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Core modified oxybenziporphyrins: new aromatic ligands for metal–carbon bond activation†

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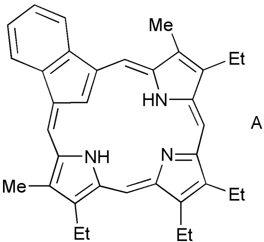
Successful syntheses of two new aromatic core modified oxybenziporphyrins by a simple '3 + 1' methodology and the first aromatic core modified oxybenziporphyrin palladium complex are reported.

Syntheses of new aromatic porphyrin derivatives continue to attract the attention of the chemists due to their diverse applications in biology, medicine, catalysis and material science.[1] This led to the discovery of many new porphyrin analogues such as carbaporphyrin[2] **1**, N-confused porphyrin[3] **2**, and benziporphyrin[4] **3** *etc*. Even though macrocycles **1**, **2** and **3** contain a CNNN core, **1** and **2** were found to be aromatic while **3** was non-aromatic. The non-aromatic nature of **3** was attributed to strong 6π arene aromaticity of the benzene ring relative to the porphyrinoid aromaticity. Addition of a suitably placed hydroxy group on the benzene ring in **3** led to the retention of aromaticity due to keto–enol tautomerism.[2] A recent report[4c] shows that this ligand is capable of forming a Pd–C bond, which was not known previously. In this communication we wish to report the first examples of aromatic core modified oxybenziporphyrins containing OCNN and SCNN cores. Such core modifications not only alter the electronic structure of the ring but also provides variable cavity size for metal coordination, where M–C, M–N and M–X (X = O or S) bonds can be created inside a single porphyrin unit.

A '3 + 1' acid catalysed MacDonald condensation has been successfully utilised by various groups[5] to synthesize new porphyrin analogues. In the present synthesis, a similar methodology was followed by the reaction of modified tripyrrane **4** or **5** with 5-formylsalicyaldehyde in the presence of 10 equivalents of trifluoroacetic acid in dichloromethane at room temperature. After two hours of stirring under nitrogen atmosphere, condensation of reagents was found to be complete and was monitored by TLC. The reaction was neutralised with triethylamine and oxidised by DDQ. Purification was done by column (alumina basic; grade III) chromatography using dichloromethane as eluent, which yielded **6** in 28% yield and **7** in 15% yield. Reaction of **6** with $PdCl_2$ in benzonitrile under reflux followed by chromatography (alumina neutral) afforded **8** in 77% yield (Scheme 1).



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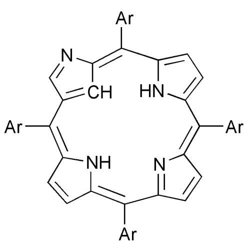

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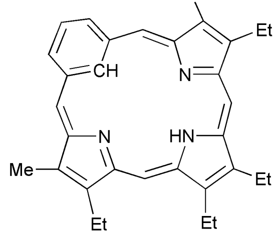

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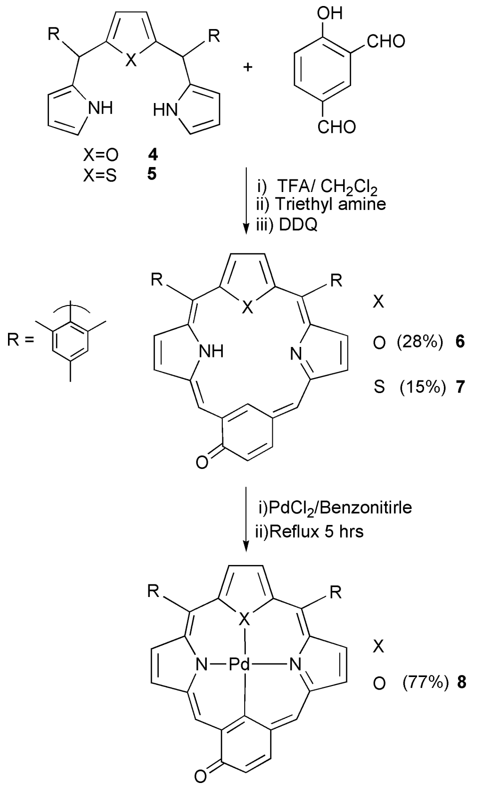

