OXIDATION OF N^{21},N^{22}-ETHENO-BRIDGED 5H-PHLORINS TO THE MONOCATIONIC N^{21},N^{22}-ETHENO-BRIDGED 5-ALKYLPORPHYRINS BY Cu(BF$_4$)$_2$.

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Abstract: Whereas N^{21},N^{22}-(1,2-diphenyletheno)-octaethyl-5H-phlorin was air-oxidized to the corresponding porphyrin with loss of the 5-exo hydrogen exclusively, the 5-endo hydrogen was lost by the oxidation of the 5-exo-alkyl-5H-phlorin derivatives with Cu(BF$_4$)$_2$ to give the corresponding 5-alkylporphyrins as monoprotonated forms which could be deprotonated from the 5-meso methylene affording 5-(exomethylene)phlorins.

Phlorins in which a porphyrin chromophore is reduced by two electrons with the π-conjugation of a porphyrin ring being interrupted at a meso position are so air-sensitive that fully characterized phlorins have so far been limited to a few examples.[1] We have recently demonstrated that the introduction of a N^{21},N^{22}-bridging group into a porphyrin causes the molecular strain which deforms a porphyrin ring out of the planar structure and greatly enhances reduction of porphyrins to phlorins.[2] In this case, a hydride and carbanions attack on the 5-meso position of N^{21},N^{22}-bridged porphyrin hydroperchlorates from the same side (exo side) as the bridge. Now, it is necessary to elucidate the nature of the oxidation reaction of N^{21},N^{22}-bridged 5H-phlorins back to the porphyrins in order to utilize N^{21},N^{22}-bridged porphyrins as redox active materials functionally similar to NAD$^+$. This paper reports on the oxidation of N^{21},N^{22}-bridged 5H-phlorins to the porphyrins and the properties of thus obtained N^{21},N^{22}-bridged 5-alkylporphyrins.

N^{21},N^{22}-(1,2-diphenyletheno)octaethyl-5H-phlorin (2) is instantly air-oxidized to regenerate N^{21},N^{22}-(1,2-diphenyletheno)(OEP)HClO$_4$ (1) in the presence of HClO$_4$ (OEP: octaethylporphyrin dianion). When N^{21},N^{22}-(1,2-diphenyletheno)-5-exo-deuterio-octaethyl-5H-phlorin (2-D)[2] which was prepared by the reaction of (1) with NaBD$_4$ was treated with acetic acid in ethanol under argon, the visible spectrum due to 2-D (λ_{max} 397, 643 nm in ethanol) immediately changed to that with absorption maxima at 412, 437, 526, 563, 740 nm in ethanol indicating the formation of the monoprotonated 5H-phlorin (3). 3 was air-oxidized and the compound 1 recovered after the

treatment with 10% $HClO_4$ contained no deuterium to the limit of detection by 270 MHz ^{1}H-NMR. It was confirmed by the control experiment using the meso-d_4 analogue of 1 with $HClO_4$ that the work-up with 10% $HClO_4$ does not cause H-D exchange at the meso position of 1. Therefore, the 5-exo-hydrogen of 2 is lost exclusively upon air-oxidation under acidic conditions. On the other hand, N^{21},N^{22}-(1,2-diphenyletheno)octaethyl-5-alkyl-5H-phlorins (4a - 4e)[3] which were prepared by the reaction of 1 with natrium cyanide, lithium phenyl acetylide, kalium acetone enolate, lithium acetophenone enolate, and cyanomethyl lithium, respectively, turned out quite air-stable even under acidic conditions existing as monoprotonated forms. In fact, 4c (λ_{max} 392 and 638 nm; Fig. 1. (a)) in ethanol was converted into the monoprotonated form (λ_{max} 413, 435, 523, 560, and 725 nm; Fig. 1. (b); virtually the same as the spectrum of 3) by the addition of acetic acid and did not show further spectral change even if benzoquinone is added, whereas the same treatment of 2 resulted in the formation of 1 instantly. This fact is consistent with the low reactivity of the endo side hydrogen and the presence of 5-meso-substituents of 4a-e at the exo side. However, 4a-e were effectively oxidized by 5 - 10 molar excess amounts of $Cu(BF_4)_2$ in CH_2Cl_2 - CH_3CN (1 : 1) to generate N^{21},N^{22}-(1,2-diphenyletheno)-5-alkyl-(OEP)$HClO_4$ (5a - 5e) in excellent yields after the treatment with a 10% $HClO_4$ aqueous solution. The UV-Vis spectral pattern of 5a-e are quite similar to that of 1 with the absorption maxima being red-shifted by 10 - 20 nm (Fig. 1. (c)). The ^{1}H-NMR spectra of 5a-e show two singlets with 2 : 1 intensity due to the meso protons and signals due to the 5-substituents as summarized in Table 1.

