Fused core-modified *meso*-aryl expanded porphyrins†

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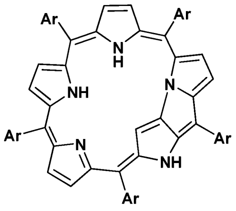
The synthesis and characterization of the first examples of singly and doubly fused expanded porphyrins containing dithienothiophene (DTT) cores are reported.

Expanded porphyrins receive considerable attention from chemists and material scientists due to their potential applications in opto-electronic devices and sensors.[1] Various modifications have been carried out on them such as core-modification,[2a] confusion[2b] and fusion[3] which lead to modulation in electronic structure, conjugation and electrochemical properties. Osuka and co-workers first reported fusion in expanded porphyrins in N-fused pentaphyrin[3a] **1** followed by many reports mainly involving pyrrolic nitrogens.[3] However, there are only few reports where fusion does not involve pyrrolic nitrogen(s). Recently sapphyrins derived from benzodipyrrole (**2a**) and benzodifuran (**2b**) have been reported by using 3 + 2 approach.[4] Very recently, Wu and co-workers reported rubyrins with phenanthrene-fused pyrrole rings which serve as a Hg^{2+} sensor.[1e] To the best of our knowledge, there are no other reports on expanded porphyrins where fusion does not involve pyrrolic nitrogen(s). Thus, it is important to synthesize fused expanded porphyrins by easy and efficient methods using a rational approach so that the design principles used can be applied to generate a variety of fused skeletons. In this communication we report that we have succeeded in designing efficient methodology to synthesize a range of expanded porphyrins using a preformed fused precursor. The fused precursor is dithienothiophene (DTT) **3** which has an electron rich rigid core and has been used as a building block for many electronic and opto-electronic materials.[5] We speculated that the incorporation of a planar DTT core in expanded porphyrins can lead to conformational rigidity resulting in planar fused macrocycles with increased aromaticity, which is a basic requirement for any macrocycle for use in optical materials. The versatility of the method was demonstrated by synthesizing singly and doubly fused rubyrins and fused heptaphyrins using appropriate conditions. It has been shown that these macrocycles are almost planar and show aromatic characteristics.



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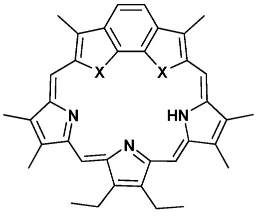
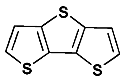


X = NH 2a ; X = O 2b



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The key precursor required for the synthesis was fused bithiophene diol **4**. This was synthesized by dilithiation of **3** followed by the addition of aldehydes in THF to give fused bithiophene diols (DTT diols) **4** in 60–70% yield. Thus the [4 + 2] MacDonald type condensation of DTT-diols **4** with modified tetrapyrranes **5** in the presence of 1 equivalent of trifluoroacetic acid (TFA) as a catalyst followed by oxidation with *p*-chloranil in air gave mono-fused rubyrins **6a–c** in ~20% yields as a single product (Scheme 1). The mass spectra peaks at m/z = 1010.66 [M]$^+$ and 1107.31 [M + 1]$^+$ for **6a** and **6c** indicated formation of the mono-fused rubyrins. The ^{1}H NMR spectrum of **6a** in CDCl$_3$ shows a sharp singlet at δ = 10.76 ppm corresponding to the β-CH of the DTT moiety (Fig. 1). The four bithiophene protons resonate as two doublets at 11.82 and 10.52 ppm. Two sets of pyrrolic protons resonate closely at 9.04 and 9.02 ppm. The mesityl phenyl protons are observed at 7.46 ppm. These assignments are based on the correlations found in the ^{1}H–^{1}H COSY spectrum. The aromaticity of fused rubyrins estimated by ^{1}H NMR chemical shifts are in comparison to rubyrin without fusion. For example on protonation with TFA the bithiophene and pyrrole protons were shifted by 0.8 and 1.1 ppm compared to 0.29 and 0.35 ppm for the same protons for a similar rubyrin without fusion.[6] Furthermore the NH protons are also more shielded and appear (at 233 K) at −7.15 ppm compared to −5.15 ppm observed for rubyrin without fusion (ESI†). Overall, the chemical shift difference (δ) between most shielded (pyrrolic NH) and deshielded (β-CH) protons of **6a** is 20 ppm compared to 17 ppm for rubyrin without fusion suggesting an increase in the aromaticity upon fusion.

