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Quick Synthesis of the First Double Porphyrin Double Calix[4]arene

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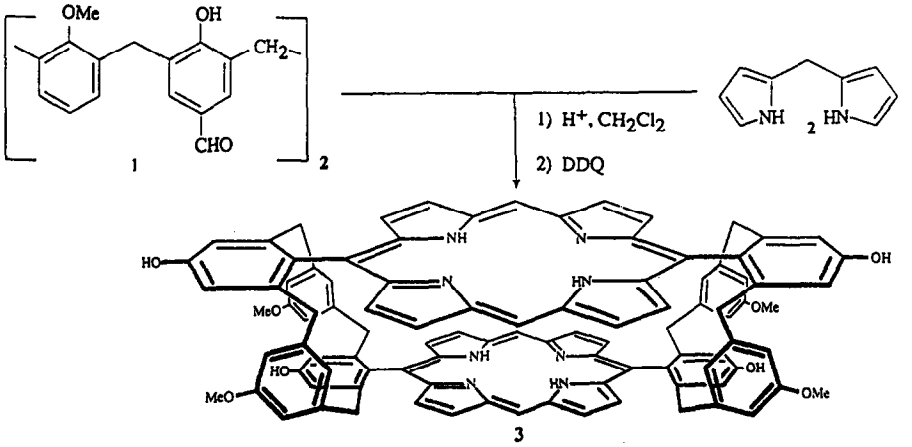
Abstract: The condensation of dipyrrylmethane and calix[4]arene 1,3 dialdehyde in dilute conditions afforded in very low yield the first double porphyrin linked by two calix[4]arene units.

For many years, there has been a growing interest in cofacial porphyrins, especially since the determination by X-ray diffraction of the structure of the reactive center of the photosynthetic bacterium *Rhodopseudomonas viridis*[1]. Such species are also of great interest, in particular regarding the multi-electronic reductions of dioxygen or dinitrogen[2], and various links between cofacial porphyrins have been used[2,3]. Similarly, numerous compounds associating porphyrins with organic structures such as crown ethers[3], cyclodextrins[4-6] and binaphtyls[7,8], which could be considered as supramolecular binding sites, have been reported in the literature during the past six years. We report hereafter the one-step synthesis and characterization of the first cofacial porphyrins linked by two calix[4]arene moieties.

The dialdehyde **1**[9] and the dipyrryl methane **2**[10] (2 equivalents) were synthesized according to literature procedure and were reacted at room temperature, under very dilute conditions in dichloromethane, in the presence of catalytic amounts of trifluoroacetic acid[11]. After 20 h stirring under argon, the crude mixture was readily oxidized by an excess of dichloro-dicyano-quinone in refluxing dichloromethane for 2 h. Extraction with water and drying the organic phase over magnesium sulfate allowed for removal of most of the tarry products. The dichloromethane phase was concentrated before purification by chromatography. After several tedious separations (SiO_2, CH_2Cl_2/MeOH and SiO_2, CH_2Cl_2/acetone), compound **3** was isolated as a purple microcrystalline powder in 0.4% yield (mp>300°C).



3

The low yield obtained is higher than the statistical yield (ca. 0.01%) predicted when combining randomly 12 reactive centers located on 6 distinct molecules. The tetrapyrrolic compound obtained was first detected by UV-VIS measurements, showing typical Q bands absorption (λ_{max}nm/e mol.L^{-1}.cm^{-1}: 416/16x10^4, 510/14 000, 548/8 400, 582/4 300, 638/1 600).

The nature of the product was then confirmed by FAB Mass Spectrometry (calculated mass 1518.9, found 1518.7), and by ^1H NMR measurements[12]. The two calix[4]arene moieties are in a cone conformation as testified by the presence of the AB quartet (J_{AB}=12.9 Hz) at 4.83 and 3.85 ppm, corresponding to the methylene bridges of the calixarenes.

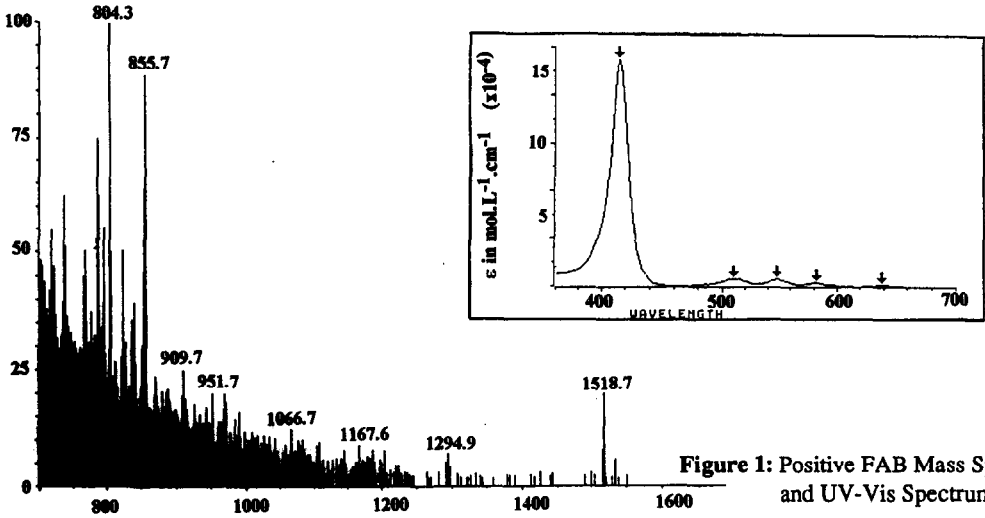


Figure 1: Positive FAB Mass Spectrum and UV-Vis Spectrum of 3.

Attemps to improve the yield by the use of guests inside the calix[4]arene moiety as templates are under progress.

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12. ^1H NMR of 3 at 200 MHz, reference $CHCl_3$ at 7.26 ppm: 10.37 (s, 4H, CH porph.), 10.20 (s, 4H, OH_{phenol}), 9.50 (d, J_{AB}=4.5 Hz, 8H, Hβ pyrrole), 9.38 (d, J_{AB}=4.5 Hz, 8H, Hβ' pyrrole), 8.11 (s, 8H, H-ArOH), 7.33 (d, J_{AB}=7.3 Hz, 8H, H_m-$ArOCH_3$), 7.00 (t, J_{AB}=7.4 Hz, 4H, H_p-$ArOCH_3$), 4.83 (d, J_{AB}=12.9 Hz, 8H, CH_2calix), 4.35 (s, 12H, OCH_3), 3.85 (d, J_{AB}=12.9 Hz, 8H, CH_2calix), -2.88 (s, 4H, NHporph.).

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