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meso-Aryl Core-Modified Fused Sapphyrins: Syntheses and Structural Diversity

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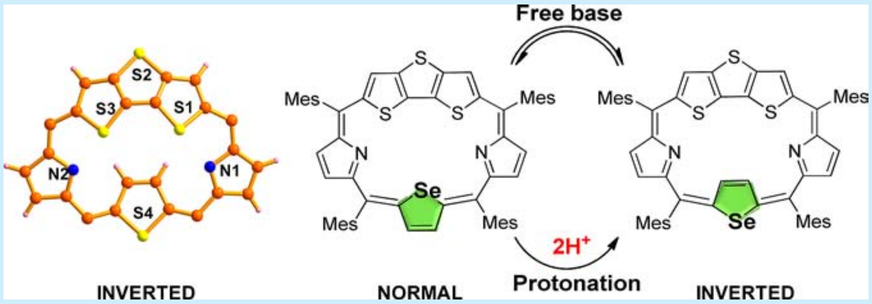
Ⓢ *Supporting Information*

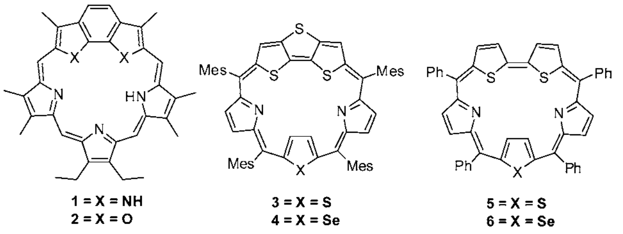


ABSTRACT: Two new, fused core-modified expanded porphyrins, sapphyrins **3** and **4**, were synthesized by a simple acid-catalyzed condensation of electron-rich and rigid precursor, dithienothiophene (DTT) diol, and core-modified tripyrrane. These sapphyrins exhibit structural diversity depending upon the heteroatom present in the macrocyclic framework, where the thiophene ring is inverted in **3**, while the selenophene ring in **4** exists in normal and inverted form in the free base and addition of two protons shifts the equilibrium to inverted form.

Structural diversity in expanded porphyrins is attracting the attention of researchers.[1] Structural diversity affects the electronic structure of the ring, the conjugation pathway, as well as physical and chemical properties.[2] More recently, it has been demonstrated that the aromaticity[3] [$(4n+2)\pi$ Hückel vs $4n\pi$ Möbius)][4] can be controlled by a careful control of conformation of the macrocycle by external stimuli such as protonation,[5] temperature,[6] solvent,[7] etc.[8] Thus, it is important to recognize the structural diversity in expanded porphyrin systems.

Rigidifying the expanded porphyrin in one particular conformation, mainly in the planar conformation, is of foremost importance as it directly relates to its physical and chemical properties.[9,10] There is a series of reports describing the synthesis of conformationally rigid expanded porphyrin by metal coordination, protonation by acid, and solvent/temperature control.[11,12] However, recently the fused and internally meso-bridged approaches to control the conformation and retain the planarity is found to be a promising technique.[13−18] Such approaches do not alter the porphyrin intrinsic properties and give rise to interesting structural features. The first fused expanded porphyrin, N-fused pentaphyrin was reported by Furuta, Osuka, and co-workers, where the pentaphyrin ring contains a fused tripentacyclic ring in the macrocyclic framework.[19] Sapphyrin is the first expanded porphyrin synthesized serendipitously by Woodward and co-workers and well established by Sessler and co-workers.[20−22] Since then, a wide variety of β-alkyl, *meso*-aryl, and the corresponding core-modified sapphyrins were synthesized and utilized for various applications;[20] however, the respective fused sapphyrins are not known in the literature. Recently, the bipyrrole-fused sapphyrin **1** reported by Lee and co-workers which showed unique absorption features and aromaticity attributed to the fused ring in the macrocycle.[15] The same group, along with Sessler and co-workers, also synthesized the benzodifuran-fused sapphyrin **2** and demonstrated the neutral molecule binding.[18] Recently, our group has reported the DTT fused singly and doubly fused rubyrins which exhibited the enhanced photophysical properties, planarity and aromaticity than its nonfused congeners, owing to the conformational rigid molecular structure imposed by DTT moiety.[14] Such results encouraged us to introduce fusion in the core-modified sapphyrins, herein, we wish to report the synthesis, spectral, structural characterization and electrochemical studies of DTT fused *meso*-aryl core modified sapphyrins **3** and **4**.