Similarly, doubly fused rubyrins were synthesized by simply condensing DTT-diols **4** with pyrrole under modified Lindsey's conditions with 1 eq. of TFA. The rubyrins were obtained in ~15% yield as a single product. The proposed structure was initially confirmed by the mass spectrum peak at m/z = 1040 [M]$^+$ for **7a**. The ^{1}H NMR spectrum confirms the symmetrical nature of the molecule. For example in the aromatic region the ^{1}H NMR spectrum of **7a** contains three singlets at 10.92, 9.24 and 7.56 ppm, corresponding to DTT, pyrrole and phenyl protons which are slightly deshielded compared to normal and mono fused rubyrins. On protonation, similar to **6a**, the CH protons were more deshielded and the NH proton appears at −7 ppm (ESI†).

The final proof of the proposed structures came from single crystal X-ray crystallography.[7] The crystal structure of **6a** is shown in Fig. 2.‡ The unit cell contains two molecules. Due to

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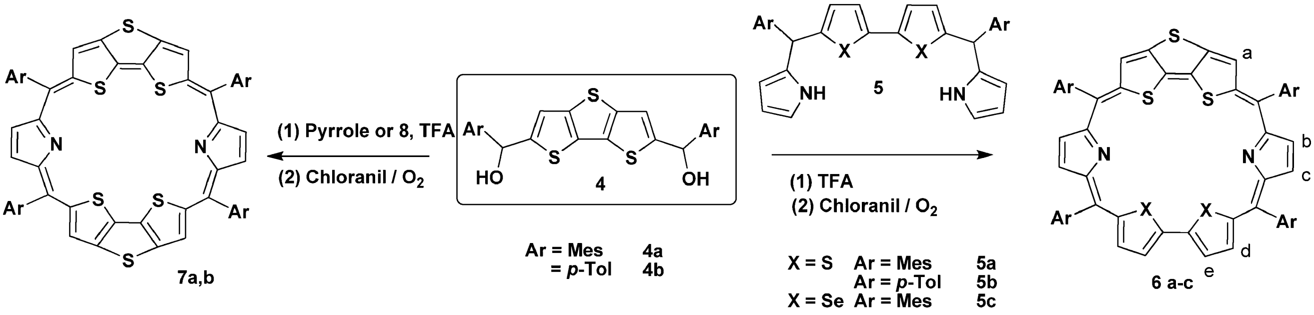
† Electronic supplementary information (ESI) available: Detailed experimental procedures, characterization data and preliminary crystal structures of **6c** and **7a**. CCDC 694219–694221. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000387e



Scheme 1 Syntheses of mono and doubly fused rubyrins.

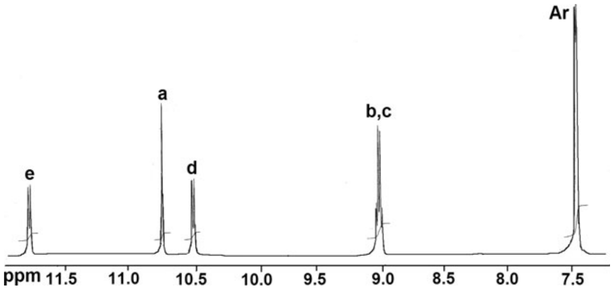


Fig. 1 ^{1}H NMR spectrum of **6a** in the downfield region in CDCl$_3$ (for labeling (a–e) see Scheme 1).

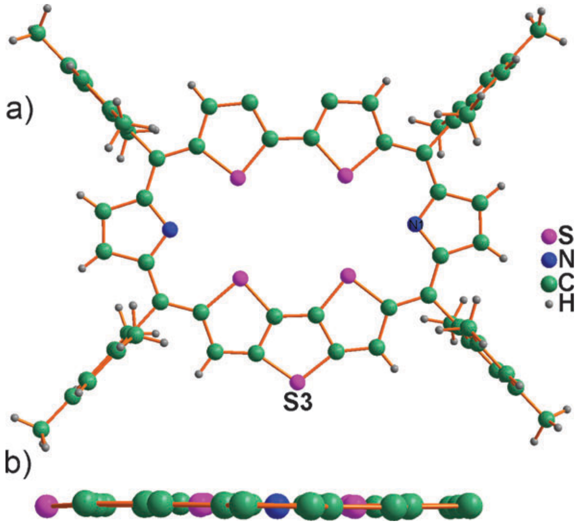
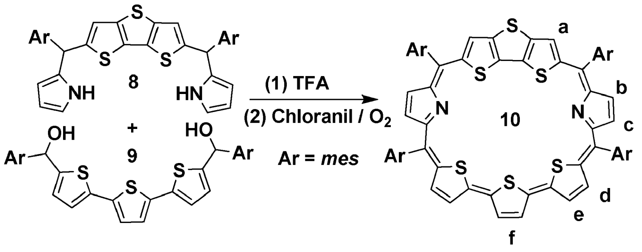