We have already shown that 1 is not deprotonated from the porphyrin nitrogen but is decomposed by the attack of a hydroxide ion on the 5-meso position followed by the ring cleavage under basic conditions.[2] In contrast, 5-acetonyl-, 5-benzoylmethyl-, and 5-cyanomethylporphyrins, 5c-e,
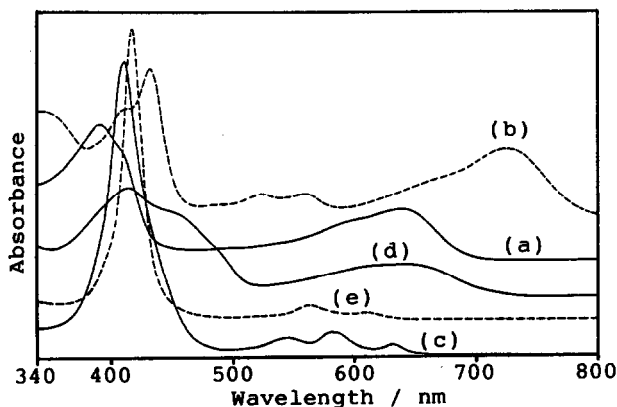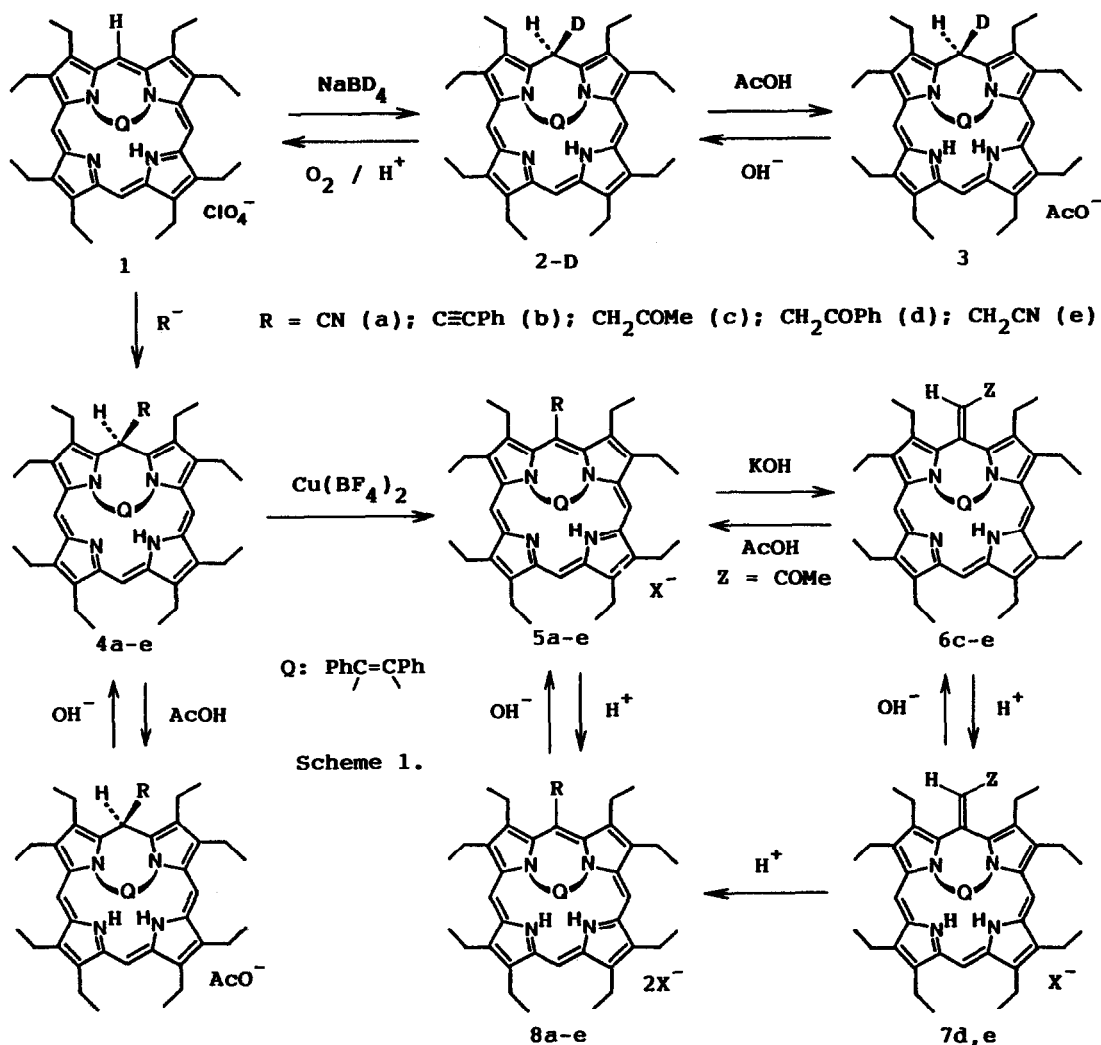