Chart 1. Fused and Nonfused Core-Modified Sapphyrins



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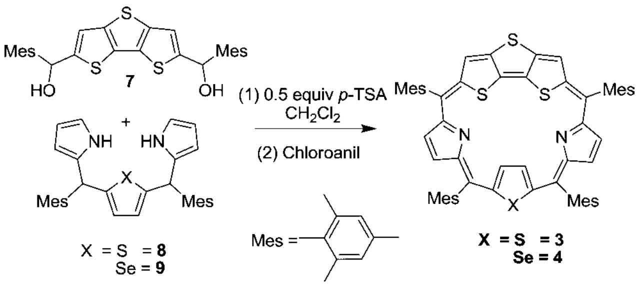
The synthesis of monofused sapphyrins is shown in Scheme 1, where we have adopted the [3 + 2] acid-catalyzed condensation reaction of DTT-diol 7[14] and core-modified tripyrrane (8 or 9).[23] In a typical synthetic procedure, equal molar amounts of 7 and 8 in CH_2Cl_2 were stirred for 1 h using 0.5 equiv of *p*-toluenesulfonic acid (*p*-TSA) as catalyst. After oxidation with 2,3,5,6-tetrachloro-*p*-benzoquinone (chloranil), the products were purified initially by basic alumina and followed by repeated neutral alumina column chromatography. A greenish brown color fraction eluted with CH_2Cl_2/hexane (10:90) was identified as sapphyrin 3 in 10% yield. While the condensation reaction of 7 and Se-tripyrrane 9 under similar reaction condition afforded 4 in 8% yield.

Scheme 1. Synthesis of Core-Modified Sapphyrins



The sapphyrins 3 and 4 were characterized by standard spectral characterization techniques such as ESI-mass spectra, NMR, UV−vis absorption spectra, electrochemical studies, and 3 further confirmed by single-crystal X-ray analysis. The initial clue for the proposed structural composition came from the mass spectrometric analysis where 3 and 4 showed molecular ion signals at *m*/*z* 929.3019 [M + H^+] and 976.2456 [M^+], respectively, which are consistent with the exact composition of the macrocycle (Supporting Information).

The ^1H NMR spectrum of 3 in CD_2Cl_2 at 298 K is shown in Figure 1. The sharp singlet peak at 8.4 ppm corresponds to the *β*-CH of the DTT moiety. The pyrrolic *β*-CH protons resonate as two doublets centered at 8.1 and 7.8 ppm, which was further confirmed by $^1H-^1H$ COSY spectral analysis. The *meso*-mesityl protons are observed as two distinguished singlets at 7.2 and 7.1 ppm, which reveal the two nonequivalent chemical environments for the mesityl protons. The mesityl methyl protons are in the upfield region between 1.0 to 2.6 ppm. The thiophene *β*-CH protons which is opposite to the DTT moiety is inverted and resonated as a singlet at 2.15 ppm, where both the *β*-CH protons are experiencing the aromatic ring current effect. The aromaticity of the fused sapphyrins 3 estimated by ^1H NMR chemical shifts are in comparison to sapphyrins without fusion 5. For example, upon protonation of 3 with TFA, the DTT and pyrrole protons are deshielded by 1.1 and 1.6 ppm and observed at 9.49 and 9.55 ppm, respectively, whereas the inverted thiophene ring is further shifted to upfield by 1.53 ppm and resonated at 0.62 ppm. Furthermore, the protonated NH protons are shielded and appeared at −2.7 ppm for 3 compared to −3.1 ppm for 5. Overall, the chemical shift difference (Δ*δ*) between the most shielded (pyrrolic NH) and deshielded (*β*-CH) protons of 3 is 11.1 ppm compared to 12.1 ppm for sapphyrins without fusion 5 suggesting a decrease in the aromaticity.

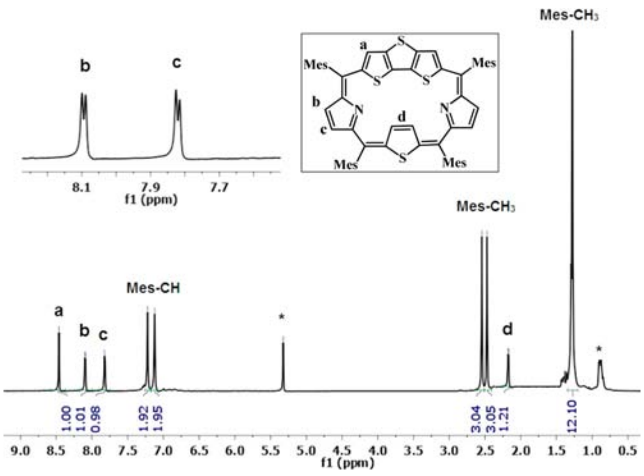


Figure 1. ^1H NMR spectrum of 3 in CD_2Cl_2 at 298 K. *Residual solvent peak and impurity grease peak.

