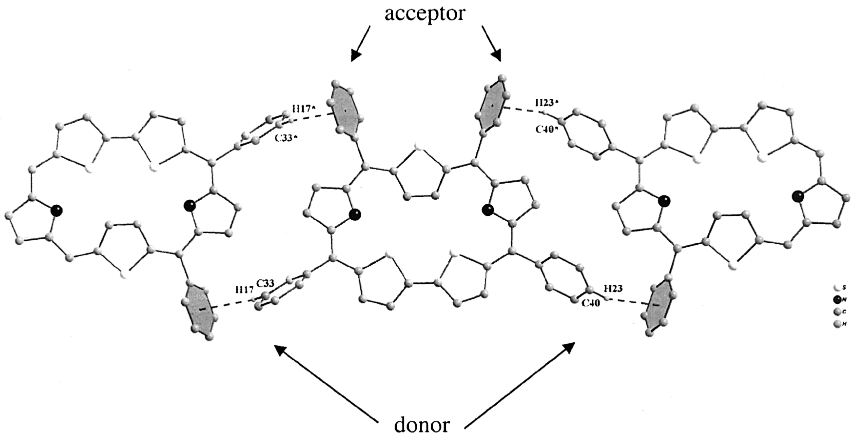
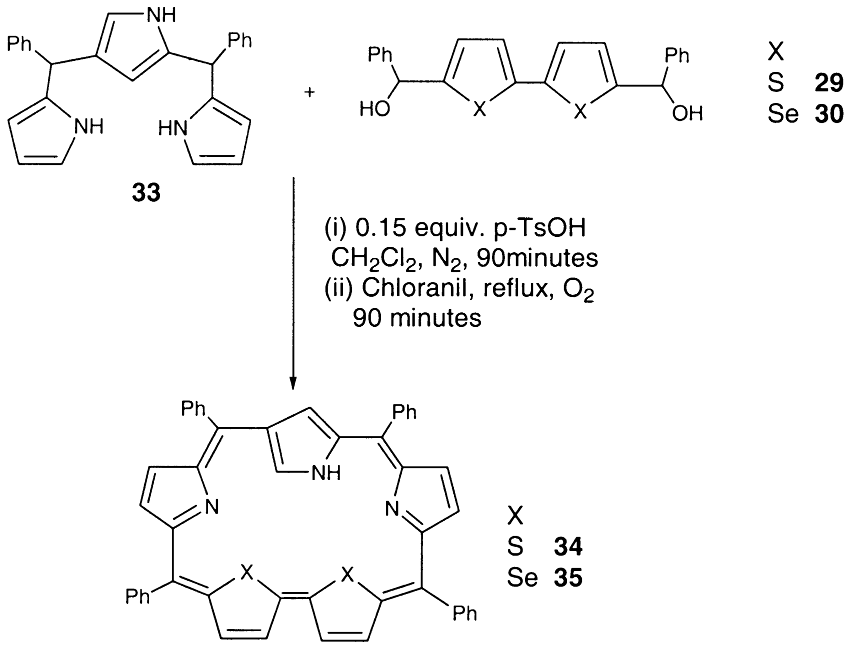


FIGURE 6 One dimensional array formed by **26** through C—H---π interactions. Noninteracting atoms are omitted for clarity.

and the remaining two meso phenyl rings act as proton acceptor. The metric parameters involved in the C—H---π interactions are 3.048(1) Å, 2.782(48) with their respective angles being 127.17(2)°, 146.92(2)°, respectively. This is an interesting example within a single sapphyrin molecule; both proton donor and acceptor interactions of the meso aryl rings are observed.

22 π Meso Aryl N-Confused Sapphyrin

The first 22-π-meso-aryl N-confused sapphyrin was reported by our group through a 3 + 2 MacDonald condensation reaction[33] (Scheme 8). The X-ray structure of **34** indicates that N-confused pyrrole opposite to bithiophene unit is inverted and makes a dihedral angle of 25.17° with respect to the mean plane containing 4 meso carbons. Four meso carbons are almost planar [deviations from the mean plane shown by meso carbons are C(5) 0.03, C(10) −0.02, C(20) 0.02, and C(24) −0.03 Å]. The dihedral angles for the other heterocyclic rings are 5.03°, 7.7°, 3.07° and 4.76°. There are two independent molecules present in the asymmetric unit cell, and a closer look into the packing revealed the presence of inter- and intramolecular hydrogen bonds. Specifically, there are 4 intramolecular hydrogen bonding interactions in each molecule involving C—H---N [2.82 Å, 110.57°, and 2.74 Å, 112.93°], C—H---S [3.35 Å, 121.42°, and 3.38 Å, 120.25°], N—H---N [2.69 Å, 114.74°, and 2.8 Å, 111.54°], and N—H---S [3.36 Å, 120.47°, and 3.35 Å, 122°], giving



SCHEME 8

rise to an 8-membered ring in chair conformation (Figure 7(a)). A further closer look at the packing diagram reveals the presence of two types of intermolecular hydrogen bonds: (1) one β-CH of the thiophene ring of one molecule with one of the core nitrogens of the pyrrole ring of the other molecule present in the unit cell [3.42 Å, 113.78°], and (2) the aromatic CH group of the meso-phenyl ring are involved in hydrogen bonding with the heteroatom [S/N] present in the core of the other molecule [C(36)-H(21)---S(3) 3.94 Å, 164.29°; C(80)-H(48)---S(1) 4.03 Å, 154.57°; C(26)-H(12)---N(2) 3.67 Å, 135.30°; and C(96)-H(62)---N(6) 3.36 Å, 121.24°]. These interactions are responsible for holding the molecule in a supramolecular array (Figure 7(b)). The torsion angle involving C(23)-C(24)-C(1)-N(1) is 12.5° and C(23)-C(24)-C(1)-C(2) is −160.1° for one molecule, while the similar torsion angles for the other is 15.8° and −163.4°. The differences in two types of pyrrole rings (confused and normal) also are reflected in bond distances; the C_α-C_β, C_β-C_β distances of confused pyrrole ring significantly are lower and higher, respectively, than those of normal pyrroles present in the macrocycle, suggesting the modified electron delocalization pathway.

