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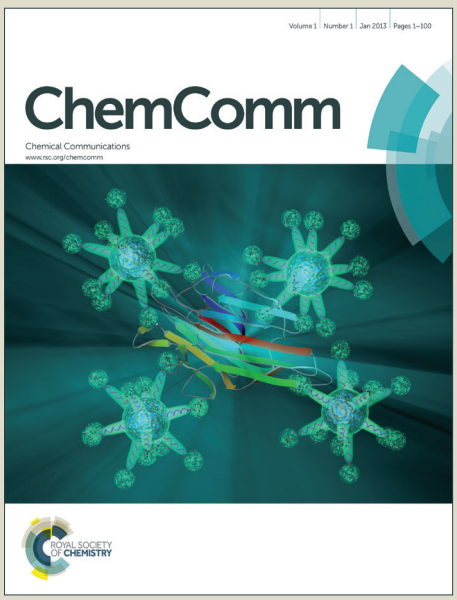

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Fused Core-Modified Planar Antiaromatic 32π Heptaphyrins: Unusual Synthesis and Structural Diversity

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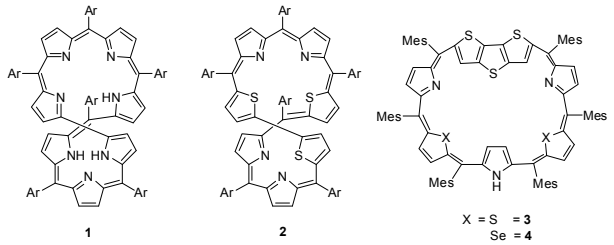
The condensation reaction of fused dithienothiophene (DTT) diol with core-modified tripyrrane led to acid and its concentration dependent product formation, sapphyrin and heptaphyrin. The single crystal X-ray analysis of sulphur and selenium heptaphyrin exhibits planar conformation owing to fusion. The experimental and theoretical calculations revealed the Hückel 4nπ antiaromatic electronic structure.

Intriguing structural diversity and aromaticity of expanded porphyrins continue to attract the attention of researchers.[1] Expanded porphyrins exhibit structural diversity such as planar, inverted, figure-eight, Möbius band, confused, fused and bridged forms depending upon the number and type of *meso* substitution and core-modification.[2-6] Structural diversity has the significant impact on the electronic structure, conjugation pathway, aromaticity and physical & chemical properties of the macrocycle. [2-6] Thus, the role of structural diversity is important in expanded porphyrin chemistry.

Recently, expanded porphyrins and core-modified expanded porphyrins provide the platform for studying the aromaticity in the annulene type molecules. Moreover, it shows different aromatic properties such as Hückel aromatic, antiaromatic, nonaromatic and Möbius aromatic electronic structure depending upon the oxidation state and conformation.[3] Especially, antiaromatic electronic structures are realized by simple and easy methods such as suitable functional group substitution, metal coordination, protonation and by external stimuli.[4–7] There are series of notable strategies for the synthesis of antiaromatic macrocycle. For example, Osuka and co-workers synthesized the *meso*-2-imidazolyl substituted planar antiaromatic hexaphyrins and octaphyrins.[8] Anand and co-workers described the synthesis of planar antiaromatic expanded isopholorins.[9] Recently, we reported the doubly fused 36π octaphyrin which undergoes conformational change from figure-eight to extended planar form along with aromaticity change from nonaromatic to Hückel antiaromatic by simple protonation.[10]

Heptaphyrins are expanded porphyrins where seven heterocyclic rings are connected by seven *meso*-carbon bridges in the macrocyclic framework.[11–19] The syntheses of heptaphyrins are well known in the literature. For example, Sessler and co-workers reported the two and five *meso*-carbon bridged heptaphyrin with nonaromatic and aromatic characteristics.[11,20] Osuka and co-workers described the synthesis of four, six (**1**) and seven *meso*-bridged heptaphyrins, where **1** is nonaromatic in solution.[17,21] Our group reported series of core-modified heptaphyrins with four,[12,13] five[18] and six-*meso* (**2**)[15] carbon bridges, where **2** is aromatic (Chart 1). Despite the number of *meso* links in the macrocycle, till date, the reported heptaphyrins are confined to non-fused derivative with different conformational behaviours and are either aromatic or nonaromatic.[11-23] Herein, we report the synthesis of fused core-modified heptaphyrins with six *meso* bridges which maintains planarity both in freebase as well as protonated state and follows 4nπ Hückel antiaromatic character.