Interestingly, the ^1H NMR spectrum of 4 in $CDCl_3$ at 298 K contains double the number of distinguished peaks especially in the aromatic region and is shown in Figure 2a. Analysis of ^1H

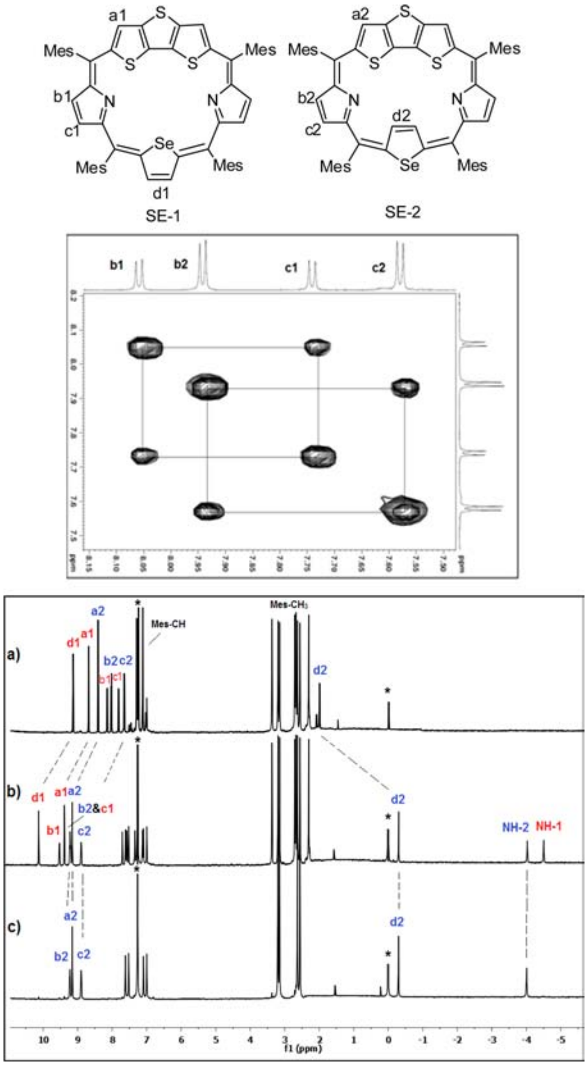


Figure 2. ^1H NMR spectrum of 4 in $CDCl_3$ at 298 K: (a) before protonation, (b) after protonation by TFA, and (c) 5 h after protonation. Inset: COSY spectrum before protonation. Top: Structures of two different conformers of 4. *Residual solvent and TMS peaks.

NMR based on relative peak intensities and correlation in ^{1}H$-$^{1}H COSY spectrum (Figure 2 inset) reveals that there are two different conformers of **4** (SE-1 and SE-2) (Figure 2). In one of the conformers, selenophene ring is in normal form (where Se atom is inside and β-CH protons are outside the macrocyclic ring) (SE-1), whereas in another conformer selenophene ring is in inverted form (where the Se atom is outside and the β-CH protons are inside the macrocyclic ring) (SE-2) (Figure 2a). In SE-1, the selenophene β-CH protons (d1) are resonated at 8.94 ppm, whereas in SE-2, the respective protons are at 2.21 ppm (d2) due to shielding effect. The β-CH protons of DTT are at 8.51 (a1) and 8.25 ppm (a2) for SE-1 and SE-2, respectively. The two doublets with lesser intensities are resonated at 8.05 (b1) and 7.67 ppm (c1) and assigned to the pyrrole β-CH protons of SE-1, where as the respective protons in SE-2 are with higher intensities and resonated at 7.87 (b2) and 7.51 ppm (c2), respectively. These assignments are based on the correlations found in the ^{1}H$-$^{1}H COSY spectrum of **4** at room temperature (Figure 2 inset). Similarly, two sets of mesityl phenyl CH and methyl protons were observed.