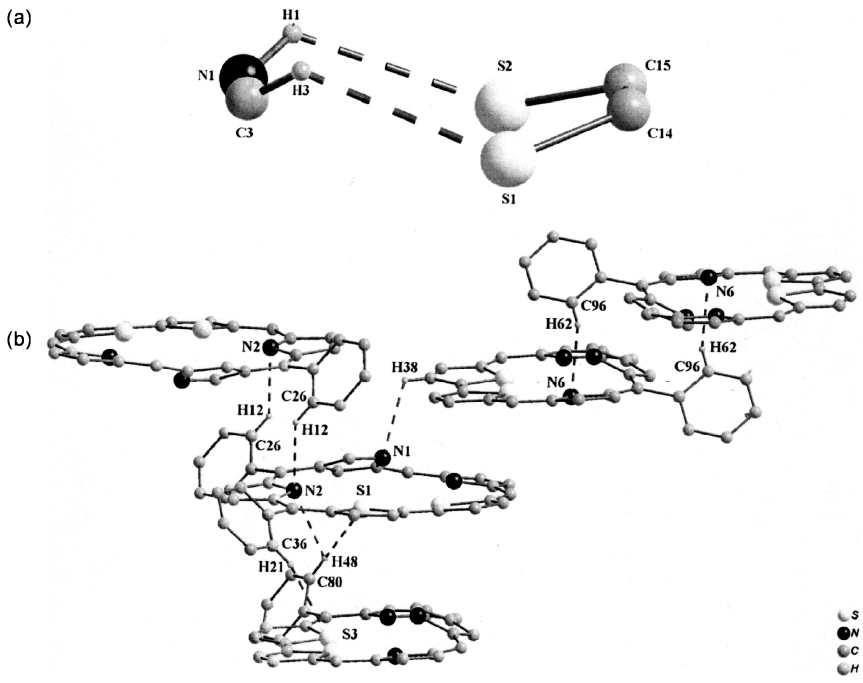


FIGURE 7 (a) Intramolecular hydrogen bonding between inverted N-confused pyrrole moiety and sulfur atoms of bithiophene unit leading to an eight membered chair conformation in **34**. (b) Intermolecular hydrogen bonding in **34** leading to supramolecular array. Noninteracting hydrogens are omitted for clarity in both the cases.

22 π Meso Aryl Smaragdyrin

Removal of one meso carbon from a sapphyrin skeleton leads to a new ring system with 22 π electrons, which has been named as smaragdyrin[1,2] (Chart 2). The structural relationship between sapphyrin and smaragdyrin is analogous to that between a porphyrin and a corrole, which are ubiquities in natural systems, performing diverse biological functions. Thus, smaragdyrin skeleton contains only three meso carbon bridges and two direct pyrrole-pyrrole links and can be considered as an expanded corrole. The chemistry of smaragdyrin is not as well developed as the chemistry of their sapphyrin analogues because of the difficulties encountered in the synthesis as well as its inherent instability. Even though Johnson and coworkers[34] were successful in the synthesis of partially β-substituted smaragdyrin, its instability toward acid and light prevented them from pursuing further studies. Only in 1997,

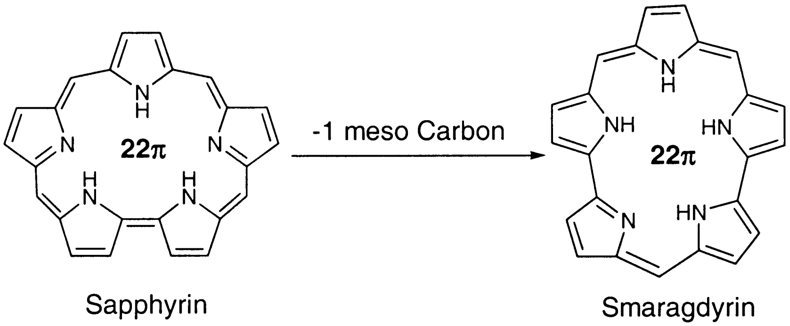
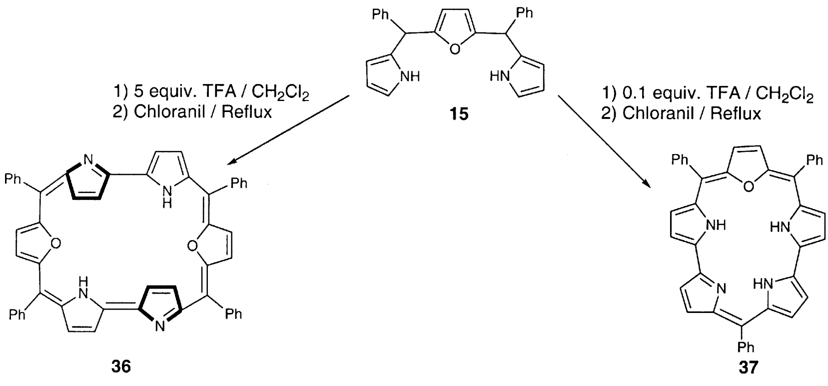


