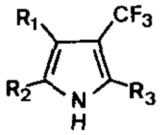
ELECTRON-DEFICIENT PORPHYRINS. 1. PERFLUOROALKYLPORPHYRINS

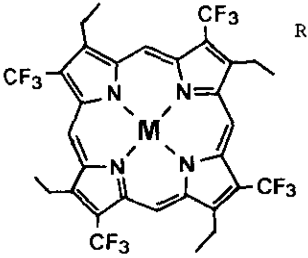
H. Ogoshi, M. Homma, Y. Aoyama, and K. Aoyagi
Department of Material Science, Technological University
of Nagaoka, Nagaoka, Niigata 949-54, Japan

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 $Pb(OAc)_4$ to give pyrrole (3) (74%). Hydrogenolysis of (3) to give (4) followed by decarboxylative condensation in the presence of $Cu(OAc)_2$ or $Zn(OAc)_2$ led to the formation of the Cu(II) or Zn(II) complex of the tetraperfluoroalkyl 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).



(1) $R_1 = COCH_3$, $R_2 = CH_3$
$R_3 = CO_2Bz$
(2) $R_1 = C_2H_5$, $R_2 = CH_3$
$R_3 = CO_2Bz$
(3) $R_1 = C_2H_5$, $R_2 = CH_2OAc$
$R_3 = CO_2Bz$
(4) $R_1 = C_2H_5$, $R_2 = CH_2OAc$
$R_3 = CO_2H$



(5a) M = Cu(II)
(5b) M = Zn(II)
(5c) M = 2H

Electronic Absorption Maxima (nm)

comp	solvent	Soret		β	α	
5a	CH_2Cl_2	405		532	568	
5b	CH_2Cl_2	403		533	565	
5c	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