Scheme 1

The structures of new macrocycles **6**, **7** and **8** were confirmed by a variety of spectroscopic techniques.‡ The FAB mass spectra confirmed the composition, and infrared spectra showed a strong peak in the region of 1600 cm^{-1} due to the presence of a keto group. The detailed ^1H and 2D NMR spectral analysis† confirmed the proposed structure. Briefly, the inner CH proton resonates as a sharp singlet at −3.5 ppm for **6**, −4.32 ppm for **7**, while the NH pyrrole proton resonates as a broad singlet at −4.7 ppm for **6** and −2.09 ppm for **7** suggesting the effect of diatropic ring current on these protons. The *meso* hydrogens appear in the deshielding region and the estimated $\Delta\delta$ (difference in chemical shift of most shielded and the most deshielded proton) is 15.2 ppm for **6** and 15.12 ppm for **7**, clearly confirming the aromatic nature of these macrocycles. As expected hydrogens α and β to the keto group appear as a doublet at ≈ 7.3 ppm and at ≈ 8.7 ppm respectively and their chemical shifts are in accord with an α,β unsaturated keto subunit.[5b] Additional evidence for the aromatic nature of **6** and **7** comes from UV-Visible spectral data, where strong Soret type

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† Electronic supplementary information (ESI) available: See FAB mass, UV-Vis, ^1H, 2D NMR spectra. http://www.rsc.org/suppdata/cc/b1/b111155h/

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(split) bands appear in the region 430–480 nm (log $\varepsilon \approx 5$) and multiple Q-bands in the region 500–750 nm confirm the porphyrinoid nature of macrocycles. These absorption bands are found to be approximately 30 to 35 nm red shifted relative to the all aza analogue, due to the substitution of a heteroatom in the porphyrin core.[6] The metallation led to the expected changes in the absorption spectra (Fig. 1) where a lesser number of Q-bands were observed, typical of metalloporphyrins.

The monocations **6a** and **7a** were generated by careful titration with TFA (15 µL of 10% v/v in $CDCl_3$). The inner CH proton resonates as a sharp singlet at -5.03 ppm for **6a** and at -4.85 ppm for **7a** suggesting the retention of aromatic character upon mono-protonation. However further addition of TFA resulted in deshielding of this proton signal relative to **6a** and **7a** and the magnitude of deshielding is proportional to the concentration of TFA added. For example, the further addition of 35 µL, 65 µL, 125 µL of 10% TFA–$CDCl_3$ solution(v/v) to **6a** resulted in the observation of CH proton signal at -4.62, -4.09 and -3.03 ppm while for **7a** the signals were at -4.65, -4.38 and -3.78 ppm respectively. Furthermore the NH protons of **6a** were seen at 3.26 ppm and at 3.3 ppm at 273 K while for **7a** only a broad signal at 3.5 ppm was observed at 233 K. Excess addition of TFA can result in the formation of dicationic species either as a non-aromatic form represented by the diprotonated hydroxybenziporphyrin[5b] structures **6b** and **7b** or as an aromatic protonated carbonyl moiety as in **6c** and **7c**. The fact that the inner CH proton still experiences considerable diatropic ring current even in excess TFA indicates that the dicationic species can be better represented as **6c** and **7c** rather than **6b** and **7b**. This is in contrast to the observation made for the all aza analogue.[5b] The appearance of pyrrole NH signals at the deshielded region is attributed to the structural change experienced by the macrocycle upon diprotonation, typical of meso aryl porphyrins.[7] UV-Visible titration data with TFA also support such a conclusion.†

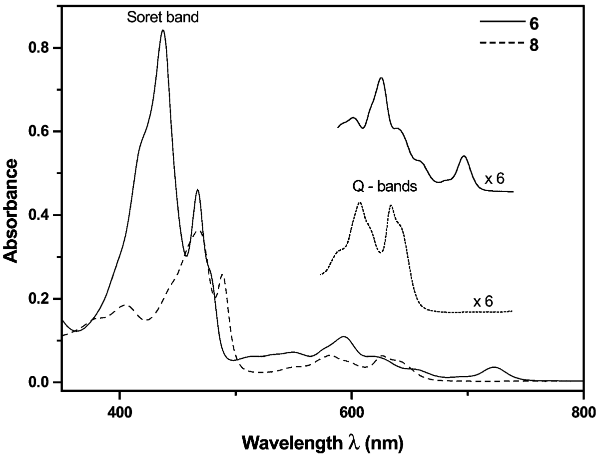
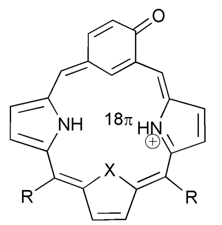
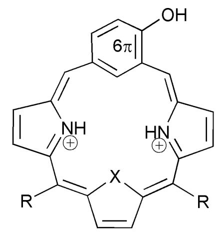


