HYPOCHROMISM ENCOUNTERED IN DIMERIZATION OF PORPHYRIN

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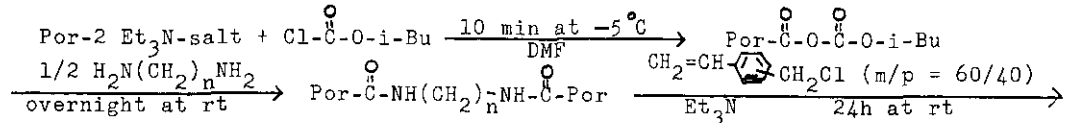
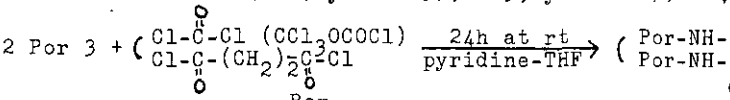
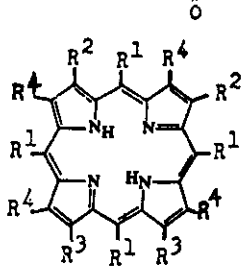
Optical molar absorptivities per monomer unit in chloroform for the porphyrin dimers prepared via the amide linkage indicated marked decreases as compared with those for the corresponding monomers. Dimers were prepared as follows.



2-Dn VB esters (n=2, yield 23%; n=3, yield 27%; n=4, yield 24%; n=6, yield 27%)





Porphyrin (Por)

Por No	R^1	R^2	R^3	R^4
1	H	$CH=CH_2$	CH_2CH_2COOH	CH_3
2	HOOC-C6H4-	H	H	H
3		H	H	H

Porphyrin	Concentration, $x10^{-3}$ g.l^{-1}	Absorptivity[b] per monomer unit
1-Me ester[c]	-	1.71 (407 nm)
1-Dimer Me ester[c]	4.71	1.14 (405 nm)
1-Dimer VB[a] ester	6.52	1.40 (407 nm)
1-Tetramer Me ester[c]	-	0.83 (405 nm)
2-VB[a] ester	1.20	6.22 (420 nm)
2-D2 VB[a] ester	1.20	2.59 (421 nm)
2-D3 VB[a] ester	1.20	3.56 (420 nm)
2-D4 VB[a] ester	1.20	2.76 (421 nm)
2-D6 VB[a] ester	1.20	3.88 (420 nm)
2(Mg)-VB[a] ester	2.41	4.63 (430 nm)
2(Mg)-Dimer VB[a] ester	3.63	3.10 (430 nm)
3	2.81	1.54 (420 nm)
3-D1	3.61	1.07 (419 nm)
3-D2	3.61	1.23 (421 nm)

a VB: vinylbenzyl.
b Soret band; $x\ 10^5$ l.cm^{-1}.mol^{-1}.
c Cf. Reference 1; solvent, CH_2Cl_2

This hypochromism is dependent upon the kind of porphyrin, the degree of oligomerization, and the kind and length of the chain connecting the porphyrin units, and is considered to indicate the existence of the interactions between two porphyrin rings and therefore a marked tendency of the linked porphyrin rings to hold the stacking structure even in dilute solutions.

Reference:

1. H. Kamogawa, H. Inoue, M. Nanasawa, J. Polm. Sci. Polym. Chem. Ed., 18 2209 (1980).