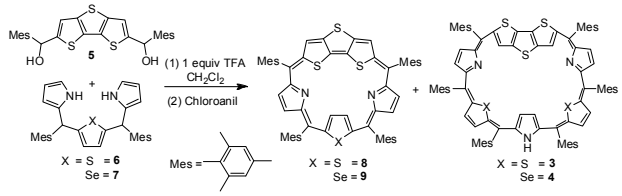


1 2

Chart 1: Non-fused normal (**1**), core-modified (**2**) and fused (**3** & **4**) heptaphyrins

Tripyrranes are prone to acidolysis in the presence of acid. Earlier, we have shown that the modified tripyrranes are not stable under reaction conditions and undergo acid-catalyzed fragmentation.[13] This can be suppressed by varying the acid and its concentration. However, tripyrrane acidolysis results in interesting products in addition to the expected product. Such a serendipity product (**3** or **4**) was observed while synthesizing the mono-fused sapphyrins (**8** or **9**). The synthetic methodology is shown in Scheme 1. We have adopted [2+3] acid-catalyzed condensation reaction of DTT-diol[10] **5** with thia-tripyrrane[13] **6** followed by oxidation afforded mono-fused sapphyrin **8** in 4% yield.[24] To our surprise, along with **8**, the hitherto unknown heptaphyrin **3** was also formed in 6% yield. Under the similar reaction condition, the acid-catalyzed condensation of **5** with selena-tripyrrane **7** afforded **9** in 3% yield and **4** in 4% yield, respectively. Increasing the acid concentration led to reduce the yields of **3** and **8**, while decreasing the acid-concentration led to more of sapphyrin product. By changing the acid-catalyst to *p*-toluenesulphonic acid (*p*-TSA) or methanesulphonic acid (MSA), at 0.5 equiv, **8** was isolated as sole product with better yield, however, while increasing the concentration no drastic change in the yield distribution was observed (Table S1, ESI). The

mechanism for the formation of **3** or **4** is not clear. However, this can be rationalized by considering the fragmentation of modified tripyrrane **6** in the presence of acid-catalyst and the recombination of the fragmented product with **6** and DTT-diol **5** to generate the porphyrinogen intermediate which on oxidation can afford fused core-modified [32]heptaphyrin (1.1.1.1.1.1.0) **3** (Scheme S1, ESI).



Scheme 1: Synthesis of sapphyrins and heptaphyrins

The composition of **3** and **4** was established from elemental analysis and mass spectrometry data. The compounds **3** and **4** showed parent ion signal at m/z 1338.4881 [M+H$^+$] and 1434.3769 [M+H$^+$], respectively, which are consistent with the exact composition of the macrocycle (Fig. S1 and S2, ESI). The solution structure was arrived at by a detailed analysis of ^{1}H NMR and ^{1}H-^{1}H COSY spectrum of **3** and **4** in $CDCl_3$. The ^{1}H NMR spectrum of **4** is shown in Figure 1. The DTT protons (a) are resonated as a singlet at 16.69 ppm, while the β-CH and NH proton of pyrrole ring (b) which is opposite to the DTT unit is observed as a singlet at 15.26 ppm and a broad signal at 3.86 ppm, respectively (Fig. 1(i)). This is further confirmed by D_2O exchange experiments. The pyrrole rings (c, c'), which are adjacent to the DTT moiety and the selenophene units (d, d'), are appeared as doublet of doublet centred at 5.29 ppm and 8.06 ppm, respectively. These signals are further confirmed by correlation in the COSY spectrum (Fig. S6, ESI). The *meso* mesityl-CH protons are observed between 6.6 to 6.8 ppm, while the *meso*-mesityl

