

Formation of N^{21},N^{22} -Etheno-Bridged Meso-Tetraphenylphlorins

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N^{21},N^{22} -(1,2-Diphenyletheno)-meso-tetraphenylporphin hydroperchlorate was reduced by $NaBH_4$ to the 5H-phlorin and deprotonated by $NaOH$ to the free base. However, the N^{21},N^{22} -hydroxymethyletheno derivative underwent intramolecular attack of the bridge hydroxy group on the 10-meso position to give the novel 10H-phlorin under basic conditions.

N^{21},N^{22} -Bridged porphyrins in which adjacent two pyrrolic nitrogens of a porphyrin are bridged by a one- or a two-carbon group have recently been prepared by us and others.¹⁻³⁾ These N^{21},N^{22} -bridged porphyrins show novel properties arising from the extraordinarily strained molecular structure and the high basicity. We have recently shown that N^{21},N^{22} -bridged octaethylporphyrin hydroperchlorates undergo regio- and stereoselective attack of a hydride and carbanions on the 5-meso position, which is surrounded by the N^{21},N^{22} -bridge, from the same side as the bridge to give novel N^{21},N^{22} -bridged 5H-phlorins.⁴⁾ This paper describes the reaction behaviors of N^{21},N^{22} -etheno(TPP) $HClO_4$ (TPP = meso-tetraphenylporphin dianion) under basic conditions in comparison with those of the OEP analogues (OEP = octaethylporphyrin dianion).

N^{21},N^{22} -(1,2-Diphenyletheno)(TPP) $HClO_4$ (**1**) was obtained in 90% yield when (TPP) Co^{II} was treated with diphenyl acetylene in the presence of excess $Fe(ClO_4)_3$ and then a 10% $HClO_4$ solution was used for a work-up process.^{2,3)} Although the OEP analogue of **1** could not be deprotonated but was decomposed due to the ring cleavage initiated by the attack of a hydroxide ion on the meso-position, **1** was cleanly deprotonated to give the free base (**2**),⁵⁾ in 83% yield, which shows a Soret absorption at 441 nm and a four-banded visible absorption typical of free base porphyrins (see Fig. 1), when a CH_2Cl_2 solution of **1** was vigorously shaken with a 10% $NaOH$ aqueous solution and then the resulting porphyrin residue was extracted into diethyl ether. Thus, meso-tetraphenyl substituents in the case of TPP