Fig. 2 Crystal structure of **6a**. (a) Top view with 30% probability thermal ellipsoids. (b) Side view (*meso* aryl groups and hydrogens are omitted for clarity).‡

the pseudo-symmetrical nature of the macrocycle the S3 atom is in positional disorder and refined with 0.5 occupancy factor. Crystal structure analysis reveals the complete planarity of the molecule as envisaged. As expected, the fused bithiophene unit is planar and deviation from the molecular plane defined by the four *meso* carbons is very small (1.256(30)°). Similarly, the pyrrole plane is also coplanar with the molecular plane making the molecule completely flat. This is the first time such a flat structure has been observed for rubyrins. In all other rubyrins (all aza and core-modified) reported earlier, two or more heterocyclic units are canted.[6,8] The *meso* phenyl groups are almost perpendicular due to the bulkiness of the mesityl group, typical of *meso*-aryl expanded porphyrins. The preliminary crystal structures of **6c** and **7a** also show planar structure (ESI†). In **6c**, S and Se atoms are in positional disorder due to pseudo-symmetry. However, compared to all thia analogue **6a** the biselenophene unit is slightly tilted with respect to the mean plane, probably due to the bigger size of Se compared to S.

This methodology was extended to obtain a higher order macrocycle such as fused heptaphyrin. For this the precursor required was fused tetrapyrrane **8** which was obtained under Lindsey's conditions by treating diols **4** with excess pyrrole in the presence of 0.1 eq. of TFA as catalyst in 60% yields. The versatility of our synthetic strategy was demonstrated by the availability of an alternate route for the syntheses of doubly fused rubyrins. Thus, MacDonald condensation of tetrapyrranes **8** with diols **4** also yielded doubly fused rubyrins **7** in 15–20% yields. The fused heptaphyrin was synthesized by a condensation reaction of tetrapyrrane **8a** with terthiophene diol **9** in the presence of 1 equivalent of TFA, which gave fused heptaphyrin **10** in 23% yield (Scheme 2). The mass spectrum peak at m/z = 1093.28 $[M+1]^+$ confirms the formation of the fused heptaphyrin. The effect of the fusion is clearly visible from the analysis of the ^{1}H NMR spectrum (Fig. 3). The reduction in the number of peaks in the aromatic region compared to similar non-fused heptaphyrin clearly reveals the symmetry of the molecule. The normal heptaphyrin is not symmetric, non-planar and shows fourteen doublets for the seven heterocycles.[9] In contrast, the aromatic region in the ^{1}H NMR spectrum of **10** in CDCl$_3$ contains four singlets and four doublets. The singlets at 10.59 and 11.42 ppm have been assigned to the β-CH protons of DTT (a) and central thiophene (f) (see Scheme 2). The doublets at 11.23 and 10.16 ppm were assigned to β-CH of the other two thiophenes (d, e). The pyrrole protons (b, c) resonate closely at 8.88 and 8.76 ppm respectively as doublets. The two singlets at 7.54 and 7.48 ppm were assigned to phenyl protons of the mesityl group. It is clear from the NMR spectrum that no ring inversion takes place in sharp contrast to non-fused heptaphyrin (**11**) where one of the thiophene rings of the bithiophene unit is inverted.[9b]

The effect of conformational restriction on the spectral properties of macrocycles (Fig. 4) upon fusion was inferred from the following observations: (i) the blue shift of the Soret



Scheme 2 Synthesis of fused heptaphyrin.