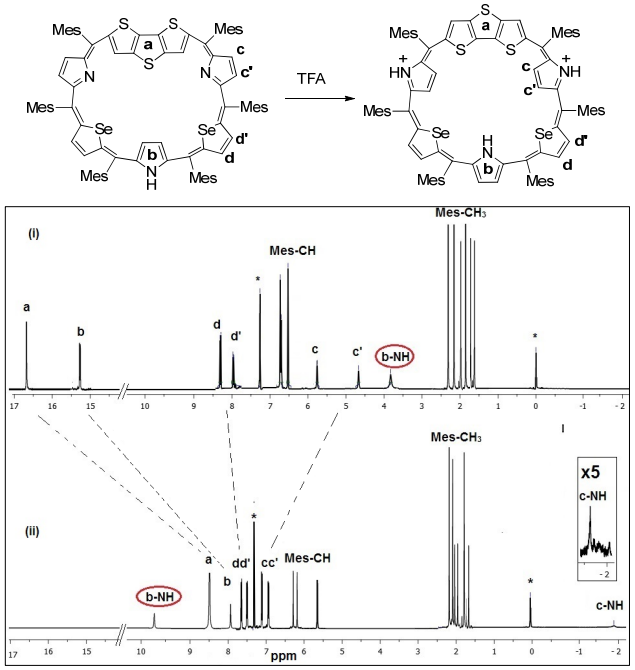


Fig 1. ^{1}H NMR spectrum of **4** in its freebase (i) and protonated form (ii) in $CDCl_3$

CH_3 protons are resonated between 1.63 to 2.19 ppm. The appearance of DTT (a) and pyrrole β-CHs (d) proton signal at downfield region and the pyrrolic NH signal in the upfield region reveal that both the units are inverted. The overall observation in **4** confirms the paratropic ring current and antiaromatic character of the 32π heptaphyrin.

Upon protonation of **4** with TFA in $CDCl_3$ (Fig. 1(ii)), the inverted β-CH protons of DTT (a) and pyrrolic (b) moiety in the freebase form is now gradually shifted to upfield, and pyrrolic NH is in the downfield region and the respective signals are at 8.35 (a), 7.82 (b) and 9.78 ppm (b, NH) with the Δδ (chemical shift difference between the inverted and normal rings which are in the freebase and protonated form) value of 8.34, 7.44 and 5.92 ppm, respectively and thus become normal. On the other hand, the normal β-CH protons of the pyrrolic units (c, c') in the freebase form are downfield shifted and centered at 7.24 ppm with Δδ shift difference of 1.95 ppm and the protonated NH is appeared in the upfield region at -1.64 ppm and thus become inverted. However, the selenophene β-CHs are slightly downfield shifted and centered at 7.38 ppm which are further confirmed by ^{1}H-^{1}H COSY analysis (Fig. S7, ESI). Overall, upon protonation, drastic structural changes were observed, however, retains the antiaromatic character as such. Similar trend was observed in the spectral analysis of **3** both in the freebase and protonated form (Fig. S3 and S4, ESI). Furthermore, the variable temperature ^{1}H NMR analysis of **3** either in the freebase form (Fig. S5, ESI) or in the protonated state reveals that there is no conformational change upon varying temperature from 343 K to 213 K. A comparison of these data with six-*meso* linked non-fused all aza derivative **1** and the corresponding core-modified heptaphyrin **2** reveals that **1** adopts figure-eight conformation and is nonaromatic,[17] while **2** is aromatic in the freebase form. Upon protonation, **2** maintains aromatic character as such in solution.[15]

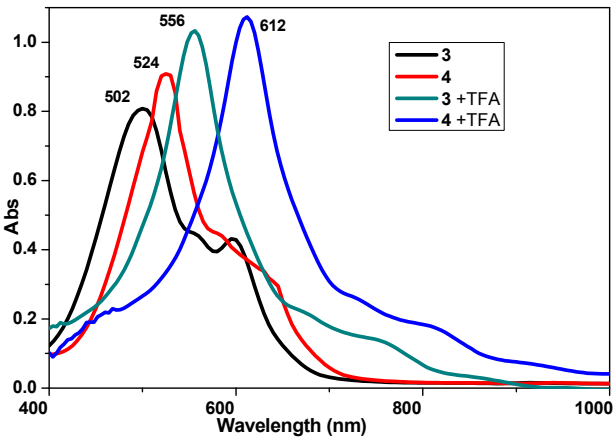


Fig 2. UV-Vis absorption spectrum of **3** and **4** in CH_2Cl_2.

