ACCOUNTS
of chemical research

Smaragdyrins: Emeralds of Expanded Porphyrin Family

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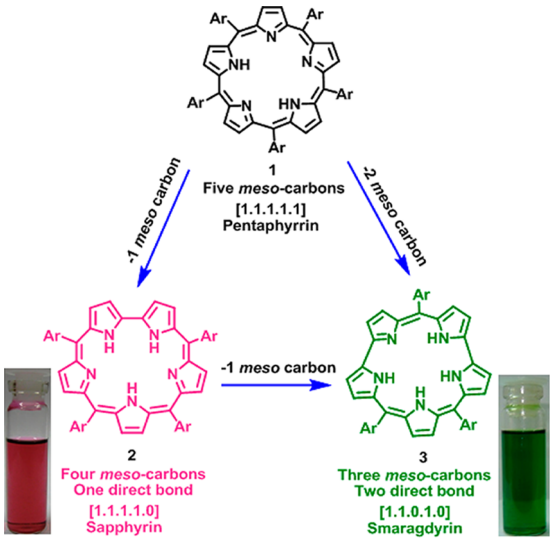
RECEIVED ON MAY 7, 2012

CONSPECTUS

Porphyrins are tetrapyrrolic 18 π electron conjugated macrocycles with wide applications that range from materials to medicine. Expanded porphyrins, synthetic analogues of porphyrins that contain more than 18 π electrons in the conjugated pathway, have an increased number of pyrroles or other heterocyles or multiple *meso*-carbon bridges. The expanded porphyrins have attracted tremendous attention because of unique features such as anion binding or transport that are not present in porphyrins. Expanded porphyrins exhibit wide applications that include their use in the coordination of large metal ions, as contrasting agents in magnetic resonance imaging (MRI), as sensitizers for photodynamic therapy (PDT) and as materials for nonlinear optical (NLO) studies. Pentaphyrin 1, sapphyrin 2, and smaragdyrin 3 are expanded porphyrins that include five pyrroles or heterocyclic rings. They differ from each other in the number of bridging carbons and direct bonds that connect the five heterocyclic rings. Sapphyrins were the first stable expanded porphyrins reported in the literature and remain one of the most extensively studied macrocycles. The strategies used to synthesize sapphyrins are well established, and these macrocycles are versatile anion binding agents. They possess rich porphyrin-like coordination chemistry and have been used in diverse applications.



This Account reviews developments in smaragdyrin chemistry. Although smaragdyrins were discovered at the same time as sapphyrins, the chemistry of smaragdyrins remained underdeveloped because of synthetic difficulties and their comparative instability. Earlier efforts resulted in the isolation of stable β-substituted smaragdyrins and *meso*-aryl isosmaragdyrins. Recently, researchers have synthesized stable *meso*-aryl smaragdyrins by [3 + 2] oxidative coupling reactions. These results have stimulated renewed research interest in the exploration of these compounds for anion and cation binding, energy transfer, fluorescent sensors, and their NLO properties. Recently reported results on smaragdyrin macrocycles have set the stage for further synthetic studies to produce stable *meso*-aryl smaragdyrins with different inner cores to study their properties and potential for various applications.

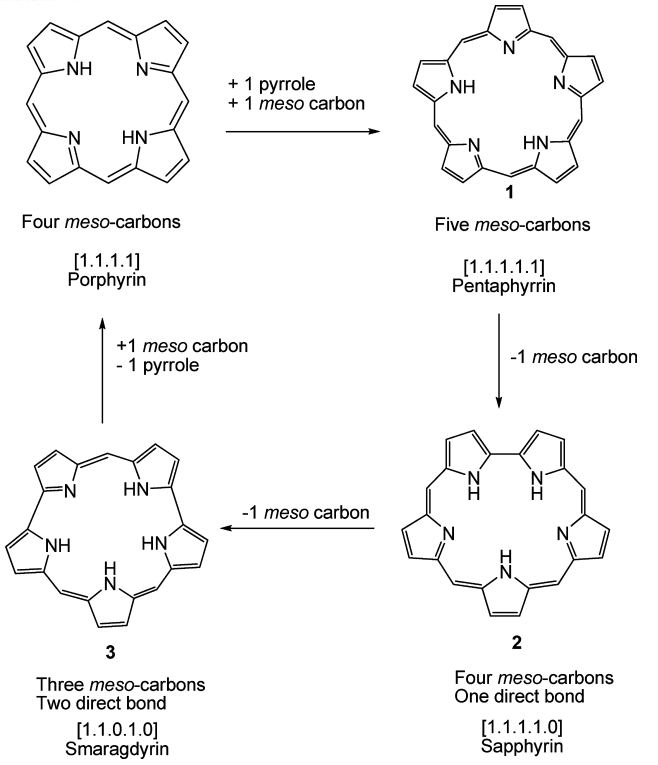
1. Introduction

Porphyrins are macrocycles containing an 18 π electron conjugation pathway. Structurally, four pyrrole rings are covalently linked to each other through four *meso*-carbon bridges. Porphyrins or the metalloporphyrins present at the active site of numerous biomolecules serve a variety of critical roles in living systems.[1] Consequently, porphyrins remain among the most widely studied of all macrocyclic systems. The scope of research on porphyrins has broadened with the emergence of core-modified porphyrins,[2] which result from the replacement of one or two pyrrole nitrogen(s) with other donor atoms such as O, S, Se, Te, C,

Published on the Web 08/31/2012 www.pubs.acs.org/accounts
10.1021/ar300136s

P, and Si in a porphyrin ring. Porphyrins, core-modified porphyrins, and related tetrapyrrolic macrocyles continued to attract the attention of researchers because of their wide variety of applications. On the other hand, the expanded porphyrins are synthetic analogues of porphyrins but differ from porphyrins in containing more than 18 π electrons in the conjugated pathway either due to an increased number of pyrroles or due to multiple *meso*-carbon bridges. In the last few decades, chemists have been fascinated with expanded porphyrins due to their special anion complexing ability, which porphyrins do not possess, and also because of their applications that range from materials to medicine.[3] Some of the significant applications of expanded porphyrins include coordination of large cations like lanthanides and actinides, anion complexation and transport, magnetic

CHART 1



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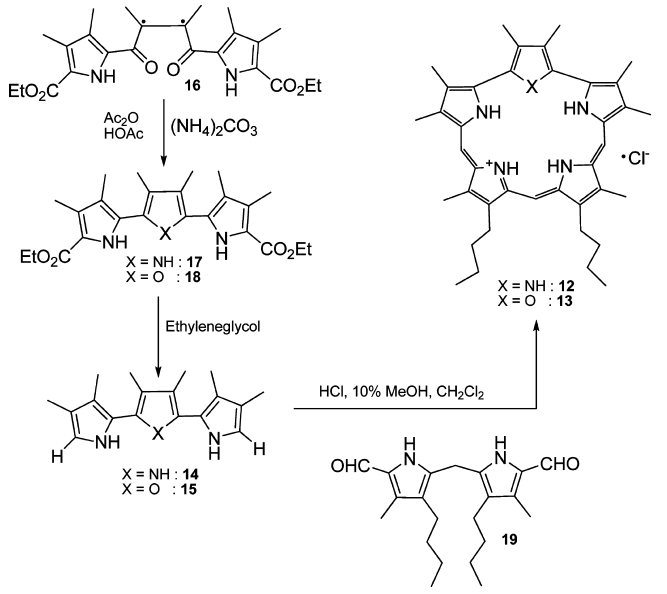

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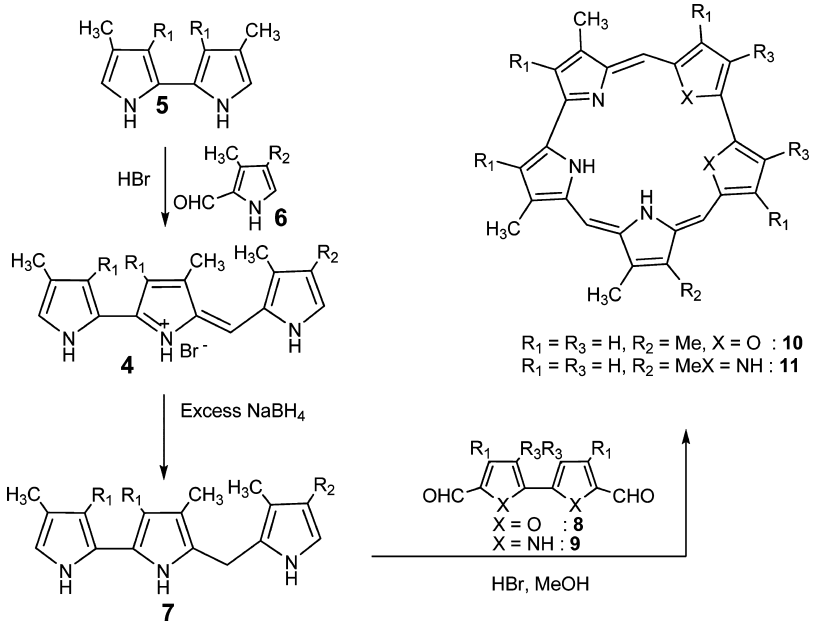