Upon protonation of **4** with a dilute solution of TFA in $CDCl_3$, the β-CH protons of the DTT, selenophene, and pyrrolic rings are deshielded by 0.75, 1.15, and 1.3 ppm for SE-1, respectively. In SE-2, the β-CH protons of the DTT and pyrrolic rings are deshielded by 0.75 ppm each, however, the inverted selenophene ring is upfield shifted by 2.73 ppm due to increase ring current effect. In addition, the two distinct protonated NH signals were observed for both isomers at −4.1 (NH-2) and −4.3 ppm (NH-1) (Figure 2b). Out of two isomers (SE-1 and SE-2), to our surprise, one of the isomers (SE-2) is found stable after 5 h, where the other isomer (SE-1) is gradually disappeared over a period of time. The stable isomer (SE-2) β-CH protons of the DTT and pyrrolic rings are resonated at 9.25, 9.32, and 8.80 ppm, the mesityl phenyl protons are observed between 7.00 to 7.60 ppm, while the inverted selenophene ring β-CH protons are at −0.32 ppm and the protonated NH protons are at −4.1 ppm, respectively (Figure 2c). Variable-temperature ^{1}H NMR analysis of **3** and **4** either in the free base form or in the protonated state reveals that there is no conformational change upon varying temperature from 323 to 223 K (Suporting Information).

The electronic spectral analysis of **3** and **4** in CH_2Cl_2 is shown in Figure 3. Compound **3** exhibits a sharp Soret band at 495 ($\varepsilon = 0.58 \times 10^5\ M^{-1}cm^{-1}$) nm and four Q-like bands between 500 and 900 nm, which is typical of aromatic expanded porphyrins. A comparison of these data with fused β-substituted sapphyrins **1** and nonfused core-modified sapphyrins **5** (S3N2) reveals the following: (a) Both the Soret (29 nm) and Q-like bands (43 nm) are red-shifted with only marginal changes in the ε-values as compared to **1**; on the other hand, **3** exhibits a small blue shift of the Soret band (12 nm) and a red shift of the Q-band (39 nm) with a significant decrease in the ε values as compared to nonfused sapphyrins **5**.[23,24] Upon protonation of **3**, the imine nitrogens are protonated and the Soret band is red-shifted by 30 nm and appeared at 525 nm which indicate the extension of π-electron conjugation. The results are comparable with nonfused congener **5**; where there is a slight red shift of Soret band (1 nm) and blue shift of the Q-like band (12 nm), with moderate increase in the ε-values. A similar trend was observed in the electronic spectral analysis of **4** in CH_2Cl_2, where the free base sapphyrins shows the Soret band at 502 nm which upon protonation exhibits the band at 532 nm with the red shift of 30 nm. However, as observed from the NMR spectral analysis, the UV−vis absorption spectrum of the most stable isomer (SE-2) is recorded after 5 h which shows 11 nm blue-shifted Soret band and appeared at 521 nm. The increase in the ε-value as well the extension in the π-electron conjugation of **4** suggests the heavier heteroatom effect as compared to **3**. In addition, the spectral trend as observed in the case of **3** and its nonfused derivative **5**, the fused derivative **4** and its protonated derivative shows similar spectral changes as compared to the nonfused derivative **6**. Furthermore, the emission spectrum of **3** shows a weaker band at 836 nm which upon protonation is blue-shifted by 21 nm and appears as an intense band at 811 nm with 5-fold increase in the emission intensity. Similar trend was observed in the emission spectral analysis of **4** both in the free base as well as in the protonated form (Supporting Information). These results are consistent with *meso*-aryl sapphyrin.[25,26] The emission intensity is mainly due to the fused DTT moiety which is part of the macrocyclic framework. It is pertinent to point out here that there is no emission intensity observed in the case of respective nonfused sapphyrin (**5** and **6**) derivatives which reflects the absence of DTT moiety (Supporting Information).

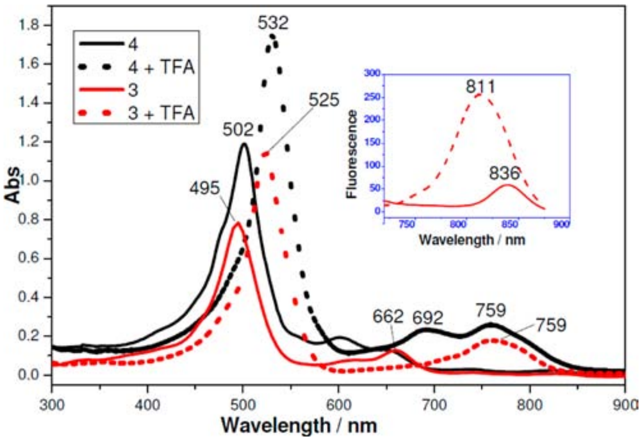


Figure 3. Electronic absorption spectrum of **3**, **4**, and its protonated derivatives in CH_2Cl_2. Inset shows the emission spectrum of **3** and its protonated derivative.

