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First structural characterization of core modified 10,15-*meso* aryl azuliporphyrins: observation of C–H$\cdots\pi$ interaction between pyrrole β-CH and mesityl ring†

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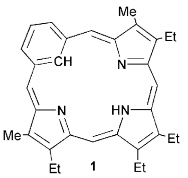
First successful syntheses and structural characterization of new core modified *meso* aryl azuliporphyrins by a simple [3 + 1] methodology are reported.

Research on the syntheses of new porphyrin analogues containing one or more carbon atoms in the place of pyrrole nitrogens is gaining momentum.[1] Such molecules are interesting from several points of view. They build a linkage between annulene and porphyrin chemistry, exhibit interesting aromatic behaviour because of the competition between the aromaticity of the small cyclic subunit and the 18π porphyrin unit,[2] and form complexes with transition metals through the formation of M–C bonds leading to interesting organometallic species.[3] This has led to the syntheses of benziporphyrin **1**, carbaporphyrin **2**, N-confused porphyrin **3**[4] and azuliporphyrin **4**. Lash and coworkers have recently pioneered the syntheses of a range of azuliporphyrins and have shown that the azulene subunit effectively interrupts π-electron conjugation pathways within the macrocycle.[2,5] The spectroscopic properties reveal that **4** has borderline porphyrin aromaticity with dipolar canonical forms making important contributions. The electronic structure and the aromaticity can be further altered by replacing one or more pyrrole nitrogens in **4** by heteroatoms such as S or Se. We have been interested in such a core modification and our recent efforts on the core modified oxybenziporphyrins have shown that the electronic structure can be significantly altered by the introduction of hetero atoms into the core.[6] In this communication, we wish to report the first examples of modified azuliporphyrins (Scheme 1). The spectroscopic and single crystal X-ray structural determinations reveal that the modified azuliporphyrin exhibits a completely planar structure in the solid state and the directed secondary C–H$\cdots\pi$ interactions between the β-CH of pyrrole ring and the *meso* mesityl π system lead to a one-dimensional array of porphyrins where the two adjacent porphryin rings are aligned perpendicular to each other to facilitate the C–H$\cdots\pi$ interactions (Fig. 1).



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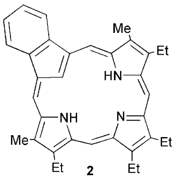

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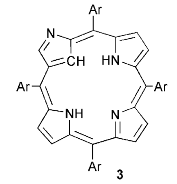

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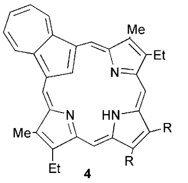

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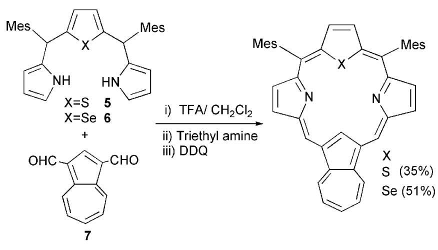
Most of the new porphyrin analogues have been synthesized through a [3 + 1] acid catalysed MacDonald type condensation[1] reaction of appropriate precursors. In the present synthesis a similar methodology was followed by the reaction of tripyrranes **5** or **6** with appropriate hetero atoms with azulene-1,3-dicarboxaldehyde **7** in methylene chloride containing ten equivalents of trifluoroacetic acid (TFA) catalyst. After 16 h, the condensation reaction was complete as monitored by TLC. The reaction mixture was then neutralised with triethylamine followed by oxidation of the macrocycle with DDQ. Purification by column (alumina, grade III) chromatography using dichloromethane as eluent, gave **8** in 35% and **9** in 51% yield.