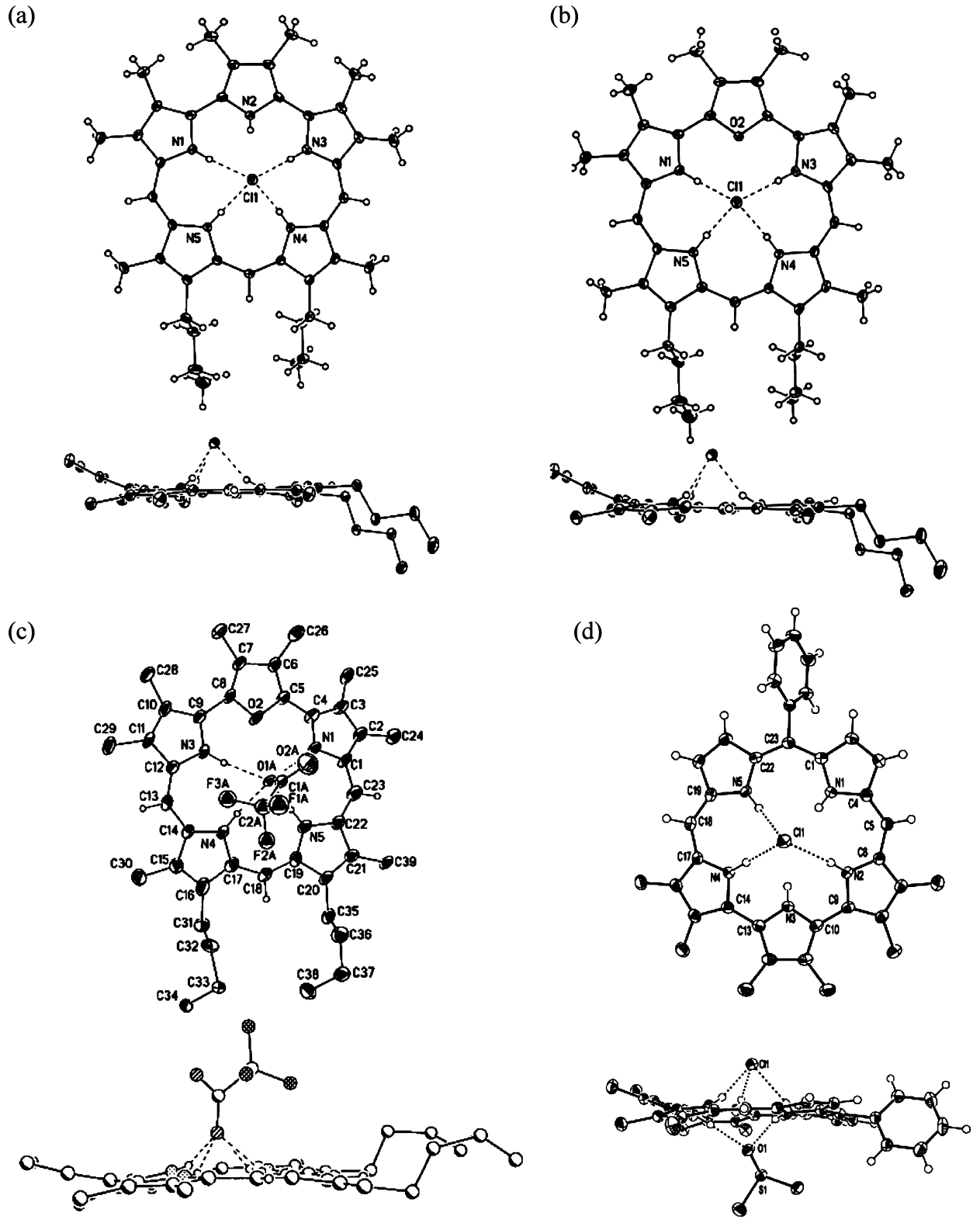

FIGURE 1. X-ray structure of (a) $\mathbf{12H^+ \cdot Cl^-}$, (b) $\mathbf{13H^+ \cdot Cl^-}$, (c) $\mathbf{13H^+ \cdot CF_3COO^-}$, and (d) $\mathbf{20aH^+ \cdot Cl^-}$.

resonance imaging (MRI) contrasting agents, photodynamic therapy (PDT) sensitizers, building blocks in nonlinear optical (NLO) materials, and issues related to aromaticity. The core-modified expanded porphyrins containing one or more heteroatoms in the place of pyrrole NH have also been known for a long time but gained momentum recently

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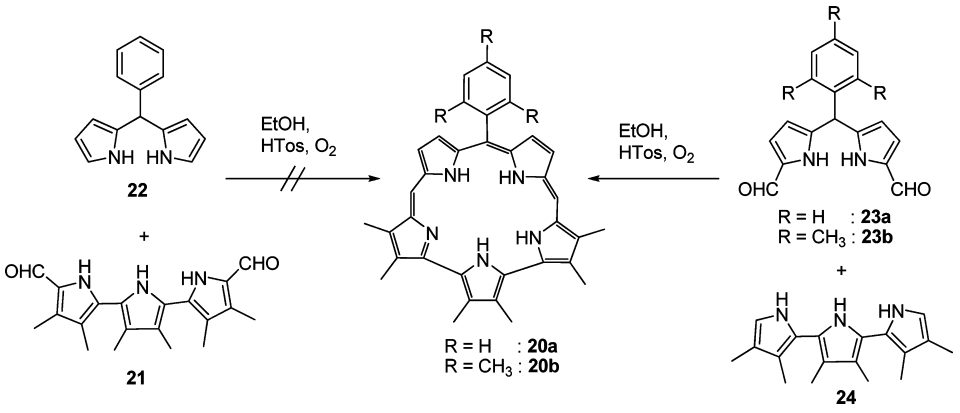

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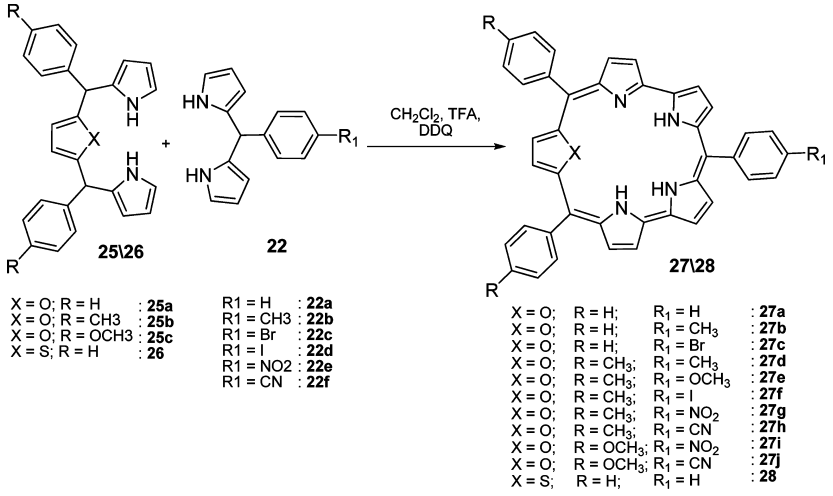


because of the availability of easier synthetic routes and interesting electronic properties.[4] Many expanded porphyrins containing more than four pyrroles or heterocycles are known today, and their potential for various applications is continuously under investigation.[3] The pioneering efforts of several research groups blossomed the expanded porphyrin chemistry and showed that the expanded porphyrins are indeed very useful synthetic analogues of porphyrins and can be used for various applications.[5] The tremendous growth in expanded porphyrin chemistry in recent years resulted in few excellent reviews covering various aspects of their chemistry by experts from the field.[3,5]

The expanded porphyrins containing five pyrroles or heterocycles are the immediate higher homologues of tetrapyrrolic porphyrins. There are three types of expanded porphyrin systems containing five pyrroles or heterocyclic rings; pentaphyrin **1**, sapphyrin **2**, and smaragdyrin **3** (Chart 1). These are 22 π electron conjugated systems containing an additional pyrrole or a heterocyclic ring compared with porphyrin but differ from each other in the number of bridging carbons and direct bonds that connect the five heterocyclic rings. Pentaphyrin contains five methine bridges; sapphyrin contains four methine bridges and one direct bond, and smaragdyrin contains three methine bridges and two direct bonds connecting the five pyrrole/heterocyclic rings. Interestingly, pentaphyrin was synthesized in 1983 by Rexhausen and Gossauer,[6] but sapphyrin is the first expanded macrocycle reported by Woodword and co-workers at an aromatic conference[7] in 1966. In 1990, Sessler and co-workers[8] serendipitously discovered that sapphyrins can bind anions, which has no precedence in porphyrin chemistry. This led to extensive investigation on sapphyrins, and today these macrocycles are important not only for anion/cation complexation studies but also for biomedical applications.[9] Interestingly, Woodword also mentioned in the same aromatic conference[7] the possibility of existence of another pentapyrrolic system