CHART 2

Sessler and coworkers[35] found that the stability of the smaragdyrin skeleton can be increased by substituting all the β-positions by alkyl substituents. They were successful in synthesizing a stable isomer of β-substituted smaragdyrin. Very recently, we were successful in the synthesis of stable meso aryl oxa smaragdyrin, **37** and reported its receptor properties towards anions and metal cations[36,37] (Scheme 9). Specifically, it has been shown that the meso aryl smaragdyrins are quite stable unlike their β-substituted analogues and can form stable metal and anion complexes. It has been shown that the Rh(I) ion binds to only two bipyrrolic nitrogens of smaragdyrin in an η^2 fashion while the Ni(II) ion binds to four bipyrrolic nitrogens in an η^4 fashion. The furan oxygen remains uncoordinated. In contrast, the Cl^- anion binds to the protonated form of smaragdyrin. The solid state structure of Cl^- complex of **37** shows the coordination of the chloride ion and chloride ion is found above the plane of the macrocycle and is held by three



SCHEME 9

N—H---Cl hydrogen bonding interactions. Specifically, out of the four pyrrole –NH groups available, only three –NH groups are involved in the N—H---Cl hydrogen bonds which are pointed toward the chloride atom. These hydrogen bonding distances compare well [3.176, 3.039, and 3.200 Å] with that observed for the monoprotonated chloride salt of a β-substituted dioxasapphyrin.[38] However, the binding seen here slightly is different from that observed for the monoprotonated chloride salt of the smaragdyrin isomer where all four nitrogens are involved in binding to the chloride anion.[35] A closer inspection into the structure reveals the formation of a dimer mediated through C—H---N interactions. One of the *meta*-protons of the meso phenyl ring is hydrogen bonded to the pyrrole nitrogen of adjacent smaragdyrin molecule [average C—H ---N distance 2.614 Å, 153.48°]. Further, this dimer is converted into one-dimensional linear structure through C—H---π and C—H---Cl interactions. The *ortho*-protons of the meso phenyl ring of one smaragdyrin molecule interact with the pyrrole π-cloud (The pyrrole ring involved is shaded in the figure.) of the adjacent molecule (C—H---π centroid distance is 2.705 Å and bond angle is 169.10°), while the *meta*-proton of the same phenyl ring is involved in a non-classical H---Cl interaction with the bound Cl^- ion of the adjacent smaragdyrin molecule. This one dimensional structure is extended to the second dimension through the interaction of the β-CH proton of the pyrrole ring of one smaragdyrin molecule with bound Cl^- ion of the second smaragdyrin molecule resulting in the formation of a two dimensional sheet like network as shown in Figure 8 (The metric parameters involved in the C—H---Cl interactions are 2.796(2) Å, 2.809(1) Å, and respective angles being 141.60°, 138.40°.).

26 π MESO ARYL RUBYRINS

Expanded porphyrins containing six pyrrole/heterocyclic rings linked through four meso carbons in a cyclic fashion are termed as rubyrins.[1,2] Thus, in a rubyrin structure there are two direct pyrrole-pyrrole links and four meso carbon bridges. They are 26 π electron systems and exhibit aromatic properties following the [4n + 2] Hückel rule. The name rubyrin arises because of its intense orange color in dichloromethane solution. Sessler and coworkers were the first to synthesize the 26 π rubyrin **39** by an acid-catalyzed condensation of appropriate precursors[1,2] (Scheme 10). Later on, Vogel's group reported the hexathia rubyrin **40** by an acid-catalyzed condensation between the dithiophene dialcohol and 3,4-diethylthiophene[39] (Scheme 11). We have reported the synthesis of meso aryl rubyrins **44–48** by either acid-catalyzed

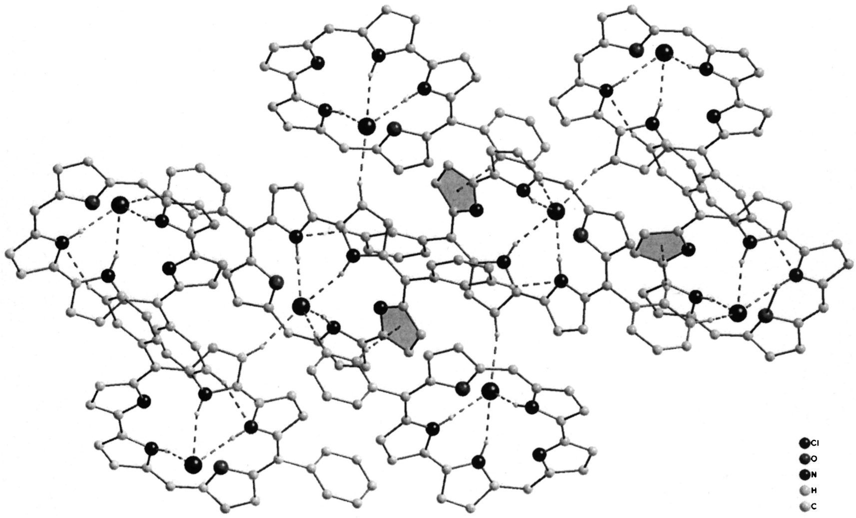
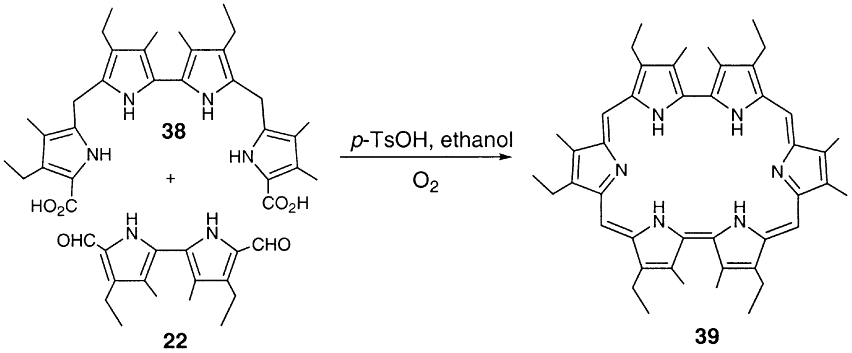
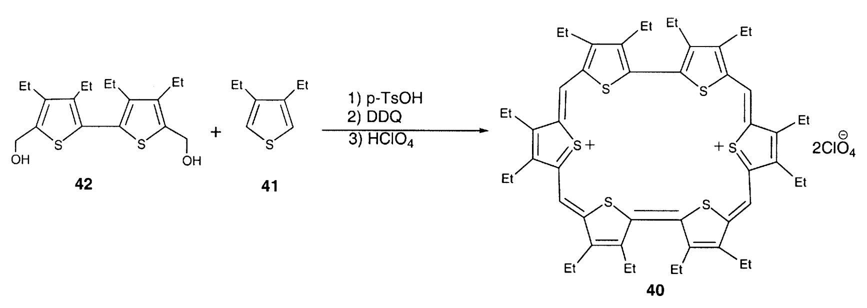


