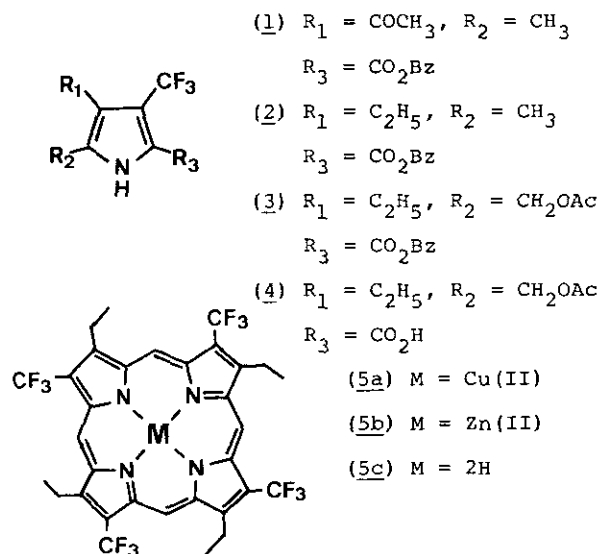


ELECTRON-DEFICIENT PORPHYRINS. 1. PERFLUOROALKYLPORPHYRINS

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The redox property of the porphyrin macrocycle can be controlled by changing the central metal. On the other hand, only a little attention has so far been paid to the possible control of metal redox property by changing the peripheral substituents of porphyrin. We are especially interested in electron-deficient porphyrins having highly electron-withdrawing, yet chemically stable substituents. The trifluoromethyl group meets this criterion.

The oximation of benzyl trifluoroacetoacetate with HNO_2 followed by reductive condensation with acetylacetone gave the trifluoromethylpyrrole (1) (25%). Reduction of (1) with borane afforded the pyrrole (2) (86%), which was treated with $\text{Pb}(\text{OAc})_4$ to give pyrrole (3) (74%). Hydrogenolysis of (3) to give (4) followed by decarboxylative condensation in the presence of $\text{Cu}(\text{OAc})_2$ or $\text{Zn}(\text{OAc})_2$ led to the formation of the Cu(II) or Zn(II) complex of the tetra-perfluoroalkyl analogue of etioporphyrin (5a, 5b). The free base porphyrin (5c) was obtained either by solid phase pyrrolysis of (4) followed by aerial oxidation or by demetallation of 5a in strongly acidic media. The absorption maxima of (5a)-(5c) are shown in the Table together with those of the free base and Cu(II) complex of octaethylporphyrin (OEP).



Electronic Absorption Maxima (nm)

comp	solvent	Soret	β	α
<u>5a</u>	CH_2Cl_2	405	532	568
<u>5b</u>	CH_2Cl_2	403	533	565
<u>5c</u>	CH_2Cl_2	407	504 539	579 633
OEPCu(II)	CHCl_3 CH_3OH	399	522	560
OEPH ₂	C_6H_6	400	498 532	568 622