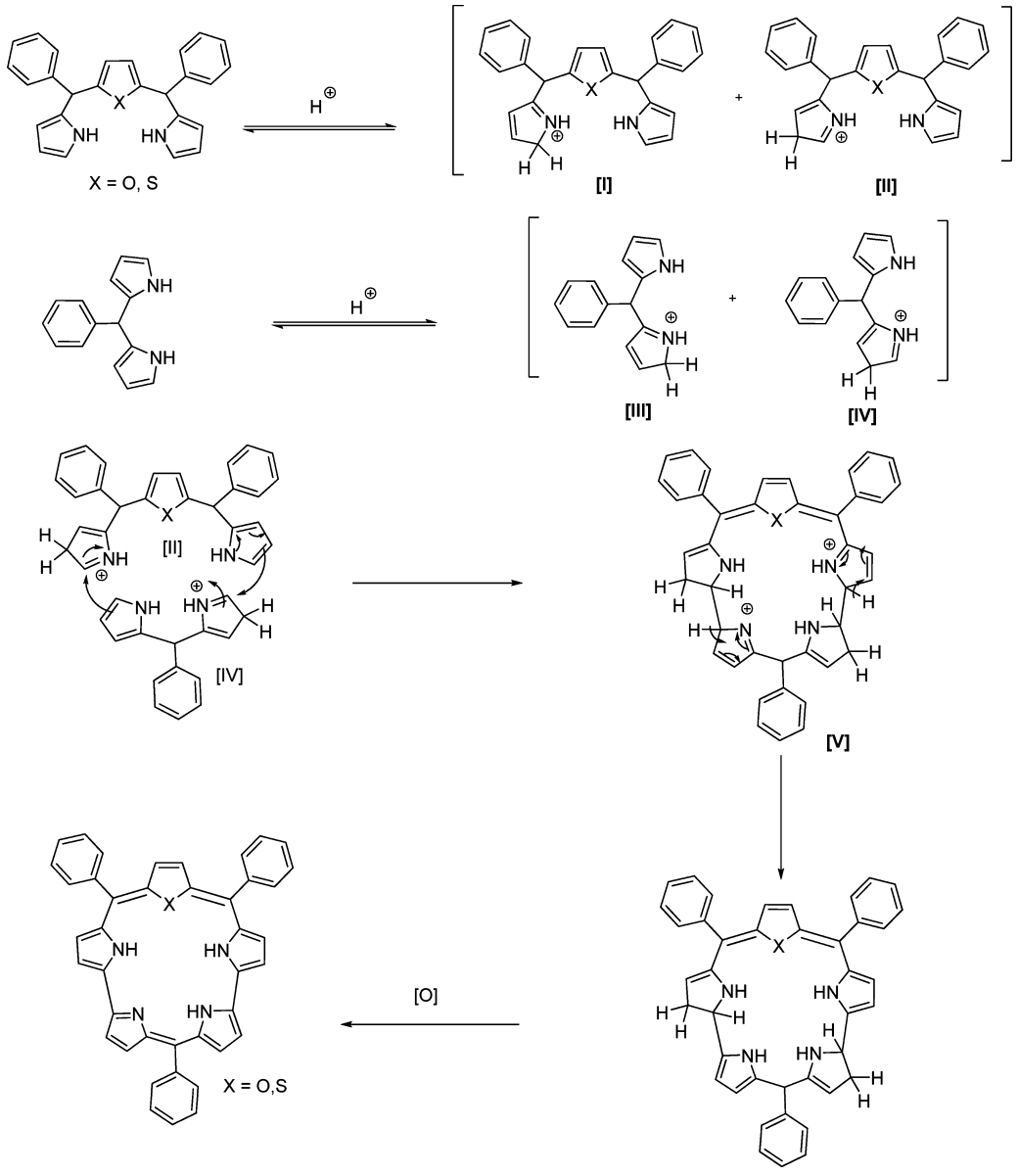


FIGURE 2. Proposed mechanism for the formation of *meso*-aryl oxasmaragdyrin and thiasmaragdyrin.

that has one methine carbon less than sapphyrin but has two direct bonds. He named this macrocycle smaragdyrin because of its intense green color in the solid state (smaragdus = emerald, precious green stone). However, unlike sapphyrins, the chemistry of smaragdyrins was not well established until recently because of their unstable nature, unavailability of stable precursors, and synthetic methodologies. In the past decade, smaragdyrins have received renewed research interest, and recently these macrocycles exhibited the potential to bind cations and anions like sapphyrins. Although sapphyrins and smaragdyrins were discovered at the same time, the developments in smaragdyrin chemistry remained relatively fewer. Hence, at this juncture, it is essential and appropriate to review the importance of smaragdyrin chemistry, which would help to elucidate the prominence of these macrocycles. The purpose of this Account is to bring the attention of readers to the less explored smaragdyrin chemistry with an emphasis on the importance of these macrocycles for potential diverse applications like those with sapphyrins in the future.

2. β- and *meso*-Aryl-Substituted Smaragdyrins

2.1. β-Substituted Smaragdyrins. In 1972, Broadhurst, Grigg, and Johnson during their rational approach for the synthesis of sapphyrins realized the possibility of synthesis of another pentaphyrin macrocycle with two direct bonds,

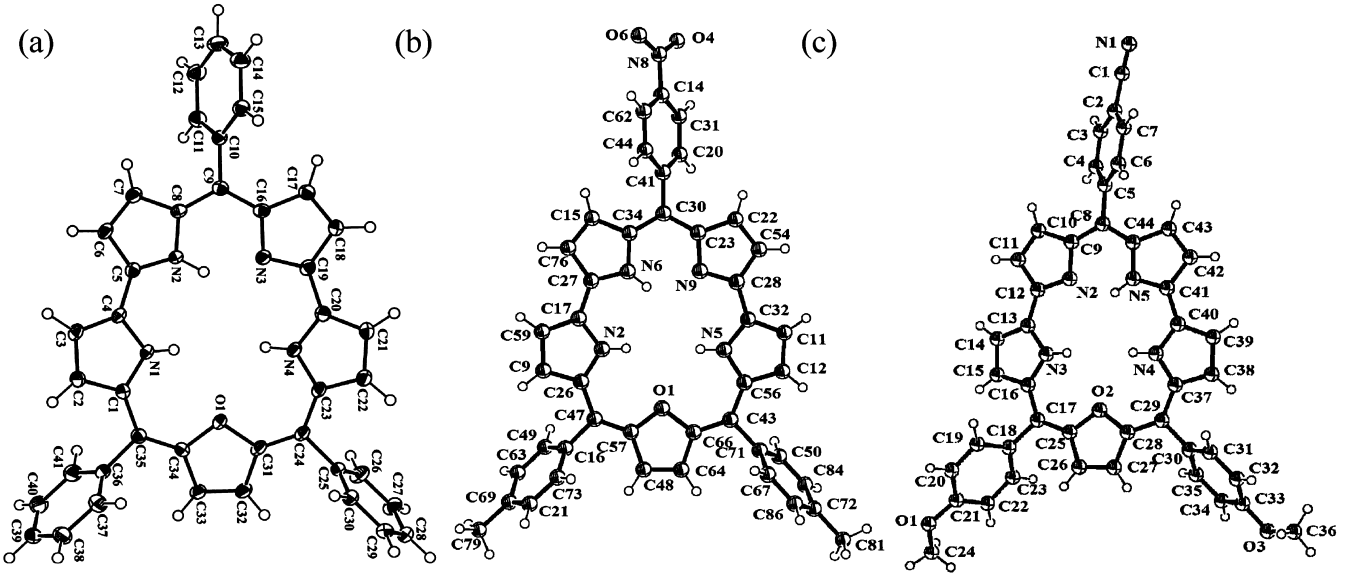


FIGURE 3. X-ray structure of (a) **27a**, (b) **27g**, and (c) **27j**.

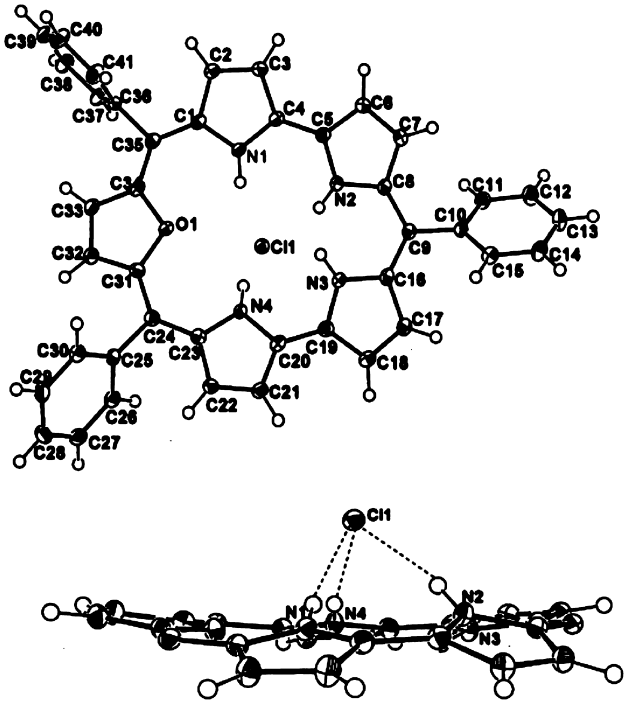


FIGURE 4. X-ray structure of **27aH**$^+$·**Cl**$^-$.

which they called norsapphyrins[10] but presently are known as smaragdyrins [1.1.0.1.0]. The norsapphyrins were synthesized over sequence of steps using precursors that have direct bonds between the heterocyclic rings as shown in Scheme 1. The pyrrolyldipyrromethene salts **4** were first synthesized by condensing alkyl-substituted bipyrroles **5** with 2-formylpyrroles **6** in the presence of a catalytic amount of HBr, and the resulting compounds **4** were reduced with excess $NaBH_4$ to the corresponding unstable pyrrolyldipyrromethanes **7**. However, the unstable **7** without isolation were condensed with the diformylbifuran **8** in $CHCl_3$ in the presence of HBr to give the first stable dioxasmaragdyrin **10** in decent yield. Under the same reaction conditions, when **7** was condensed with 5,5′-diformylbipyrrole **9**, the absorption studies indicated the formation of the aza analogue of smaragdyrin **11**, but their attempts to isolate **11** failed due to its highly unstable nature. The aromatic nature of **10** was confirmed by ^{1}H NMR spectroscopy, which showed inner NH protons in the high field region (−4.85 ppm) and the *meso*-protons in downfield region (∼10.00 ppm) due to the strong ring current effect. The dioxasmaragdyrin **10** showed several absorption bands in the 350−750 nm region, and in protonated state, the compound **10H**$^+$ showed a split Soret-like band in addition to the Q-bands. However, the chemistry of oxasmaragdyrin **10** was not further explored.