FIGURE 8 Two dimensional network formed by **37**. The appropriate interactions are shown by dotted lines. The pyrrole ring involved in C—H---π interactions are shaded. Only interacting hydrogens and meso phenyl rings are shown.

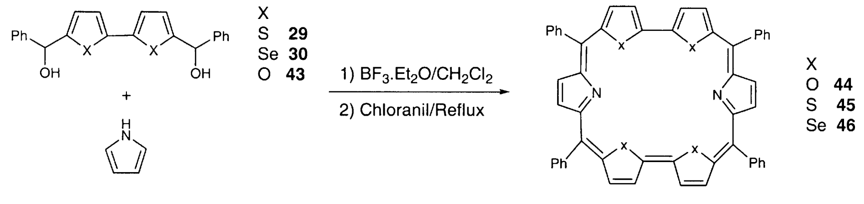


SCHEME 10

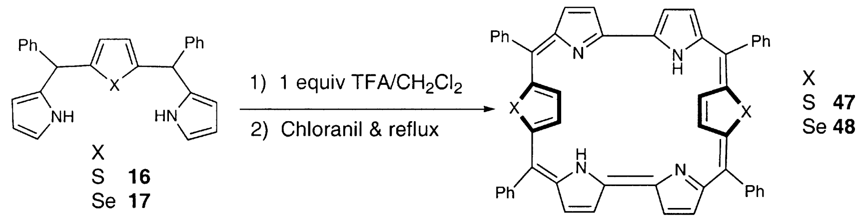
condensation reaction[27] or the oxidative coupling reaction[32] of appropriate precursors (Schemes 12 and 13). Meso-substituted rubyrins also show structural diversity similar to that observed to meso aryl sapphyrins.[9] Three different types of structures have been observed for *meso* aryl rubyrins both in solution and in solid state.[10] They are planar as in **45**, where the all the 6 heteroatoms are pointing towards the ring-current region and the β-CH protons projecting away. In the partially



SCHEME 11



SCHEME 12



SCHEME 13

inverted structure, as in **47/48**, the 2 thiophene or 2 selenophene linked to the bipyrrolic units have undergone a 180° ring flipping in such a way that the β-CH protons of thiophene/selenophene point towards the ring-current region and the sulphur/oxygen atoms point away from the ring-current region. On the other hand, **36** also shows a partially inverted structure where one of the pyrrole ring on each bipyrrolic unit exhibits a 180° ring flipping, giving rise to a new type of inverted structure.[10]

Anion Binding Studies

Protonation of two pyrrole nitrogens leads to the formation of dicationic species with two positive charges delocalized inside the cavity(2).

Thus, the diprotonated form of rubyrins are expected to have affinity for the anions. For example, spectral titrations of a methanolic solution of diprotonated [**44**.H_2]$^{2+}$ with anions result in decrease in absorbance, a blue shift of the Soret band by about 30 nm, and a blue shift of the emission band by about 15 nm together with enhanced emission intensity. These observations suggest anion binding and the binding constants evaluated by an analysis of absorption data vary as $N_3^- > \text{AMP} > F^-$ (Chart 3). It is shown that the binding constants depend on (1) the complementarity of the anion size and the cavity size available, and (2) the number of hydrogen bonding sites available inside the cavity. The lower-binding constants observed for F^- complexes reflect mis-match of the sizes of the F^- ion and the rubyrin cavity. In the core-modified rubyrins, the cavity size will be different for rubyrins depending on the size of the heteroatoms. The binding constants observed for N_3^- and CO_3^{2-} complexes are orders of magnitude lower compared to the all-aza rubyrin complexes because of the decrease in the number of hydrogen bonding sites in **44** and **45**. The higher value for the CO_3^{2-} relative to the N_3^- in part is attributed to the complete charge neutralization for CO_3^{2-} as against partial charge neutralization for N_3^- complex.[27]