Fig. 1. UV-Vis spectra of 5-acetonylphlorin 4c in EtOH (a); 4c + AcOH (b); monoprotonated 5-acetonylporphyrin 5c in CH_2Cl_2 (c); 5-(acetylmethylene)phlorin 6c in CH_2Cl_2 (d); 5c + CF_3COOH (e).

R = CN (a); C≡CPh (b); CH$_2$COMe (c); CH$_2$COPh (d); CH$_2$CN (e)

Q: PhC=CPh

Scheme 1.

were readily deprotonated from the methylene directly bound to the 5-meso position by the treatment with a 5% KOH aqueous solution to give 5-(exo-methylene)phlorins 6c-e in good yields. These compounds show UV-Vis bands typical of a phlorin chromophore (Fig. 1. (d)). Their ^{1}H-NMR spectra are indicative of the absence of both the ring current effect of a porphyrin and the molecular symmetry element. Whereas 5-(acetylmethylene)phlorin 6c could be cleanly converted back into the 5-acetonylporphyrin 5c through the protonation with acetic acid, 5-(benzoylmethylene)phlorin 6d and 5-(cyanomethylene)phlorin 6e were found to be protonated at the nitrogen to give the corresponding phlorin monocations 7d,e which also show a broad visible band around 750 nm. Treatment of 6c-e with trifluoroacetic acid resulted

Table 1. Yields and Spectral Data of N^{21},N^{22}-(1,2-Diphenyletheno)-5-Alkyl(OEP)HClO$_4$
(5a-e) and the 5-(Exomethylene)phlorins (6c-e).

	R	Yield (%)	^{1}H-NMR (δ-value, CDCl$_3$)[a]						UV-Vis(λ_{max}, CH$_2$Cl$_2$) (nm)			
			meso-H		-CH$_2$-	Z						
5a	CN	80	10.34(2H)	10.65	-				412	540	591	644
5b	C≡C-Ph	100	10.21(2H)	10.40	-	8.14(dd,2H)	7.72(m,3H)		439	556	599	650
5c	CH$_2$COMe	90	10.19(2H)	10.33	6.88	2.94(3H)			411	543	581	630
5d	CH$_2$COPh	82	10.21(2H)	10.36	7.35	8.55(d,2H)	7.74(m,3H)		412	544	581	630
5e	CH$_2$CN	90	10.24(2H)	10.41	6.70				412	543	583	634
-----(Z)-----			-----	(=CH-)	-----							
6c	COMe	90	7.50 7.45	7.28	6.62	2.44(3H)	_		413	453	640	
6d	COPh	83	7.61 7.41	7.22	6.12	8.20(dd,2H)	7.57(m,3H)		414	475	667	
6e	CN	76	7.39 7.34	7.22	5.69				410	460	595	644

a) notations for singlet and 1H-integral are omitted.

in the formation of porphyrin dications 8c-e, which show a very sharp Soret band at 420 nm and visible bands at 562 and 611 nm (Fig. 1. (e)).

In conclusion, the present work showed that (i) the 5-exo hydrogen is used exclusively in the oxidation of 1, (ii) the meso-substitution of N^{21},N^{22}-etheno-bridged (OEP)HClO$_4$ is readily achieved by the nucleophilic addition - oxidation sequence, in contrast to the electrophilic substitution of ordinary porphyrins and metalloporphyrins,[4] (iii) thus obtained monoprotonated N^{21},N^{22}-etheno-bridged 5-alkylporphyrins show novel acid - base equilibrium involving 5-(exomethylene)phlorins, the monoprotonated phlorins, and the diprotonated porphyrins with dramatic spectral changes.

Acknowledgment

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