2.2. Isosmaragdyrins. After a gap of more than 2 decades, Sessler and co-workers[11] reported the synthesis of a stable isomer of smaragdyrin, the dibutyloctamethyl derivative of isosmaragdyrin **12** [1.1.1.0.0] and its monooxa analogue **13**. The required precursors, bis-α-free terpyrroles **14** and **15** were synthesized by carrying out the ring closure reaction of diketone **16**, which resulted in the formation of a mixture of two compounds, **17** and **18**. Compounds **17** and **18** were separated by column chromatography and subjected to saponification followed by decarboxylation to afford **14** and **15**, respectively. The isosmaragdyrins **12** and **13** were synthesized via the acid-catalyzed condensation of bisformyl dipyrromethane **19** with **14** and **15**,

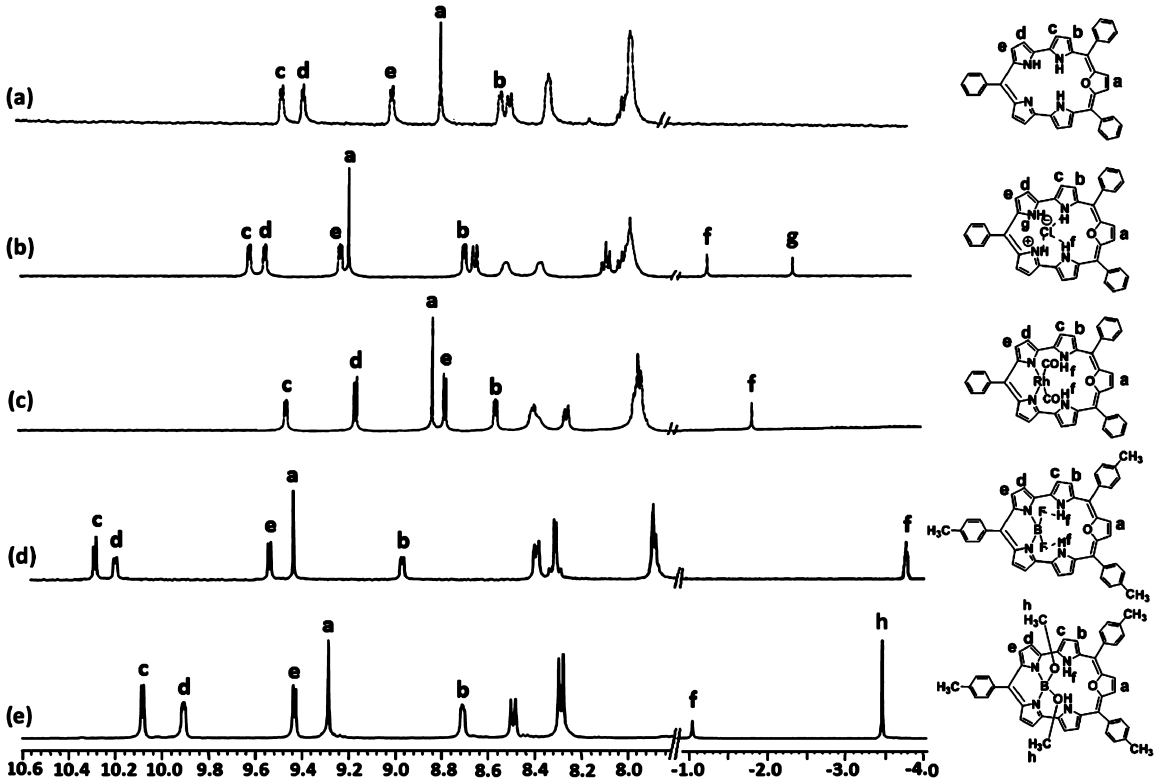
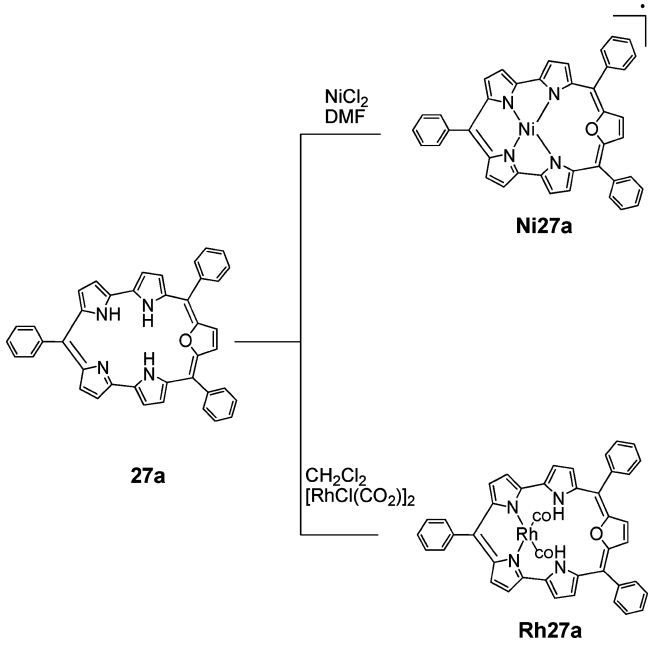


FIGURE 5. Comparison of ^{1}H NMR spectra of (a) **27a**, (b) **27aH**$^+\cdot$**Cl**$^-$, (c) **Rh27a**, (d) **29a**, and (e) **31b**.

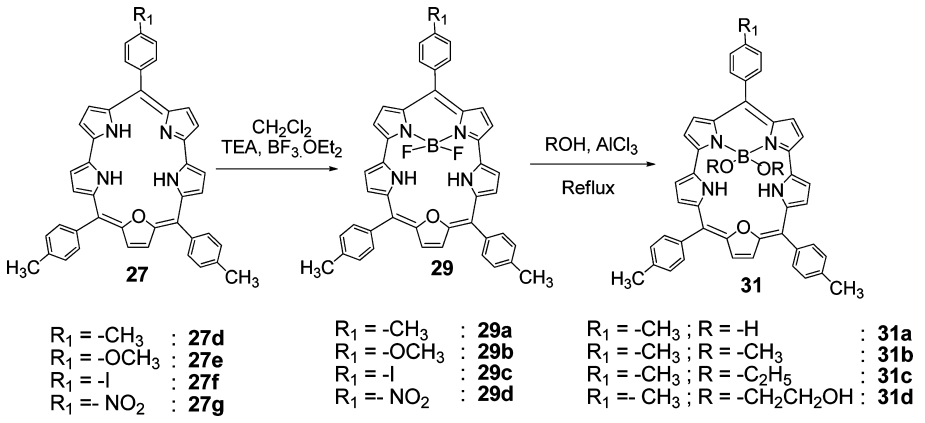
SCHEME 5



respectively, and isolated in ~40% yield (Scheme 2). The isosmaragdyrins **12** and **13** are aromatic in nature. The absorption spectra of compounds **12** and **13** showed a split Soret band along with the other Q-bands and the intensity of the Soret band of **13** is three times more than that of **12**. The authors obtained the single-crystal X-ray structures of the hydrochloride salts of **12** and **13** (Figure 1a,b). The structure of **12H**$^+\cdot$**Cl**$^-$ indicated that the macrocycle was nearly planar but the central pyrrole of the terpyrrole moiety deviated by 23.2° from the mean plane containing the other four heteroatoms. Except the nitrogen of the tilted pyrrole, all of the other four pyrrole nitrogens are bonded to the central Cl$^-$ ion.

Furthermore, the Cl$^-$ ion was also found to be 1.919 Å away from the mean plane of the macrocycle. The X-ray structure of **13H**$^+\cdot$**Cl**$^-$ exhibited the same features as the structure of **12H**$^+\cdot$**Cl**$^-$. The macrocycle **13H**$^+\cdot$**Cl**$^-$ is relatively planar with the exception of central furan being deviated by 21.2° from the neighboring pyrroles. The four pyrrole nitrogens bound to the Cl$^-$ ion whereas the furan oxygen was not involved in binding. The X-ray structure of **13H**$^+\cdot$**CF$_3$COO**$^-$ (Figure 1c) also showed similar features as the structure of **13H**$^+\cdot$**Cl**$^-$. Sessler and co-workers[12] prepared the partially β-substituted azasmaragdyrins **20**. Initially, they attempted to synthesize smaragdyrins **20a** by condensing diformylhexamethylterpyrrole **21** with 5-phenyldipyrromethane **22** in the presence of *para*-toluenesulfonic acid in ethanol at reflux, but the desired compound **20a** was not formed. However, their attempts were successful