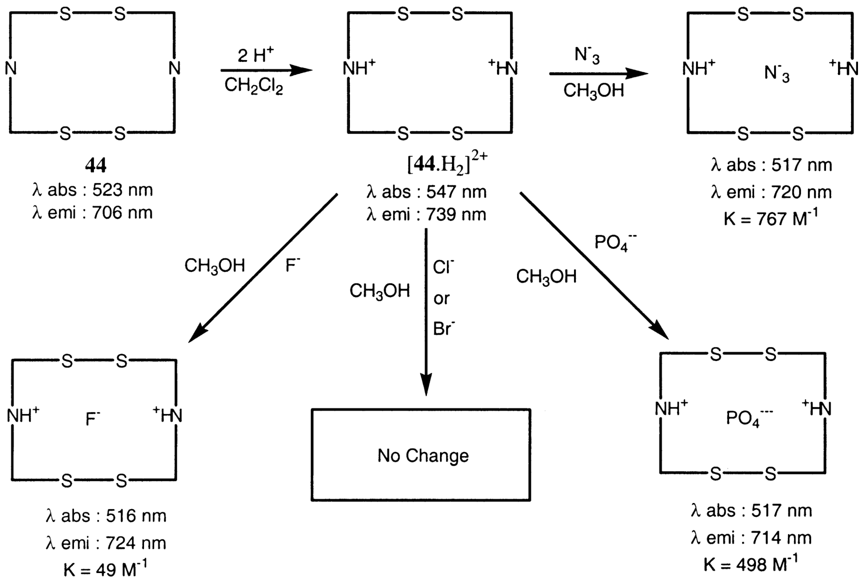


CHART 3

Supramolecular Assemblies Through C—H---π Interactions in Rubyrins

The single crystal X-ray structure of **46** as expected shows a noninverted structure with all the six hetero atoms are in the core of the macrocycle.[10] The rubyrin almost is planar with only small deviations from the mean plane. Specifically, 1 of the selenophene rings of the bis-selenophene unit is deviated by 6.18°, while the other deviates 1.45° from the mean rubyrin plane. A closer look at the packing diagram revealed the formation of a one-dimensional array of rubyrins mediated by strong C—H---π interactions between the CH proton of the meso phenyl ring of one rubyrin and the pyrrole π-cloud of the adjacent rubyrin. The C—H---π centroid distance observed is 2.644 Å with an angle of 155.53°[8] (Figure 9). The distances of the heteroatoms of the pyrrole ring which was a π-acceptor [four carbons and one nitrogen] were almost similar in the range from 2.803–2.956 Å revealing an almost symmetric interaction with the aromatic π-cloud of the heterocyclic ring. On the other hand the rubyrin **48** exhibit a inverted structure in which the two selenophene rings are inverted, and both of the selenophene rings are above the mean plane defined by four meso carbons.[40] The unit cell contains two crystallographically independent molecules with a molecule of ethanol coordinated to one of them. There are five nitrobenzene solvent molecules also present in the unit cell. Of the five nitrobenzene molecules, two pairs of nitrobenzenes are involved in a π-π [face-to-face] interaction among themselves (the π-π distances are 3.959(2) Å and 3.882(1) Å). The fifth nitrobenzene molecule is involved in a moderately strong π-π interaction with one of the pyrrole rings of the rubyrin [π-π distance 3.741 Å][3] (Figure 10). Furthermore, the two oxygens of the nitro group on the nitrobenzene are involved in

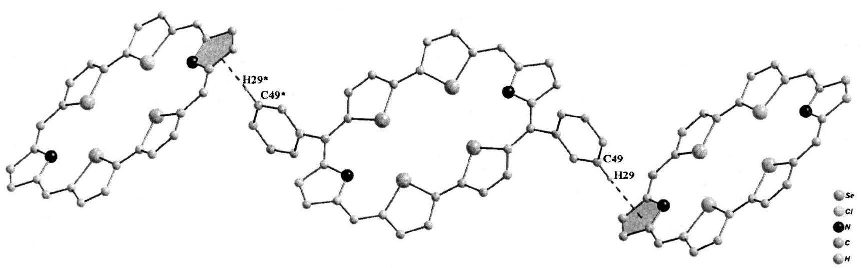


FIGURE 9 One dimensional array formed by **46** through C—H---π interactions. The pyrrole ring involved is shaded. Noninteracting hydrogens and meso phenyl rings are omitted for clarity.

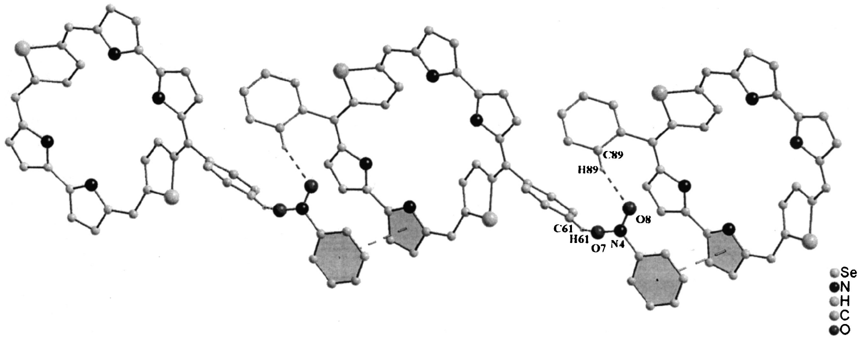


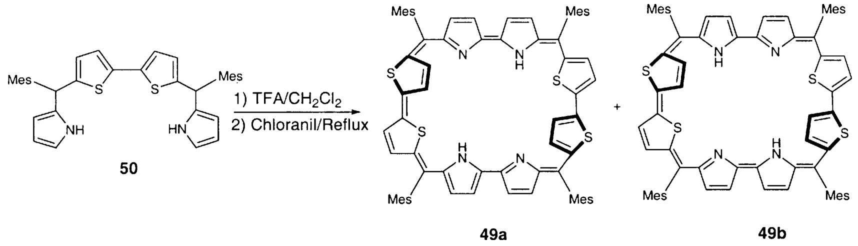
FIGURE 10 Nitrobenzene mediated one dimensional array formed by **48**. The pyrrole ring and benzene ring of nitrobenzene involved in π---π interactions are shaded. Meso phenyl rings and noninteracting hydrogens atoms that are not involved in the hydrogen bonding interactions are omitted for clarity.

two C—H---O interactions. Specifically, one oxygen is interacting with the *meta*-proton of the meso phenyl ring of one rubyrin while the other oxygen is interacting with the *para*-proton of the meso phenyl ring of the adjacent molecule leading to the formation of polymeric one dimensional array of rubyrins (The metric parameters for C—H---O interactions are 2.465(7) Å, 156.37°, and 2.531(14) Å, 133.40°). Thus, the one-dimensional array in **48** is mediated by the nitrobenzene solvent present in the crystal as solvent of crystallization.