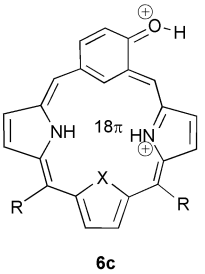
Fig. 1 Electronic absorption spectra of **6** (—) (1.91×10^{-5} M) and **8** (---) (1.23×10^{-1} M) in dichloromethane.



X = O 6a
X = S 7a



6b
7b



6c
7c

The reaction of $PdCl_2$ in benzonitrile with **6** results in the formation of metal complex **8**. The absence of inner CH and NH signals, in the NMR spectrum, imply the coordination of palladium with inner nitrogens, oxygen and carbon. The *meso* protons are slightly deshielded corresponding to free base **6**, an observation typical of metalloporphyrins. The shift of the C=O peak in the complex ($\gamma_{C=O}$ = 1588 cm^{-1}) relative to free base ($\gamma_{C=O}$ = 1630 cm^{-1}) further supports the palladium coordination. UV-Visible spectral data for the palladium complex indicate the retention of aromatic character. It should be pointed out here that very recently Latos-Grazynski *et al*[4c] reported the anionic palladium derivative of oxybenziporphyrin, which on alkylation forms both O-substituted and C-substituted metal complexes.§

In summary, we have described the syntheses of two new heteroatom substituted aromatic oxybenziporphyrins and the first metallated derivative of an oxa substituted oxybenziporphyrin, where palladium is coordinated to pyrrole nitrogens, furan oxygen and benzene carbon inside a single porphyrin unit. Further studies on the use of **8** as a catalyst for organic conversions and C–H bond activation are under way.

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Notes and references

‡ Characterization data for **6** UV/Vis (CH_2Cl_2): λ_{max} nm (log ε) = 437 (4.92), 467 (4.66), 515 (3.79), 549 (4.44), 593 (3.86), 616 (3.79), 723 (3.56); ^1H NMR (400 MHz, $CDCl_3$): $\delta = -4.70$ (br s, NH), -3.50 (s, H), 1.82 (s, 6H), 1.83 (s, 6H), 2.57 (s, 6H), 7.24 (s, 4H), 7.33 (d, H), 8.26 (t, 2H), 8.67 (m, 3H), 8.90 (d, H), 9.04 (d, H), 9.53 (s, H), 10.50 (s, H); FAB mass *m*/*z* (%): 575 [*M* + 1]; IR(KBr) $\gamma_{C=O}$: 1630 cm^{-1}.

7 UV/Vis (CH_2Cl_2): λ_{max} nm (log ε) = 442 (5.09), 472 (4.89), 558 (4.00), 600 (4.18), 727 (3.68); ^1H NMR (400 MHz, $CDCl_3$): $\delta = -4.32$ (s, H), -2.09 (br s, NH), 1.84 (s, 6H), 1.86 (s, 6H), 2.58 (s, 6H), 7.26 (s, 4H), 7.46 (d, H), 8.36 (d, 2H), 8.83 (d, H), 8.91 (d, H), 9.07 (m, 3H), 9.66 (s, H), 10.80(s, H); FAB mass *m*/*z* (%): 591 [*M* + 1]; IR(KBr) $\gamma_{C=O}$: 1628 cm^{-1}.

8 UV/Vis (CH_2Cl_2): λ_{max} nm (log ε) = 404 (4.26), 468 (4.56), 489 (4.41), 582 (3.81), 672 (3.80); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.74 (s, 12H), 2.52 (s, 6H), 7.15 (s, 4H), 7.19 (s, H), 8.26 (dd, 2H), 8.55 (d, H), 8.67 (d, 2H), 8.78 (d, H), 8.90 (d, H), 9.38 (s, H), 10.63 (s, H); FAB mass *m*/*z* (%): 678 [M^+]; IR(KBr) $\gamma_{C=O}$: 1588 cm^{-1}.

§ After the submission of this manuscript a paper 4*c* appeared in the literature and we thank one of the referees who brought it to our notice.

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