SCHEME 6



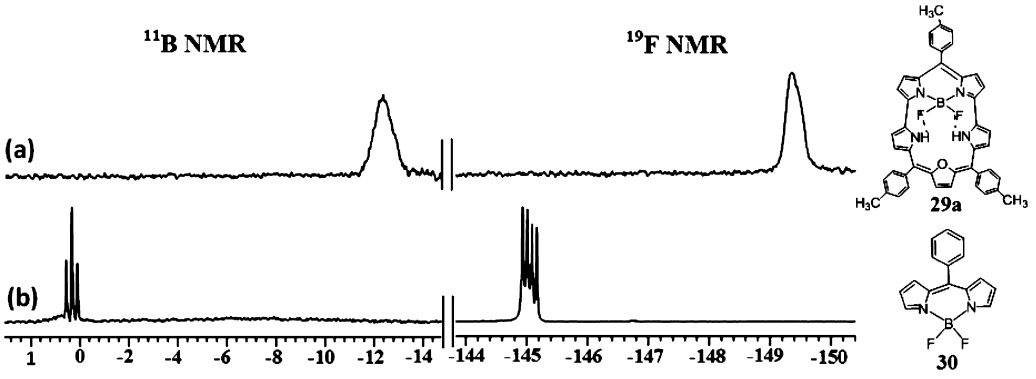


FIGURE 6. Comparison of ^{19}F and ^{11}B NMR spectra of (a) **29a** and (b) **30**.

when 1,9-bisformyl-5-phenyldipyrromethane **23a** was reacted with hexamethylterpyrrole **24** in the presence of HCl in chloroform, and they isolated the desired compound **20a** as its HCl salt (Scheme 3). The structure of **20aH**$^+\cdot$**Cl**$^-$ was confirmed by X-ray crystallography. The overall macrocycle **20aH**$^+\cdot$**Cl**$^-$ is planar except for the deviation of the middle pyrrole ring of the terpyrrole moiety from the macrocyclic plane. The crystal structure (Figure 1d) revealed that the Cl^- ion was above the macrocyclic plane and bound to three nitrogens. Sessler et al.[12] also prepared compound **20b** in the form of its HCl salt (**20bH**$^+\cdot$**Cl**$^-$) by condensing 1, 9-bisformyl-5-mesityldipyrromethane **23b** with **24** under similar reaction conditions. They carried out extensive NMR studies to conclude that isosmaragdyrins unlike sapphyrins[13] do not show pyrrole inversion in the free base or protonated forms.

2.3. *meso*-Aryl-Substituted Smaragdyrins. Chandrashekar and co-workers[14,15] succeeded in preparing the first examples of stable *meso*-aryl core-modified smaragdyrins by adopting an oxidative coupling strategy. Since the precursors containing direct pyrrole−pyrrole bonds used for the preparation of β-substituted smaragdyrins and isosmaragdyrins are very unstable and difficult to handle, these authors adopted a strategy of introducing the pyrrole−pyrrole bond in the final step of condensation. Thus, [3 + 2] oxidative coupling between 16-oxatripyrranes **25** or 16-thiatripyrrane **26** with *meso*-aryl dipyrromethanes **22** in the presence of TFA gave the corresponding smaragdyrins **27** and **28**, respectively, as major product along with the minor amount of corresponding oxa- or thiacorroles. The yields of core-modified smaragdyrins are dependent on the nature of the heteroatom in tripyrrane and the amount of acid catalyst used. By this strategy, a series of symmetrical and unsymmetrical *meso*-aryl oxasmaragdyrins **27** were prepared in high yields (Scheme 4). Interestingly, only one example of *meso*-aryl thiasmaragdyrin **28** was reported, which was obtained in low yield, and detailed studies are not available due to its instability. The authors proposed a possible mechanism[15] for the formation of core-modified smaragdyrins as shown in Figure 2. The protonation on the α and β positions of tripyrrane and dipyrromethane gave four possible intermediates **I**–**IV**. The active intermediates **II** and

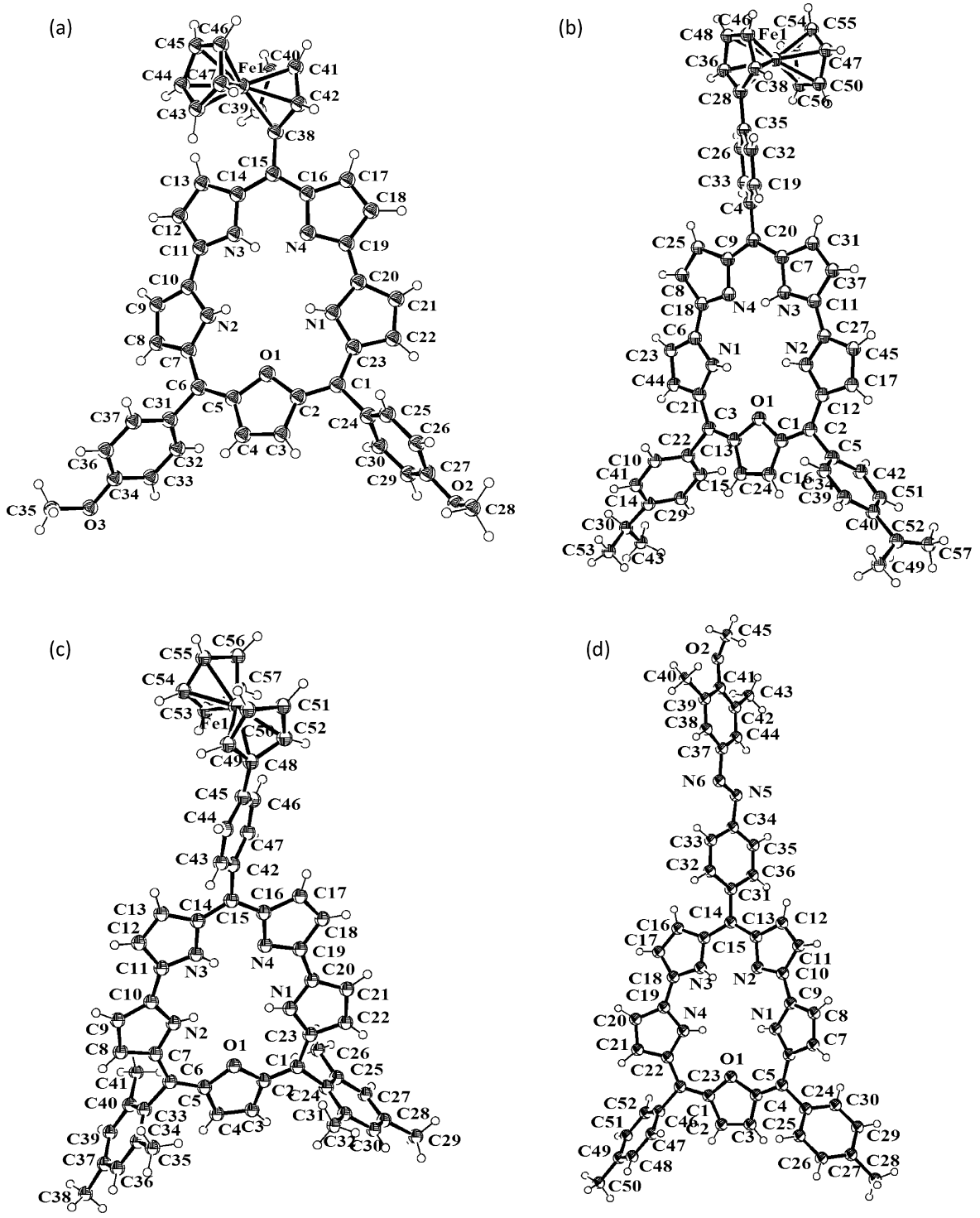
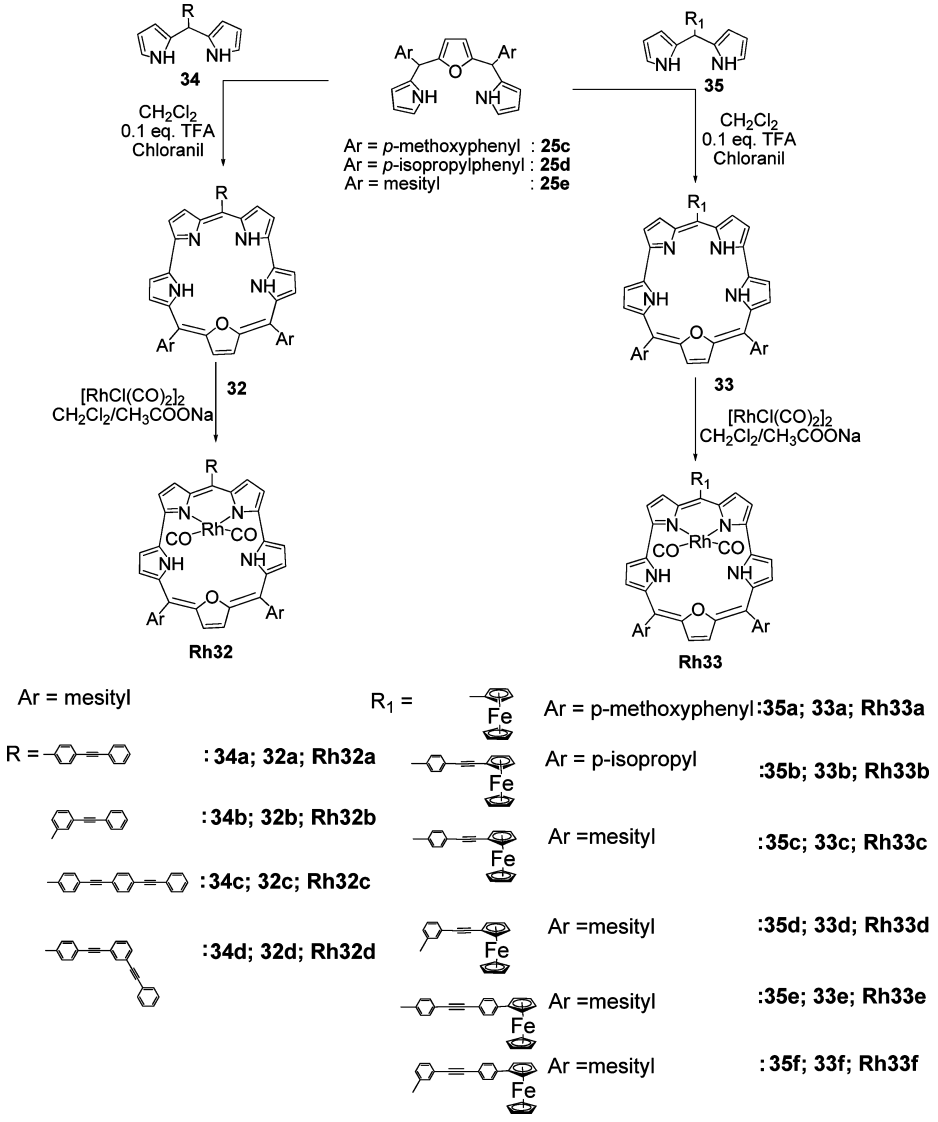


FIGURE 7. X-ray structure of (a) **33a**, (b) **33b**, (c) **33c**, and (d) **36a**.