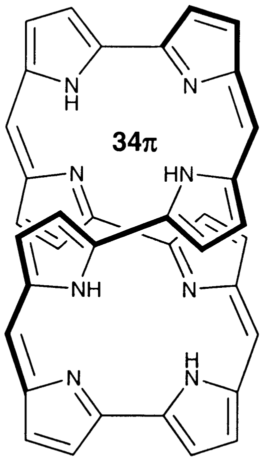
34 π MESO ARYL OCTAPHYRINS

Octaphyrins are macrocycles having eight pyrrole/heterocyclic rings that are interconnected by meso carbons in cyclic fashion. Vogel and co-workers[41] were first to report the formation of cyclooctapyrrole **51** during the synthesis of porphyrin isomer. Later, several groups reported successful syntheses of a range of octaphyrins.[1,2] However, none of them exhibit aromatic character because of their figure-eight conformation in the solid state. Recently, we were successful in (Scheme 14) synthesis-modified meso aryl octaphyrins **49**, **52**, and **53** (Chart 4), which exhibit perfect aromaticity both in solution and solid state.[42] The single crystal X-ray structure of **49** shows inversion on one thiophene ring in each of bithiophene units and the macrocycle is perfectly planar.

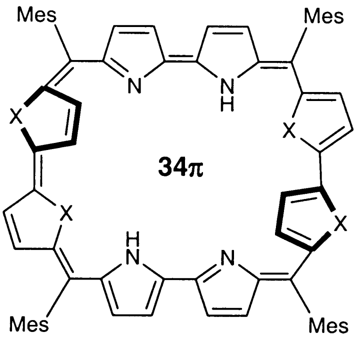
The protonated form of **49**, **52**, and **53** binds anion in both solution and solid state.[43] Specifically, **52** binds trifluoroacetate (TFA) anion in the ratio 1:2, where the TFA molecules are found above and below the plane of the macrocycle and the binding is through hydrogen bonding



SCHEME 14



51



X	
S	**49**
Se	**52**
O	**53**

CHART 4

interactions involving N—H and C—H protons of the octaphyrin with oxygen atom of the TFA anion. The X-ray structure of the anion complex (Figure 11) indicates four hydrogen bonding interactions are responsible for the binding of each TFA ion to the macrocycle. They are (1) N2-H--O1 [2.232 Å, 143.67°], (2) N2-H--O1 [2.139 Å, 146.64°], (3) C11-H--O1 [2.444 Å, 171.04°], and (4) C34-H--F2 [2.323 Å, 146.22°]. Of the above four interactions, the first two are typical electrostatic interactions. The protonation of the imino type nitrogens creates a positive charge, which attracts the counter anion [CF_3COO^-]. The other two interactions probably are induced due to the geometric features of the anion and the macrocycle in the complex. The β-CH of the inverted selenophene ring forms a strong hydrogen bond with the Oxygen of the —OH group in TFA. The proximity for the interaction is clearly evident

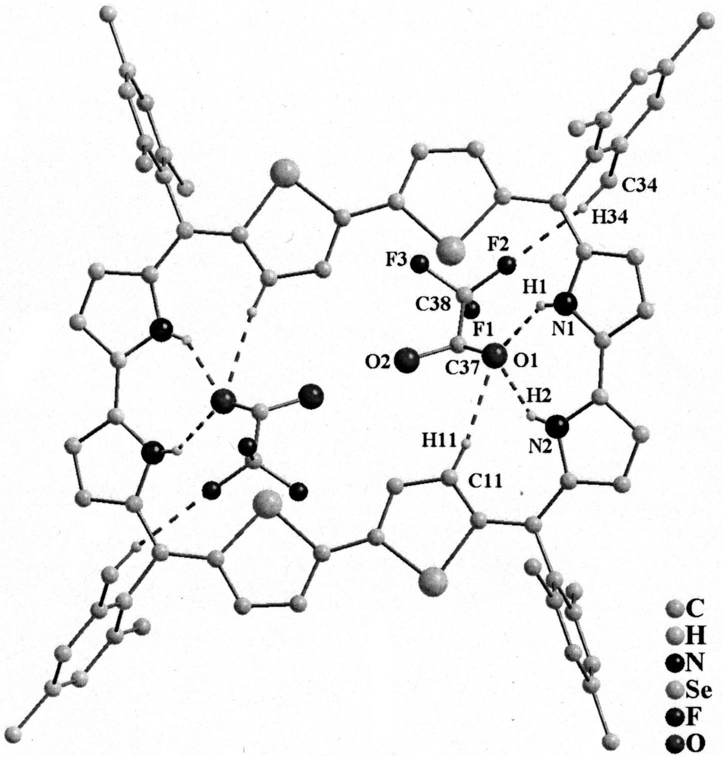


FIGURE 11 Top view of TFA bound complex of **52**. The hydrogen bonding interactions involved are shown in dotted lines. The noninteracting hydrogens are omitted for clarity.

from the near-linear bond angle, which is one of the strong reasons for the existence of this hydrogen bond. Such an interaction could be only comprehended due to the complete inversion of the selenophene ring. Due to such geometry, the β-CH of the inverted ring comes in plane with the –CO of the TFA as supported by the bond angle of 171.04°. Another important interaction observed was between the fluorine of the TFA and the hydrogen of the methyl group on the meso mesityl ring between the noninverted heterocyclic rings. Two such interactions are observed due to the binding of two anions to the macrocycle. Such type of intramolecular hydrogen bonding between the meso substituent of the macrocycle and the guest molecule defines novel binding modes between the host and the guest in expanded porphyrins.