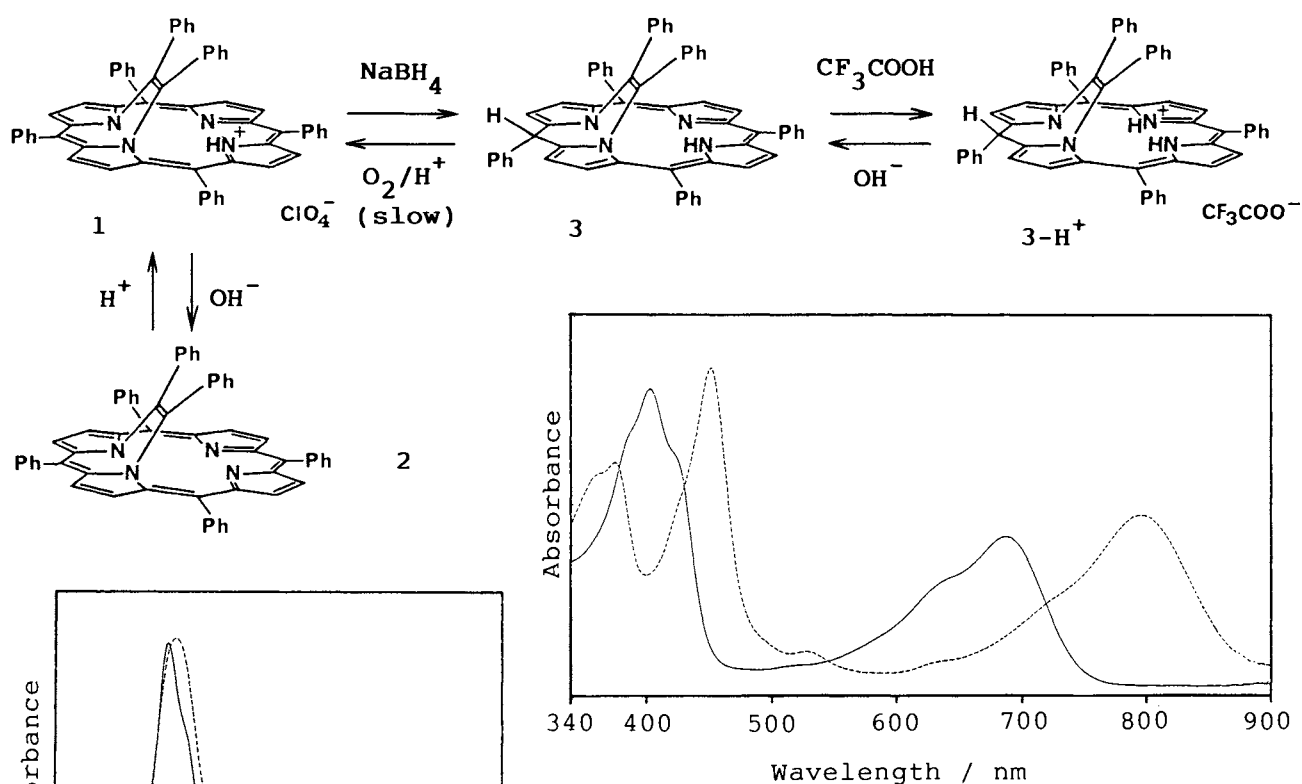


Fig. 1. UV-Vis Spectra of N²¹,N²²-(1,2-Diphenyletheno)(TPP)HClO₄ (**1**) (left:—); N²¹,N²²-(1,2-Diphenyletheno)(TPP) (**2**) (left:-----); N²¹,N²²-(1,2-Diphenyletheno)-5H-Phlorin (**3**) (upper:—); and the Monoprotonated Form (**3-H⁺**) (upper:-----).

make the porphyrin nitrogens less basic and the meso-carbons less susceptible to nucleophilic attack in comparison with octaethyl substituents at the β -pyrrolic position in the case of OEP. In accord with this, treatment of **1** with carbanions such as enolates did not lead to the nucleophilic attack on the meso-position but to the deprotonation from the porphyrin nitrogen. However, treatment of **1** with NaBH₄ resulted in the quantitative formation of N²¹,N²²-(1,2-diphenyletheno)-meso-tetraphenyl-5H-phlorin (**3**).⁶⁾ **3** shows a C_s symmetric ¹H NMR spectrum with a mirror plane passing through 5-meso and 15-meso position. Disappearance of the ring current effect in the ¹H NMR spectrum of **3** suggests that π -conjugation of porphyrin is interrupted by the addition of a hydride at the 5-meso position and probably from the same side as the etheno-bridge as we have shown in the case of the OEP analogue of **3**.⁴⁾ While the OEP analogue of **3** is immediately air-oxidized to regenerate a porphyrin chromophore under acidic conditions,⁴⁾ **3** turned out to give a stable monoprotonated form **3-H⁺** rather than undergoing air-oxidation which actually occurred in a much slower process. These redox and acid-base two-step processes are reversible and accompanied by drastic spectral change from 600 to 700 and then to 800 nm as shown in Fig. 1.

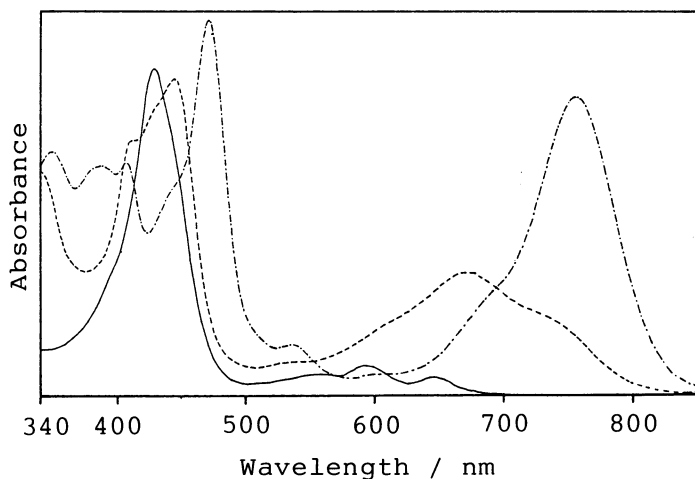
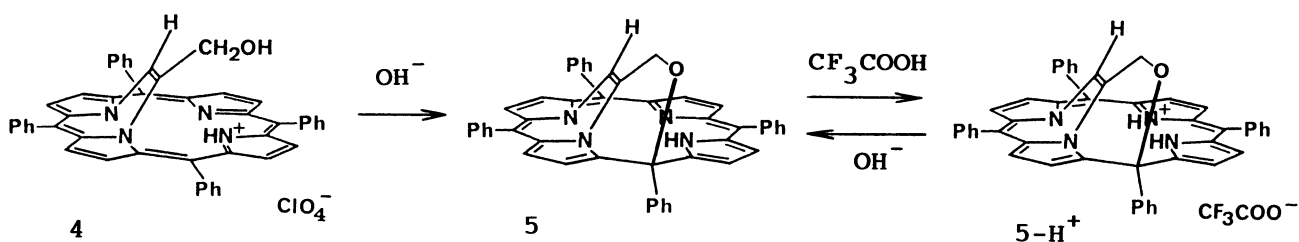