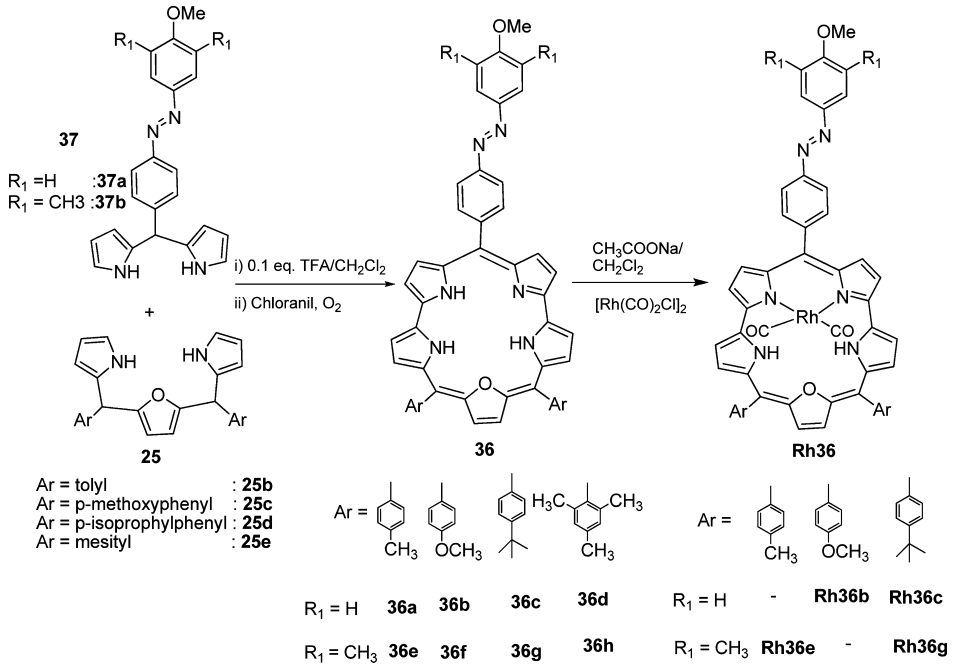
IV were chosen for an α−α coupling reaction between the tripyrrane and dipyrromethane through an intramolecular electrophilic attack to generate intermediate **V**, which on further rearrangement followed by oxidation led to the formation of smaragdyrin. However, the above-described oxidative coupling methodology has not been used so far for the synthesis of pentaazasmaragdyrin. The *meso*-aryl oxasmaragdyrins **27** are stable and exhibited characteristic spectral and electrochemical properties. ^{1}H NMR spectra of oxasmaragdyrin **27** exhibit four doublets for bipyrrole protons and one singlet for furan protons in the 8.3−9.5 ppm region revealing the aromatic character of smaragdyrins

SCHEME 7



(Figure 5a). The three inner NH protons, which are expected to appear in the high-field region due to macrocyclic ring current, were not observed even at −50 °C because of rapid tautomerism. Furthermore, the absence of β-proton resonance in the high-field region in ^{1}H NMR indicated no occurrence of heterocyclic ring inversion in *meso*-aryl oxasamaragdyrins unlike *meso*-aryl sapphyrins[4b,13] where heterocycle ring flipping was commonly observed. This is due to one less methine bridge and one extra direct pyrrole−pyrrole bond in smaragdyrin compared with sapphyrin, which restricts the flexibility of the smaragdyrin macrocycle. The electronic spectra of **27** and **28** exhibited a porphyrinoid-type Soret band at ∼445 nm and four Q-bands in the range 550−730 nm. The *meso*-aryl oxasmaragdyrins **27** are fluorescent with one band at ∼700 nm and quantum yield of 0.04. The oxasmaragdyrins **27** exhibit two reversible oxidations and two ill-defined irreversible reductions, which indicate that **27** are electron-rich and stable under oxidation conditions compared with free base porphyrins. The single-crystal X-ray analysis of oxasmaragdyrins **27a**,[14] **27g**,[16] and **27j**[16] revealed the nonplanarity of the smaragdyrin framework (Figure 3). This was attributed mainly to the strain imposed on the whole molecule by introduction of an additional pyrrole ring, direct pyrrole−pyrrole interactions, and the steric repulsion between imino hydrogen atoms. For example, in compound **27a**, N2 and N3 deviate below the mean plane (−0.0171 and −0.0041 Å) while N1 and N4 are located above the plane (0.0145 and 0.0120 Å, respectively). Furthermore, strong hydrogen-bonding interactions among the protons on the nitrogens and the heteroatom were present in these macrocycles.

SCHEME 8



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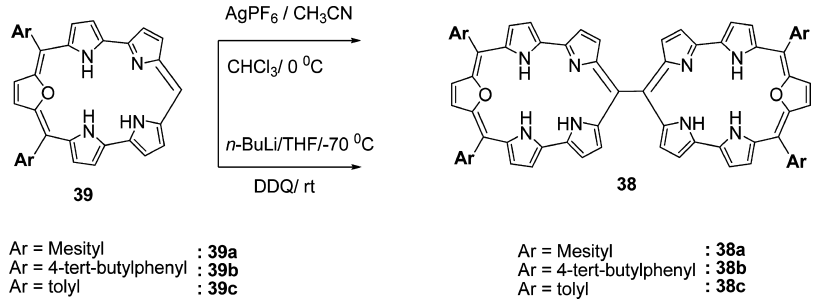

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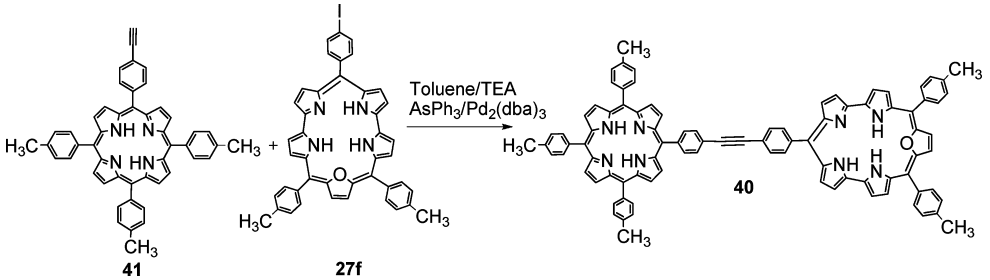
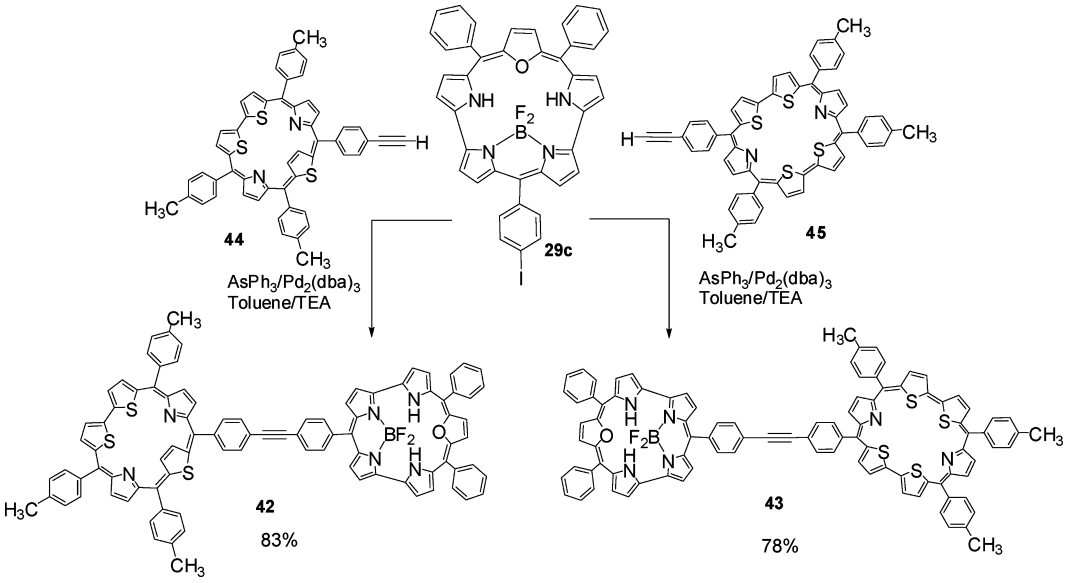