Further analysis on hydrogen bonding revealed that octaphyrins form one-dimensional supramolecular array (Figure 12) through

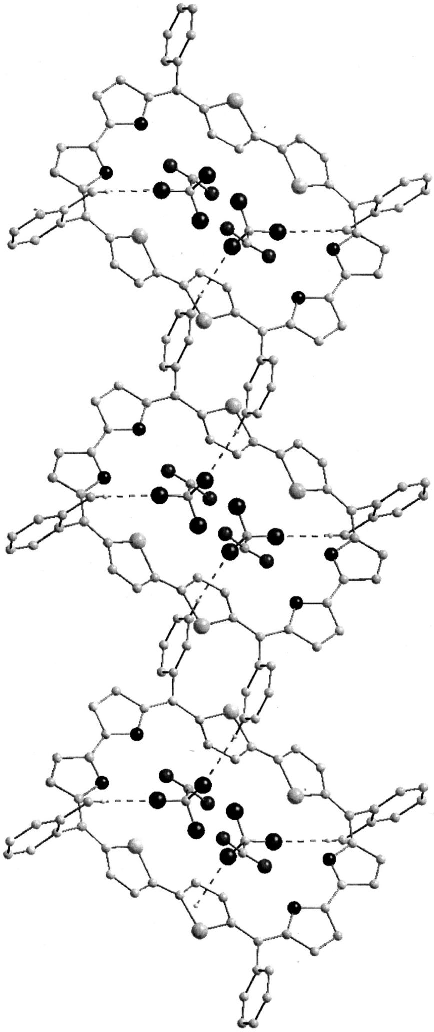


FIGURE 12 A view of the one dimensional array formed by TFA complex of **52**. The various hydrogen bonding interactions are shown in dotted lines.

intermolecular C—H--F hydrogen bonds [C—H--F: 2.55 Å; 149.43°]. This array is formed through the involvement of the aromatic CH from the meso-mesityl rings adjacent to the inverted selenophene rings and one of the fluorine from the TFA. As schematically described, two TFA molecules are sandwiched between two octaphyrins, which approximately are separated by a distance of 13 Å . To the first octaphyrin, the TFA is bound to pyrrolic nitrogens, inverted ring proton, and the methyl group of the mesityl ring. At the other end it has two fluorine atoms free. One of them forms a weak hydrogen bond with the aromatic CH of the mesityl ring from the second octaphyrin. A complementary interaction between the TFA from the second octaphyrin to the first one makes the interaction stronger. Such interactions continue to add up over each octaphyrin molecule, thus forming the supramolecular array in one dimension.

CONCLUSIONS

The examples discussed in this brief account demonstrate that self-assembling procedures provide unique and promising methods for construction of highly ordered, complex, expanded porphyrin supramolecular assemblies through noncovalent interactions. The availability of efficient synthetic methods for the synthises of expanded porphyrins and an understanding of the construction principles which govern the self assembly processes should allow one to build supramolecular architecture with unique physical and chemical properties useful for specific applications. In this direction, the recent observation of a large third-order optical susceptibility[44] of a self assembled porphyrin oligomer [$\chi^3 \sim 1 \times 10^{-9}$ esu] and the conjugated porphyrin tapes with electronic absorption into IR region is an encouraging sign to their future as photo electronic materials.[45]

REFERENCES

[1] J. L. Sessler, A. Gebauer, and S. J. Weghorn, *Porphyrin Handbook*, K. M. Kadish, K. M. Smith, and R. Guilard, Eds. (Academic Press, San Diego: 1999),Vol. II, Chap. 9, pp. 55–124.

[2] J. L. Sessler and S. J. Weghorn, *Expanded, Contracted & Isomeric Porphyrins*, (Elsevier Science Ltd.: 1997), Chap. 10, pp. 429–503.

[3] J. L. Sessler and J. M. Davis, *Acc. Chem. Res.*, **34,** 989, (2001).

[4] R. K. Pandey and G. Zheng, *Porphyrin Handbook*, K. M Kadish, K. M. Smith, and R. Guilard, Eds., (Academic Press, San Diego: 1999), Vol. VI, Chap. 43, pp. 157–230.

[5] J. H. Chou, H. S. Nalwa, M. E. Kosal, N. A. Rakow, and K. S. Suslick, *Porphyrin Handbook*, K. M. Kadish, K. M. Smith, and R. Guilard, Eds. (Academic Press, San Diego: 1999), Vol. VI, Chap. 41, pp. 43–132.

[6] H. Furuta, T. Asano, and T. Ogawa, *J. Am. Chem. Soc.*, **116,** 767 (1994).

[7] P. J Chemielewski, L. Latos-Grazynski, K. Rachlewicz, and T. Glowiak, *Angew. Chem. Int. Ed. Engl.*, **33,** 779 (1994).

[8] H. Furuta, H. Maeda, and A. Osuka, *Chem. Commun.*, 1795, (2002)

[9] A. Srinivasan, V. G. Anand, S. J. Narayanan, S. K. Pushpan, M. R. Kumar, T. K. Chandrashekar, K.-I. Sugiura, and Y. Sakata, *J. Org. Chem.*, **64,** 8693 (1999).

[10] S. J. Narayanan, A. Srinivasan, B. Sridevi, T. K. Chandrashekar, M. O. Senge, K.-I. Sugiura, and Y. Sakata, *Eur. J. Org. Chem.*, 2357 (2000).

[11] B. Y. Liu, C. Bruckner, and D. Dolphin, *Chem. Commun.,* 2141 (1996).

[12] S. K. Pushpan, A. Srinivasan, V. G. Anand, T. K. Chandrashekar, A. R. Subramanian, R. Roy, K.-I. Sugiura, and Y. Sakata, *J. Org. Chem.*, **66,** 153 (2001).

[13] G. R. Geier III and J. S. Lindsey, *J. Org. Chem.*, **64,** 1596 (1999).

[14] G. R. Geier III, D. M. Haynes, and J. S. Lindsey, *Org. Lett.*, **1,** 1455 (1999).