Fig. 2. UV-Vis Spectra of N^{21},N^{22} -(Hydroxymethyletheno)(TPP) $HClO_4$ (4) (—); the 10H-Phlorin (5) (-----); and its monoprotonated form (5-H⁺) (-·-·-·-).

N^{21},N^{22} -(hydroxymethyletheno)(TPP) $HClO_4$ (4)²⁾ was converted not into a free base but into a phlorin (5)⁷⁾ in 60% yield by treatment with a 10% NaOH solution, extraction into n-hexane, and recrystallization from CH_2Cl_2 - MeOH. 5 shows a Soret band at 446 nm and a broad visible band with the maximum absorbance at 672 nm in the UV-Vis spectrum characteristic of a phlorin chromophore as shown in Fig. 2. The comparison of the 1H -NMR spectra of 3, 4, and 5 clearly shows that 5 has a phlorin chromophore similar to 3 (see Table 1). While the bridge O-methylene protons (δ -1.08 and -1.71, $J_{gem} = 14.0$ Hz) of 4 are coupled to the OH proton with the vicinal coupling constants of 4.0 and 9.2 Hz, respectively, the bridge O-methylene protons of 5 shows only a geminal coupling (δ 3.94 and 3.68, $J_{gem} = 13.0$ Hz). This indicates that the bridge hydroxy group is deprotonated

Table 1. Selected 1H NMR Chemical Shifts of N^{21},N^{22} -Etheno-Bridged Porphyrins (1,2,4) and Phlorins (3,5) (δ -value in $CDCl_3$)

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
β -pyrrole	8.77 8.82 9.15 9.21	8.21 8.47 8.61 8.63	6.17 6.58 6.70 6.95	8.71 9.00 8.84 9.02 8.90 9.04 8.96 9.05	6.43 6.85 6.48 6.96 6.49 7.08 6.81 7.10
Bridge	2.65(o) 5.93(m) 6.34(p)	\sim 3(o) 5.80(m) 6.15(p)	6.05(o) 6.77(m) 6.87(p)	-1.08(CH_2) ^{a)} -1.71(CH_2) ^{b)} -1.28(=CH) 0.66(OH)	3.68(CH_2) ^{c)} 3.94(CH_2) 4.09(=CH)
Meso	-	-	5.04	-	-

a) $J_{gem}=14.0$ Hz, $J_{vic}=4.0$ Hz. b) $J_{vic}=9.2$ Hz. c) $J_{gem}=13.0$ Hz.

under basic conditions and the resulting alkoxide anion adds to the 10-meso position which is only accesible as judged from the molecular model, giving rise to novel 10H-phlorin structure which contains an unstrained six-membered ring. Furthermore, the 10H-phlorin 5 was also protonated to the monocation (5-H⁺) accompanied by the red shift of the visible band from 672 to 756 nm.

In conclusion, N²¹,N²²-etheno-bridged porphyrin hydroperchlorates undergo deprotonation from the porphyrin nitrogen or nucleophilic attack on the meso-position to afford free base porphyrins or phlorins depending on the basicity of the porphyrin nitrogens and the reactivity of the meso-positions, which are influenced by the peripheral substituents of porphyrin. These reversible conversions of porphyrin - phlorin chromophores would be interesting in the application to a electrochromic functional dye.

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- 4) J.-i. Setsune, M. Ikeda, T. Iida, and T. Kitao, *J. Am. Chem. Soc.*, 110, 6572 (1988).
- 5) 2: MS 793 (M+3). UV-Vis(CH₂Cl₂) λ_{max}(log ε) 441 (5.01), 544 (4.02), 585 (3.81), 628 (3.75), 677 (3.55).
- 6) 3: MS 793 (M+1). UV-Vis(CH₂Cl₂) λ_{max}(log ε) 405 (4.63), 426 (4.51), 690 (4.30).
- 7) 5: MS 669 (M+1). UV-Vis(CH₂Cl₂) λ_{max}(log ε) 446 (4.56), 672 (4.15).

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