2.3.1. Protonation and Anion Binding. Smaragdyrins form stable protonated species upon treatment with acid.[15] The protonation of **27a** (**27aH**$^+\cdot$**Cl**$^-$) led to the downfield shift of all signals in the ^{1}H NMR spectrum due to delocalization of the positive charge in the macrocycle,[15] and now the localized inner-NH protons appear at −1.06 and −2.06 in the ^{1}H NMR spectrum (Figure 5b). The protonation of **27a** also led to splitting of the Soret band and a slight red shift of all absorption bands compared with the neutral derivative. The crystal structure of **27aH**$^+\cdot$**Cl**$^-$ showed that only three out of four pyrrole-NH groups are involved in the N−H···Cl hydrogen bonding (Figure 4). Furthermore, the pyrrole

SCHEME 11



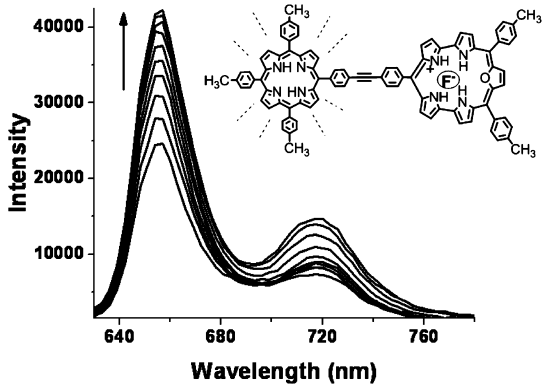


FIGURE 8. Fluorescence titration of **40H**$^+$ (1 μM) in the presence of various concentrations (0−66 μM) of F^- ions in toluene ($\lambda_{ex} = 410$ nm).

rings N1, N2, and N4, which were involved in the bonding, are tilted above the plane of the macrocycle defined by *meso*-carbons, while the pyrrole ring N3, which was not involved in coordination with Cl^- ion, is in the plane. Thus, the bonding observed in **27aH**$^+\cdot$**Cl**$^-$ is slightly different from that observed for Sessler's monoprotonated chloride salt of the isosmaragdyrin[11] **20bH**$^+\cdot$**Cl**$^-$ where all four nitrogens were involved in binding to the chloride ion. The protonated oxasmaragdyrin **27aH**$^+\cdot$**Cl**$^-$ was tested for the complexation of anions by absorption spectroscopy. However, the binding constants observed with **27aH**$^+\cdot$**Cl**$^-$ are approximately an order of magnitude lower relative to those of similar ions by the protonated form of pentaazasapphyrin.[17] The anion binding studies concluded that **27aH**$^+\cdot$**Cl**$^-$ did not have specificity toward any particular anion.

2.3.2. Metal Complexation. Exploration by various research groups[5,9b] of the metal-complexing ability of expanded porphyrins has shown that these macrocycles readily form both mono- and binuclear complexes preferably with larger metal ions such as Rh(I) and Ir(I). Sessler and co-workers[18] showed that sapphyrins can bind to Rh(I) in η^2-fashion involving one amino and one imino nitrogen of the dipyrromethane unit of the sapphyrin skeleton. Recently, the metal complexation behavior of *meso*-aryl oxasmaragdyrins was explored.[15] The rhodium complexes of oxasmaragdyrin **Rh27a** and thiasmaragdyrin **Rh28** were synthesized by treating the corresponding free base smaragdyrins **27a** and **28**, respectively, with di-μ-chlorobis[dicarbonylrhodium(I)] in CH_2Cl_2, and the nickel complex of oxasmargdyrin, **Ni27a**, was obtained by refluxing the DMF solution of **27a** with $NiCl_2$ (Scheme 5). ^{1}H NMR spectra (Figure 5c) of **Rh27a** showed two inner NH protons as a singlet in the high-field region and supported that only two out of four nitrogens are involved in the metal coordination. The crystal structure of **Rh27a** showed that the Rh(I) formed an out-of-plane square planar complex with oxasmaragdyrin by complexing in η^2-fashion involving one amino and one imino nitrogen of the dipyrromethene unit (N2 and N3) and two carbonyl groups as observed earlier for sapphyrins.[18] Interestingly, **Ni27a** did not show inner NH signals in ^{1}H NMR due to the coordination of all four bipyrrole nitrogens with the Ni(II) ion. Since free base oxasmaragdyrin has three ionizable protons, it was expected to form a Ni(III) complex. However, authors formulated **Ni27a** as a π cation radical of Ni(II)

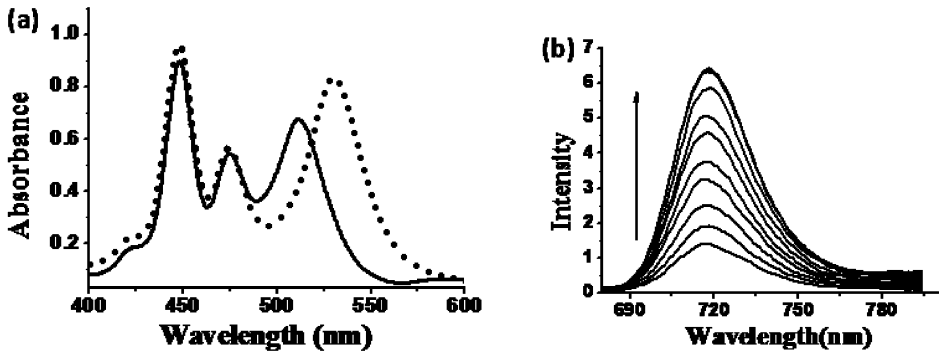


FIGURE 9. (a) Comparison of Soret absorption spectra of **42** (solid line) with $\mathbf{42H_2}^{2+}$ (dotted line). (b) Fluorescence spectral titration of $\mathbf{42H_2}^{2+}$ with increasing amounts (0−1.08 equiv) of CO_3^{2-} ions ($\lambda_{ex} = 450$ nm).

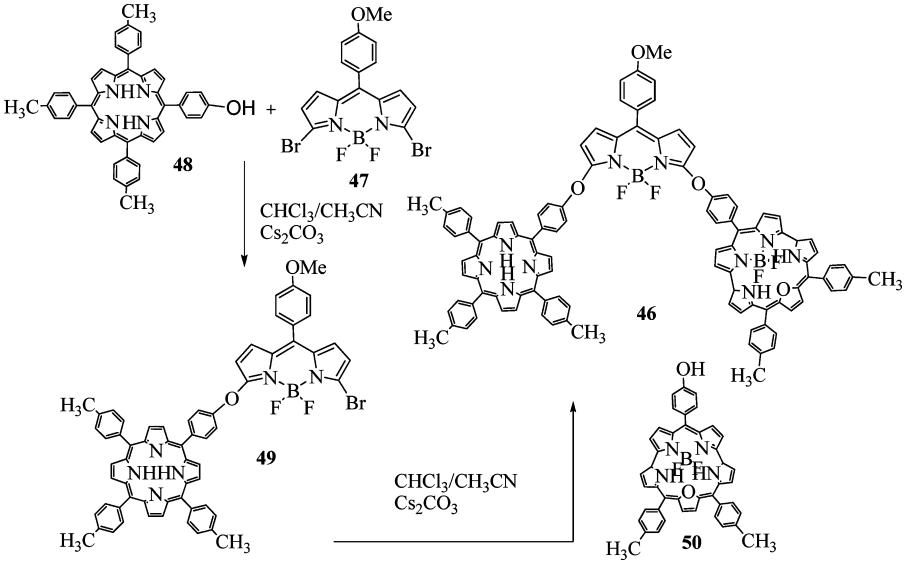
oxasmaragdyrin based on the paramagnetic nature of the complex supported by NMR and ESR studies.[15] The Rh(I) and Ni(II) derivatives exhibited a split Soret band like protonated smaragdyrin complex supporting the lower symmetry of metal complexes occurred due to distortion.

2.3.3. BF_2- and $B(OR)_2$-Smaragdyrins. Sessler and co-workers synthesized mono- and bis-BF_2 complexes of expanded porphyrins called amethyrin and [32]octaphyrin along with octaethylporphyrin and characterized them by X-ray crystallography.[19] They showed that the bis-BF_2 complex of octaethylporphyrin is not stable and undergoes ready hydrolysis to form a B−O−B bond, whereas the bis-BF_2 complexes of amethyrin and [32]octaphyrin are hydrolytically stable. Rao and Ravikanth[20] synthesized mono-BF_2 complexes of oxasmaragdyrins, **29**, by treating smaragdyrins **27** with triethylamine and $BF_3 \cdot OEt_2$ in CH_2Cl_2 at room temperature (Scheme 6). The green BF_2-smaragdyrin complexes **29** are stable and do not undergo any hydrolysis or decomplexation. In ^{1}H NMR of **29a**, the two inner NH protons appeared as an unresolved triplet further upfield (−3.6 ppm) compared with **Rh27a** (Figure 5d) due to the presence of hydrogen bonding between inner NH protons and fluoride ions of the BF_2 unit in addition to macrocycle ring current effect. ^{19}F and ^{11}B NMR also supported macrocyclic ring current effect and hydrogen bonding in **29a** and showed upfield shifted resonances compared with simple BODIPY such as 8-phenyl-4-bora-3*a*,4*a*-diaza-*s*-indacene **30** as shown in Figure 6. Similar observation was also made by Sessler and co-workers in the solid state structure of the BF_2 complexes of amethyrin and [32]octaphyrin.[19] The absorption studies of **29** showed a strong band at ∼700 nm that is three times more intense than the absorption band of **27** present in the same region. The BF_2-smargdyrins **29** are fluorescent and more electron-deficient than **27**. The authors also synthesized[20] a series of $B(OR)_2$ complexes of smaragdyrins **31** by replacing the fluoride ions of **29** with hydroxy and alkoxy groups under simple reaction conditions (Scheme 6). The ^{1}H NMR features of **31** were identical with **29** except for inner NH protons, which experienced a downfield shift due to the absence of strong hydrogen bonding present in **29** (Figure 5e). Furthermore, the axial hydroxy and alkoxy protons also experienced a strong macrocyclic ring current effect and appeared in the very high field region in ^{1}H NMR. The absorption and fluorescence features of **31** were similar to those of **29**, but their redox properties were different due to the electron-donating nature of the alkoxy groups. The $B(OH)_2$-smaragdyrin **31a** was explored for anion sensing properties by titrating with increasing amounts of various anions. NMR, UV−vis, fluorescence, and electrochemical studies indicated that **31a** acts as specific sensor for fluoride ion.