[15] T. D. Lash, T. D. Richter, and C. M. Shiner, *J. Org. Chem.*, **64,** 7973 (1999).

[16] L. Szterenberg and L. Latos-Grazynski, *Inorg. Chem.,* **36,** 6287 (1997).

[17] P. J. Chemielewski, L. Latos-Grazynski, and T. Glowiak, *J. Am. Chem. Soc.*, **118,** 5690 (1996).

[18] P. J. Chemielewski, L. Latos-Grazynski, and I. Schmidt, *Inorg. Chem.*, **39,** 5475 (2000).

[19] H. Furuta, T. Ogawa, Y. Uwatoko, and K. Araki, *Inorg. Chem.*, **38,** 2676 (1999).

[20] H. Furuta, N. Kubo, H. Maeda, T. Ishizuka, A. Osuka, H. Nanami, and T. Ogawa, *Inorg. Chem.*, **39,** 5424 (2000).

[21] T. Ogawa, H. Furuta, M. Takahashi, A. Morino, and H. Uno, *J. Organomet. Chem.*, **611,** 551 (2000).

[22] A. Ghosh, *Angew. Chem. Int. Ed. Engl.*, **107,** 1117 (1995).

[23] P.-Y. Heo, K. Shin, and C.-H. Lee, *Tetrahedron Lett.*, **37,** 1521 (1996).

[24] E. Pacholska, L. Latos-Grazynski, L. Szterenberg, and Z. Ciunik, *J. Org. Chem.*, **65,** 8188 (2000).

[25] V. J. Bauer, D. L. J. Clive, D. Dolphin, J. B. Paine III, F. L. Harris, M. M. King, J. Loder, and S. C. Wang, *J. Am. Chem. Soc.*, **105,** 6429 (1983).

[26] P. J. Chmielewski, L. Latos-Grazynski, and K. Rachelewicz, *Chem. Eur. J.*, **1,** 68 (1995).

[27] A. Srinivasan, V. R. M. Reddy, S. J. Narayanan, B. Sridevi, S. K. Pushpan, M. R. Kumar, and T. K. Chandrashekar, *Angew. Chem. Int. Ed. Engl.*, **36,** 2598 (1997).

[28] A. Srinivasan, S. K. Pushpan, M. R. Kumar, T. K. Chandrashekar, and R. Roy, *Tetrahedron*, **55,** 6671 (1999).

[29] A. Srinivasan, S. Mahajan, M. K. Kumar, S. K. Pushpan, and T. K. Chandrashekar, *Tetrahedron Lett.*, **39,** 1961 (1998).

[30] S. K. Pushpan, V. G. Anand, S. Venkatraman, A. Srinivasan, A. K. Gupta, and T. K. Chandrashekar, *Tetrahedron Lett.*, **42,** 3391 (2001).

[31] A. Srinivasan, V. G. Anand, S. J. Narayanan, S. K. Pushpan, T. K. Chandrashekar, K.-I. Sugiura, and Y. Sakata, *J. Chem. Soc., Perkin Trans.*, **2,** 1788 (2000).

[32] S. J. Narayanan, B. Sridevi, T. K. Chandrashekar, A. Vij, and R. Roy, *Angew. Chem. Int. Ed.*, **37,** 3394 (1998).

[33] S. K. Pushpan, A. Srinivasan, V. G. Anand, S. Venkatraman, T. K. Chandrashekar, B. S. Joshi, R. Roy, and H. Furuta, *J. Am. Chem. Soc.*, **123,** 5138 (2001).

[34] M. J. Broadhurst, R. Grigg, and A. W. Johnson, *J. Chem. Soc., Perkin Trans. 1*, 2111 (1972).

[35] J. L. Sessler, J. M. Davis, and V. Lynch, *J. Org. Chem.*, **63,** 7062 (1998).

[36] S. J. Narayanan, B. Sridevi, and T. K. Chandrashekar, *Org. Lett.*, **1,** 587 (1999).

[37] B. Sridevi, S. J. Narayanan, R. Rao, T. K. Chandrashekar, U. Englich, and K. R. Senge, *Inorg. Chem.*, **39,** 3669 (2000).

[38] J. L. Sessler, M. C. Hoehner, A.Gebauer, A. Andrievsky, and V. Lynch, *J. Org. Chem.*, **62,** 9251 (1997).

[39] E. Vogel, M. Pohl, A. Herrmann, T. Wiss, C. Konig, J. Lex, M. Gross, and J. P. Gisselbrecht, *Angew. Chem. Int. Ed. Engl.*, **35,** 1529 (1996).

[40] S. J. Narayanan, B. Sridevi, T. K. Chandrashekar, A. Vij, and R. Roy, *J. Am. Chem. Soc.*, **121,** 9053 (1999).

[41] E. Vogel, M. Broring, J. Fink, D. Rosen, H. Schmickler, J. Lex, K. W. K. Chan, Y.-D. Wu, D. A. Plattner, M. Nendel, and K. N. Houk, *Angew. Chem. Int. Ed. Engl.*, **34,** 2511 (1995).

[42] V. G. Anand, S. K. Pushpan, S. Venkatraman, A. Dey, T. K. Chandrashekar, B. S. Joshi, R. Roy, W. Teng, and K. R. Senge, *J. Am. Chem. Soc.*, **123,** 8620 (2001).

[43] V. G. Anand, S. Venkatraman, H. Rath, T. K. Chandrashekar, W. Teng, and K. R. Senge, *Chem. Eur. J.*, **9,** 2282 (2003).

[44] K. Ogawa, T. Zhang, K. Yoshihara, and Y. Kobuke, *J. Am. Chem. Soc.*, **124,** 22 (2002).

[45] A. Tsuda and A. Osuka, *Science*, **293,** 79 (2001).