The FAB mass spectra of **8** and **9** confirmed the proposed compositions.‡ The appearance of a singlet at 9.22 ppm for the *meso* hydrogens and another singlet at 2.87 ppm for the inner CH azulene proton in the ^{1}H NMR spectrum of **9** in $CDCl_3$ suggest the presence of two-fold symmetry along the axis passing through the centers of heteroatom and the azulene group. The calculated $\Delta\delta$ (difference in the chemical shifts of the most shielded and the most deshielded proton) of 6.35 ppm suggests that in the free base form, the aromaticity is lower than that is expected for 18π porphyrin systems. The charge separation in the dipolar resonance structure such as **10** may contribute to the reduced aromaticity. However, on protonation with TFA, there is a dramatic shift in the resonances of inner CH and the *meso* hydrogens in the opposite directions. The chemical shift of inner CH proton was dependent on the concentration of TFA used and the temperature at which the spectra were recorded.† The inner CH proton was observed at -2.66 ppm at a concentration $\approx 10\%$ v/v TFA in CD_2Cl_2 at -30 °C and the *meso* hydrogens appear at 10.9 ppm under the same conditions.† This corresponds to a $\Delta\delta$ value of 13.56 ppm suggesting high aromatic character of **9** in the diprotonated state. The further shielding of azulene inner CH upon diprotonation suggests a change of electron delocalization pathway from **9** to **11** (Scheme 2). In the electronic absorption spectra† of **9**, typical porphyrin like Soret and Q-bands were observed in the region 350–700 nm and upon protonation the absorption bands experience a red shift ($\approx$ 20–35 nm) with 1.5 increase in the ε values suggesting that the tropylium character as in **11** promotes the porphyrin aromaticity upon protonation. The deshielding of tropylium protons by ≈ 1 ppm upon protonation also supports such a conclusion. This is also in



Scheme 1

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† Electronic supplementary information (ESI) available: FAB mass, UV–VIS, ^{1}H and 2D NMR spectra. See http://www.rsc.org/suppdata/cc/b2/b204642c/

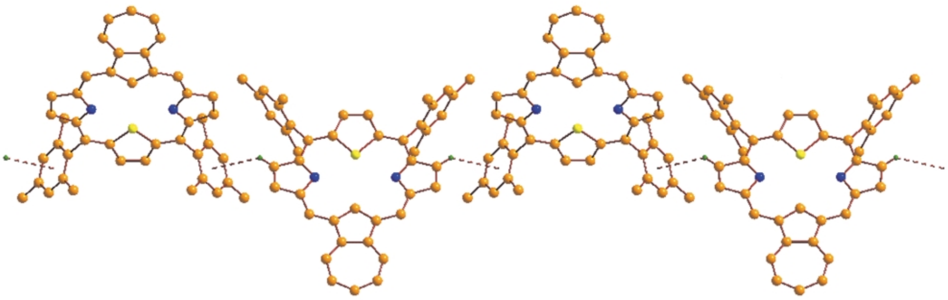
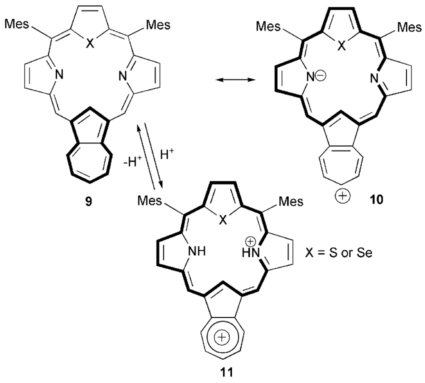


Fig. 1 One-dimensional network in the crystal structure of **8** held by C–H$\cdots\pi$ interactions (non-interacting hydrogen atoms are omitted for clarity, orange: carbon; blue: nitrogen; yellow: sulfur; green: hydrogen).



Scheme 2

accord with the conclusions of Lash and coworkers for the all aza azuliporphyrins.[2]