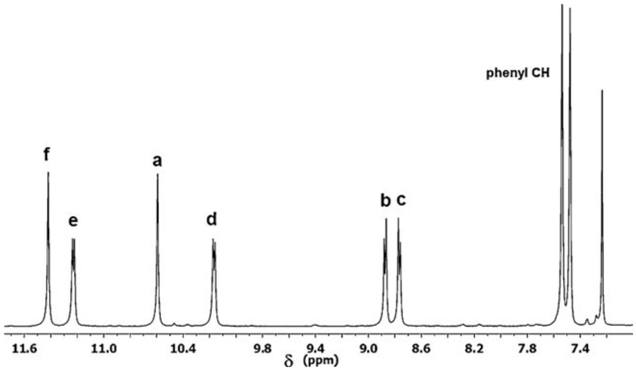


Fig. 3 ^{1}H NMR spectrum of **10** in the downfield region in CDCl$_3$ (for labeling (a–f) see Scheme 2).

band on fusion (6 nm for mono-fused (**6a**) and 10 nm for doubly fused (**7a**)), (ii) the increase in the molar extinction coefficient by 4 times upon fusion in rubyrins (**6**, **7**),[10] and the 1.5 times increase in fused heptaphyrins (**10**),[10] (iii) the increase in planarity of **10** relative to **11**, (as reflected by ^{1}H NMR) and (iv) the dramatic downfield shift of a, a′ protons of **11**[9a] from −0.6 ppm to 10.6 ppm in **10**.

In conclusion we have synthesized a new range of mono and doubly fused core-modified expanded porphyrins containing DTT cores. We also demonstrated that fused expanded porphyrins can be designed by choosing appropriate precursors. In rubyrins fusion resulted in increased aromaticity, probably due to their flat structure. By introducing fusion, we were also able to restrict the conformation of the heptaphyrin. Possibly, fusion can be used as a tool for attaining planarity/rigidity in larger expanded porphyrins. Research in this direction is underway.

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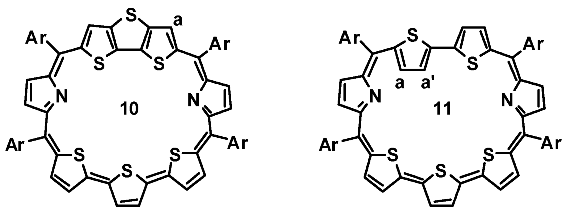

Fig. 4 Effect of fusion: conformational restriction.

Notes and references

‡ Crystal data for **6a** C$_{64}$H$_{52}$N$_2$S$_5$:[9] crystals were grown by slowly diffusing dry *n*-hexane over a chloroform solution of **6a**. Green rectangular, monoclinic, space group $P2_1/n$, a = 14.6226(29) Å, b = 15.0918(30) Å, c = 15.9295(32) Å, α = 90.00°, β = 114.978(30)°, γ = 90.00°, V = 3186.6(13) Å^3, T = 293(2) K, Z = 2, μ(Mo-Kα) = 0.218 mm^{-1}, F(000) = 1060. 45977 reflections were measured, of which 5924 were unique (R_{int}) = 0.0430, R_1 = 0.0948, wR_2 = 0.2006, final R_1 ($I > 2\sigma(I)$) = 0.0843, wR_2 = 0.1933, GOF on F^2 = 1.047. CCDC 694219. The S3 atom is in positional disorder and refined with 0.5 occupancy factor, where two independent molecules are overlapped with opposite orientation.

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10 The electronic spectral data for **6a**, **7a** and **10** are as follows: **6a**. UV-Vis (CH$_2$Cl$_2$) [$\lambda_{\max}$ (nm) ($\varepsilon \times 10^{-5}$)]: 517 (6.10), 536 (3.10), 606 (0.09), 659 (0.30), 711 (1.30), 822 (0.05); (CH$_2$Cl$_2$/TFA): 538 (4.70), 559 (3.40), 783(0.30) and 831(1.00). **7a**. UV-Vis (CH$_2$Cl$_2$) [$\lambda_{\max}$ (nm) ($\varepsilon \times 10^{-5}$)]: 513 (3.80), 540 (2.10), 606 (0.09), 665 (0.17), 710 (0.82), 800 (0.06); (CH$_2$Cl$_2$/TFA): 535 (2.40), 566 (1.64), 766 (0.17), 843 (0.77). **10**. UV-Vis (CH$_2$Cl$_2$) [$\lambda_{\max}$ (nm) ($\varepsilon \times 10^{-5}$)]: 553 (2.00), 579 (1.38), 797 (0.70); (CH$_2$Cl$_2$/TFA): 613 (1.60), 860 (0.12), 933 (0.70).