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.

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 $^1$H and $^2$D NMR spectral analysis confirmed the proposed structure. Briefly, the inner CH proton resonates as a sharp singlet at $\approx$ 3.5 ppm for 6, $\approx$ 4.32 ppm for 7, while the NH pyrrole proton resonates as a broad singlet at $\approx$ 4.7 ppm for 6 and $\approx$ 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 $D_d$ (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 $\alpha$ and $\beta$ to the keto group appear as a doublet at $\approx$ 7.3 ppm and at $\approx$ 8.7 ppm respectively and their chemical shifts are in accord with an $\alpha,\beta$ unsaturated keto subunit. Additional evidence for the aromatic nature of 6 and 7 comes from UV-Visible spectral data, where strong Soret type transitions are observed.
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 CDCl₃). The inner CH proton resonated as a sharp singlet at 4.09 and 4.38 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 dicaticonic species either as a non-aromatic form represented by the diprotonated hydroxybenziporphyrin 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 dicaticonic 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. 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.

UV-Visible titration data with TFA also support such a conclusion.

The reaction of PdCl₂ 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 (ν_C=O = 1588 cm⁻¹) relative to free base (ν_C=O = 1630 cm⁻¹) further supports the palladium coordination.

The 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. 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 oxza 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.

We thank Department of Science and Technology, New Delhi, India for the research grant provided.

Notes and references

Characterization data for 6 UVVis(CHCl₃): λmax nm (log ε) = 437 (4.92), 467 (4.66), 515 (3.79), 549 (4.44), 593 (3.86), 616 (3.56); HNMR (400 MHz, CDCl₃): δ = -4.70 (br s, NH), -3.50 (s, H, 1.82 (s, 6H), 1.83 (s, 6H), 2.57 (s, 4H), 7.24 (s, 4H), 7.33 (d, H), 8.26 (t, 2H), 8.67 (m, 3H), 9.80 (d, H), 9.04 (d, H), 9.53 (s, H), 10.50 (s, H); FAB mass m/z (‰): 575 [M + 1]; IR(KBr) ν_C=O: 1630 cm⁻¹.

UVVis(CHCl₃): λmax nm (log ε) = 442 (5.09), 472 (4.89), 558 (4.00), 600 (4.18), 727 (3.68); HNMR (400 MHz, CDCl₃): δ = -4.32 (s, H, 2.09 (br s, NH), 1.84 (s, 6H), 1.86 (s, 6H), 2.58 (s, 4H), 7.26 (s, 4H), 7.46 (d, H), 8.36 (2H), 8.83 (d, H), 8.91 (d, H), 9.07 (m, 3H), 9.66 (s, H), 10.85 (s, H); FAB mass m/z (‰): 591 [M + 1]; IR(KBr): 1628 cm⁻¹. 8UVVis(CHCl₃): λmax nm (log ε) = 404 (4.26), 468 (4.56), 499 (4.41), 582 (3.81), 672 (3.80); HNMR (400 MHz, CDCl₃): 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 (2H), 8.78 (d, H), 8.90 (d, H), 9.05 (s, H), 10.63 (s, H); FAB mass m/z (‰): 678 [M+]; IR(KBr) ν_C=O: 1588 cm⁻¹.

After the submission of this manuscript a paper 1 appeared in the literature and we thank one of the referees who brought it to our notice.