The final confirmation has come from the single-crystal X-ray structure, where the macrocycle **3** crystallizes in the monoclinic system (Figure 4). As predicted from the NMR analysis, the thiophene ring which is opposite to the DTT moiety is inverted and inside the macrocyclic framework. The nonbonding distance between two pyrrole rings (N1 and N2) is 6.5 Å, which is comparable with the nonfused core-modified derivative **5**,[23] is sufficient enough to accommodate the two β-Cs (C_{58}−C_{59}) inside the ring. All the heterocyclic rings and *meso*-aryl units deviated from the mean macrocyclic plane defined by the four meso carbon atoms C1−C10−C32−C38 are 28.02° (DTT), 10.62° (N1), 9.45° (N2), 18.30° (thiophene) (Figure 4b), and 72.53−88.92° (*meso*-aryl units). In addition, the DTT moiety is bent by 16.68° (S1) and 17.48° (S3) from the mean S2 plane (C4−C5−C6−C7−S2) and forms the macrocyclic ring. The crystal analysis of **3** shows a 1-D array formed from the intermolecular C−H···π interactions between one of the *meso*-aryl methyl C−H (C16−H16c) units and *meso*-mesityl π cloud of the neighboring macrocyclic ring with the distance and angle of 2.75 Å and 156°, respectively (Supporting Information).

The redox behaviors of **3** and **4** were studied by cyclic voltammetry and differential pulse voltammetry. Both **3** and **4** (Supporting Information) exhibit two reversible oxidation and two reversible reduction couples, which supports the aromatic

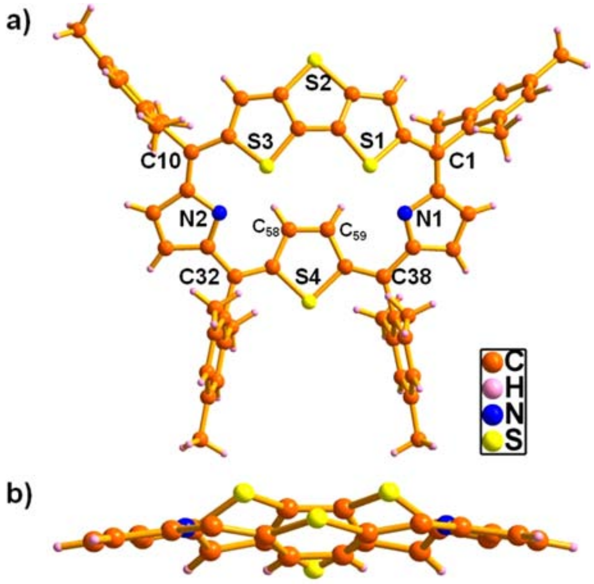


Figure 4. Single-crystal X-ray structure of **3**: (a) top view and (b) side view; *meso*-aryl groups are omitted for clarity in the side view.

nature. The ΔE_{redox} value calculated from the difference of first oxidation and first reduction potential for **3** and **4** are 1.596 and 1.584 V and indicate significant decreases in the ΔE_{redox} value relative to *meso*-aryl porphyrins (2.26 V) and comparable results with the corresponding nonfused derivatives (**5** and **6**). These results suggest a decrease in the HOMO−LUMO gap in **3** and **4** relative to porphyrins. Thus, the observed red shifts of the Soret and Q-bands in the electronic spectral analyses are consistent with this.

Overall, the introduction of fusion in the macrocyclic framework leads to series of spectral changes as compared to the nonfused sapphyrin derivatives, which results in (a) blue shift (12 nm in **3** and 5 nm in **4**) of the Soret band in the free base form; (b) a significant reduction in the molar extinction coefficient; (c) marginal change in aromaticity as reflected from the NMR spectral analysis (11.1 ppm vs 12.1 ppm in **3**, 12.65 ppm vs 12.5 ppm in **4**); and (d) significant emission intensity both in the free base as well as in its protonated form.[23,24] Nevertheless, as compared to the fused congeners (**1** and **2**) and higher homologues (singly and doubly DTT fused rubyrins), compounds **3** and **4** exhibit structural diversity in the core-modified fused system for the first time.[14]

In conclusion, we have synthesized two new fused core-modified sapphyrins containing a DTT core by a simple and efficient acid-catalyzed condensation reaction. We have also demonstrated the structural diversity in **3** and **4** where the thiophene ring was inverted in **3** and two different conformers of the selenophene (both normal and inverted) ring in **4** in its free base form. Introduction of fusion resulted in a decrease in aromaticity, probably due to ring inversion. The role of fusion can further be explored by studying the photodynamics and anion receptor properties which are currently underway in our research group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedure, spectral data for all the new compounds, and crystal data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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