Further confirmation of the molecular structure came from single crystal X-ray analysis of **8**§ (Fig. 2). The molecule shows a completely planar structure with azulene subunit in the plane defined by the four *meso* carbons. The two *meso* mesityl rings are almost perpendicular to the mean plane of the *meso* carbon atoms [dihedral angles: 100.942(26), 78.925(26)°]. The changes in the delocalization pathway due to the replacement of pyrrole NH by thiophene sulfur is obvious from the altered bond distances of C_β–C_β and C_α–S bonds relative to the free heterocycle. [C_β–C_β and C_α–S for **8** is 1.360(3) and 1.748(2) Å respectively, while for the free thiophene are 1.42 and 1.71 Å respectively]. The aromatic nature is evident from the fact that C_β–C_β distances are smaller than C_α–C_β distances [C_β–C_β pyrrole 1.352(3) Å, C_α–C_β pyrrole 1.457(3) Å; C_β–C_β thiophene 1.360(3) Å, C_α–C_β 1.416(3) Å]. There is a strong intramolecular C–H$\cdots$S hydrogen bonding [bond distance 2.532(1) Å; bond angle 177.00(18)°] interaction inside the azuliporphyrin cavity. The observed bond distance is one of the shortest known in the literature.[7a]

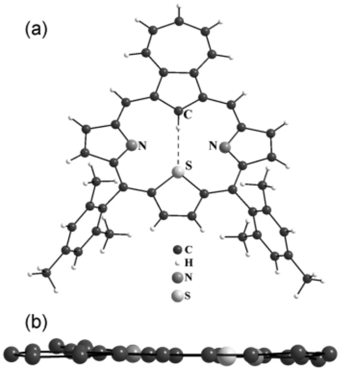


Fig. 2 Crystal structure of **8**: (a) Top view (dotted lines show the intramolecular hydrogen bonding); (b) side view showing the planarity of the molecule (mesityl rings and the hydrogens are omitted for clarity).

The interesting aspect of the structure is the observation of intermolecular C–H$\cdots\pi$ interactions[7a] between one of the β hydrogen of the pyrrole ring and the π cloud of the *meso* mesityl ring. Such an interaction is possible only if the two adjacent porphyrin rings are perpendicular to each other and indeed a detailed analysis of the structure indicates the formation of one-dimensional network of porphyrins held by such C–H$\cdots\pi$ interactions (Fig. 1). The metric parameters for the interactions are, C–H distance 0.950(2) Å; H$\cdots\pi$ distance 2.79(1) Å; C–H$\cdots\pi$ angle 137.10(12)°. These are in excellent agreement with the values observed by Kochi and coworkers for similar interactions in arenediazonium tetraphenylborate system reported recently.[7b]

In summary, we have successfully described the syntheses and characterization of thia and selena azuliporphyrins by a [3 + 1] methodology and the single crystal X-ray structure of the thia derivative exhibits a planar structure and directed secondary C–H$\cdots\pi$ interactions are responsible for the formation of one-dimensional supramolecular arrays in the solid state.

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Notes and references

‡ *Characterization data*: for **8**: UV/Vis (CH_2Cl_2): λ_{max}/nm (log ε) 395 (4.99), 477 (sh) (4.7), 494 (4.95), 670 (4.20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.49 (d, 2H, *J* 9.52 Hz), 9.31 (s, 2H), 8.33 (d, 2H, *J* 4.4 Hz), 8.16 (s, 2H), 7.81 (m, 3H), 7.55 (d, 2H, *J* 4.4 Hz), 7.09 (s, 4H), 2.74 (s, 1H), 2.45 (s, 6H), 1.92 (s, 12H).For

9: UV/Vis (CH_2Cl_2): λ_{max}/nm (log ε) 397 (4.89), 465 (sh) (4.79), 492 (4.96); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.34 (d, 2H, *J* 9.04 Hz), 9.22 (s, 2H), 8.32 (m, 4H), 7.65 (m, 3H), 7.54 (d, 2H, *J* 4.12 Hz), 7.09 (s, 4H), 2.87 (s, 1H), 2.45 (s, 6H), 1.95 (s, 12H).

§ *Crystal data* for **8**: $C_{44}H_{36}N_2S$, M = 624.81, orthorhombic space group *Pbam*, D_c = 1.137 Mg m^{-3}, Z = 8, a = 16.6722(6), b = 17.9438(7), c = 24.4007(9) Å, V = 7299.8(5) Å^3, T = 84(2) K, final $R1$ = 0.0578, $wR2$ = 0.1510, GOF = 1.041. CCDC 186274. See http://www.rsc.org/suppdata/cc/b2/b204642c/ for crystallographic data in CIF or other electronic format.

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