The electronic spectral analysis of **3** and **4** in its freebase and protonated form in CH_2Cl_2 is shown in Fig. 2 which exhibits typical Soret like band at 502 nm and 524 nm, respectively. The ε values for these bands are the order of 10^4 which clearly indicate the antiaromatic characteristics in conjunction with 32π electronic circuit. Protonation by dilute TFA led to 54 and 88 nm bathochromic shift of Soret band and appeared at 556 and 612 nm for **3** and **4** respectively with only marginal increase in the ε values, which attribute to the extension in the π electron

conjugation. In addition, the electrochemical analysis **3** and **4** shows two quasi-reversible reduction and oxidation peaks with $\Delta E_{(ox1\text{-}red1)}$ value of 1.510 V and 1.491 V, respectively. These observations further support the antiaromatic electronic structure of **3** and **4** (Fig. S8 and S9, ESI).[15]

The final confirmation of **3** and **4** has come from the single crystal X–ray structural analysis. As predicted from the spectral analyses, **3** contains a DTT unit, three pyrrole and two thiophene units which are connected through the six *meso*-carbon bridges by mesityl units where the DTT moiety and pyrrole units are inverted (Fig. 3). The non-bonding distance between two thiophene rings (S1 and S2) is 8.1Å, which is sufficient enough to accommodate pyrrolic (N2) two β-Cs inside the ring.[24] The DTT unit is in positional disorder where two of the DTT units are overlapped each other. Analysis of the crystal structure reveals that the DTT unit in **3** is deviated by 28.8°, while the *meso*-mesityl rings are almost perpendicular to the mean macrocyclic plane, the other units such as thiophene and pyrrole units are hardly deviated from the mean plane, thus maintaining the planarity. Similar trend was observed in the single crystal X-ray analysis of **4** (Fig S12 and S13, ESI), where the DTT unit is deviated by 28.7°. On the other hand, the crystal analysis of **1** and **2** reveals that the **1** maintains planarity in the protonated form where three pyrrolic rings are inverted and deviated from the plane.[17] However, **2** adopts figure-eight conformation in the solid state.[15]

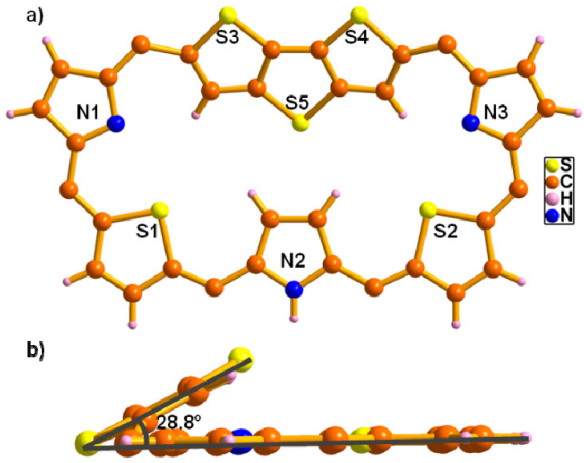


Fig 3. Single crystal X-ray structure of **3**. a) Top view and b) side view; *meso*-mesityl groups are omitted for clarity.

Further evidence for the antiaromatic nature of **3** and **4** was obtained by computing the nucleus-independent chemical shift (NICS)[25] values by employing density functional theory method M06L/6-31G** as implemented in Gaussian 09 suite of programs. The NICS(0) values from the crystal structure are found to be δ = +24.6 and +22.26 ppm, for **3** and **4** respectively. For the protonated derivatives, the NICS(0) values are +24.1 and +24.02 ppm for $\mathbf{3.2H^+}$ and $\mathbf{4.2H^+}$, respectively. These large positive NICS(0) values are in complete agreement with Hückel 4nπ-electron rules for antiaromatic electronic systems and are in line with the experimental results obtained from ^{1}H NMR analysis.

In summary, we have successfully synthesized the first example of fused core-modified heptaphyrin with six *meso* links. We have also demonstrated the planar and antiaromatic characteristic of fused heptaphyrin by experimentally and further proved by theoretical calculations. The photophysical properties of these novel rigid macrocycles are currently underway in our research group.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures and characterization of all new compounds and crystallographic data for compounds **3** and **4**.
See DOI: 10.1039/b000000x/

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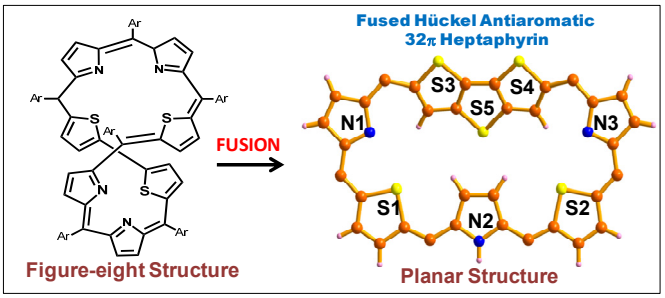
TOC Graphic



The novel core-modified fused heptaphyrins were synthesized and exploited its 4nπ Hückel antiaromatic electronic strucuture.