3. Smaragdyrin Conjugates

Chandrashekar and co-workers reported the synthesis of series of 22 π smaragdyrin conjugates and their corresponding Rh(I) derivatives bearing phenylacetylene substituents,[21,22] **32** and **Rh32**, and ferrocene-containing substituents,[16,22−24] **33** and **Rh33**. The synthetic strategy involved was the same [3 + 2] acid-catalyzed oxidative coupling reaction of **34** or **35** with **25** (Scheme 7). The crystal structures of **33a**,[24] **33b**,[24] and **33c**[23] were reported (Figure 7a−c). The structures showed similar deviations of heterocyclic rings from planarity like their earlier structures of smaragdyrins **27** suggesting that structural deviation upon introduction of ferrocene directly as well as through spacer at the *meso*-position is minimal. The absorption and emission properties of **32** and **33** depend on the nature of the substituent, nature of the linker group, and spacer length. The absorption and emission bands experienced bathochromic shifts, and the shifts increased on extension of conjugation. The fluorescence quantum yield in **32** increased linearly with

SCHEME 12



increased conjugation, whereas conjugates **33** are weakly fluorescent due to photoinduced electron transfer. The electrochemical properties of **32** and **33** revealed that smaragdyrin ring oxidation become easier with the increase of conjugation and in the presence of ferrocene moiety.

Recently, it has been shown that expanded porphyrins with a large number of π electrons are more promising nonlinear optical (NLO) materials with larger two photon absorption (TPA) cross-section values ($\sigma^{(2)}$) than the porphyrins.[25] The TPA studies of **32**, **33**, and their Rh(I) derivatives showed that the $\sigma^{(2)}$ values increased with the increase of conjugation.

Smaragdyrin–azobenzene conjugates[26] **36** were synthesized by condensing **37** with **25b** under [3 + 2] oxidative coupling reaction conditions, and their Rh(I) complexes **Rh36** were also prepared (Scheme 8). The X-ray structure of **36** was nearly flat with small deviations of the macrocycle from the mean plane (Figure 7d). The structure also revealed that the azobenzene unit was in its (*E*) form. The absorption spectra of **36** showed absorption features of smaragdyrin along with a band at 340 nm corresponding to the azobenzene chromophore. The fluorescence studies supported a possibility of energy transfer from the azobenzene moiety to the smaragdyrin unit. The conjugates **36** and **Rh36** were more difficult to oxidize compared with **27a** and **Rh27a**, respectively, due to the electron-withdrawing nature of the azobenzene moiety. Although the irradiation experiments carried out at 360 nm indicated the conversion of (*E*) isomer to (*Z*) isomer, the instability of the (*Z*) isomer resulted in the decomposition of the smaragdyrin macrocycle.

4. Smaragdyrin-Based Dyads and Triads

Although an extensive body of literature is available on multiporphyrin arrays,[27] the reports on multiexpanded porphyrin arrays and porphyrin-expanded porphyrin arrays are relatively very few.[28] Chandrashekar and co-workers[29] reported the first example of *meso–meso* linked smaragdyrin dyads **38** by treating *meso* free smaragdyrin monomers **39** either with $AgPF_6$ or with *n*-BuLi (Scheme 9). On the basis of theoretical calculations, the authors proposed a twist angle of 71° to 64° between the smaragdyrin units in dyads **38**, which resulted in enhanced conjugation leading to a red shift of the absorption spectra by 25 nm compared with the smaragdyrin monomer **39**. The *meso–meso* linked smaragdyrin dyads **38** showed a sharp Soret band with negligible exciton coupling.

Ravikanth and co-workers reported the synthesis of diphenyl ethyne bridged porphyrin–smaragdyrin dyad[30] **40**, BF_2-smaragdyrin–sapphyrin dyad[31] **42**, and BF_2-smaragdyrin–rubyrin dyad[31] **43** by coupling iodo- (**27f**, **29c**) and ethynyl- functionalized (**41**, **44**, and **45**) porphyrin/expanded porphyrin monomeric building blocks under mild Pd(0) coupling reaction conditions (Schemes 10 and 11). The fluorescence studies carried out on dyad **40** supported an efficient singlet–singlet energy transfer from porphyrin unit to oxasmaragdyrin unit as noted previously[28a] in noncovalent porphyrin–sapphyrin dyad. Furthermore, the protonation studies of the dyad **40** monitored by absorption spectroscopy indicated that it is possible to protonate the smaragdyrin unit selectively. The addition of anions to $\mathbf{40H}^+$ resulted in the binding of anion at the protonated

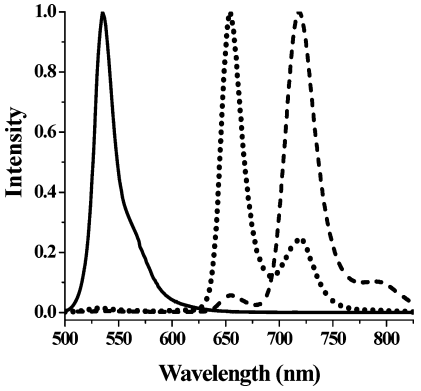


FIGURE 10. Comparison of emission spectra of triad **46** (dashed line) with its associated reference compounds **47** (solid line) and **49** (dotted line).

smaragdyrin site, which was reflected in the gradual enhancement of porphyrin fluorescence (Figure 8); hence the dyad **40** can be used as a fluorescent sensor for anions.

The dyads[31] **42** and **43** possess the following properties, which are favorable for using these dyads in fluorescent sensor applications: (1) thiasapphyrin and thiarubyrin macrocycles are nonfluorescent, and BF_2-smaragdyrin macrocycle is fluorescent; (2) the protonated sapphyrin and rubyrin can bind anions because of their large cavity size and availability of inner pyrrole NH protons; (3) BF_2-smaragdyrin cannot be protonated (Figure 9a) and cannot bind anions because the pyrrolic NHs are engaged in hydrogen bonding with fluorides of the BF_2 group. Hence, the anion sensing experiments carried out on protonated dyads $\mathbf{42H_2}^{2+}$ and $\mathbf{43H_2}^{2+}$ with various concentrations of CO_3^{2-} ions (Figure 9b) resulted in the gradual enhancement of the intensity of the emission of BF_2-smaragdyrin unit, indicating that the dyads can be used for fluorescent sensor applications.

Khan and Ravikanth synthesized[32] trichromophoric system **46** containing porphyrin, BODIPY, and BF_2-smaragdyrin units and studied its photophysical properties. The triad **46** was synthesized by reacting 3,5-dibromo BODIPY **47** with hydroxyporphyrin **48** affording BODIPY−porphyrin conjugate **49**, which was subjected to further reaction with hydroxy BF_2-smaragdyrin **50** resulting in the formation of trichromophoric system **46** (Scheme 12). A comparison of normalized emission spectra of **47**, **49**, and **46** recorded in $CHCl_3$ using excitation wavelength of 488 nm at which the BODIPY unit absorbs relatively strongly is shown in Figure 10. The fluorescence studies of trichromophoric system **46** indicated that the emission from the BODIPY and the porphyrin units was quenched by 99% and the major emission was noted from the BF_2-smaragdyrin unit because the singlet state energy level of the BF_2-smaragdyrin unit is lower than those of the other two chromophoric units.

5. Conclusions

Sapphyrins and smaragdyrins, the pentapyrrolic 22 π electron conjugated macrocycles, were discovered during the same time, but the chemistry of sapphyrins was extensively investigated whereas the smaragdyrin chemistry remained almost at infancy. This is due to lack of proper synthetic strategies and also because of inherent instability of the smaragdyrins compared with the sapphyrins. However, the recent [3 + 2] oxidative coupling strategy helped in the synthesis of stable *meso*-aryl oxasmaragdyrins. The studies showed that smaragdyrins are as interesting as sapphyrins in terms of binding anions and cations and also can be used for various applications like sapphyrins. Though some stable *meso*-aryl smaragdyrins can be synthesized now, there is more scope to synthesize several other types of stable smaragdyrins with different inner core atoms. There is also a tremendous scope to use smaragdyrins as ligands for metal coordination chemistry. Furthermore, the rich spectral, electrochemical, and photophysical properties of smaragdyrins can be exploited for various applications. It is our hope that more research will be carried out on these fascinating macrocycles to explore their complete potential for various applications.

Y.P. thanks IIT-Bombay and CSIR-SRF for a fellowship, M.R. thanks BRNS, and T.K.C. thanks DST (J. C. Bose fellowship) for financial support. We also thank our co-workers whose names appear in the references. Special thanks to Mr. Avijit Ghosh for his help in replotting X-ray structures.

BIOGRAPHICAL INFORMATION

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FOOTNOTES

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