

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

Jun-ichiro SETSUNE,^{*} Yoshihiro ISHIMARU, and Teijiro KITAO⁺
 Department of Chemistry, Faculty of Science, Kobe University,
 Nada, Kobe 657

⁺Department of Applied Chemistry, College of Engineering
 University of Osaka Prefecture, Sakai, Osaka 591

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)HClO₄ (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)HClO₄ (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% HClO₄ 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

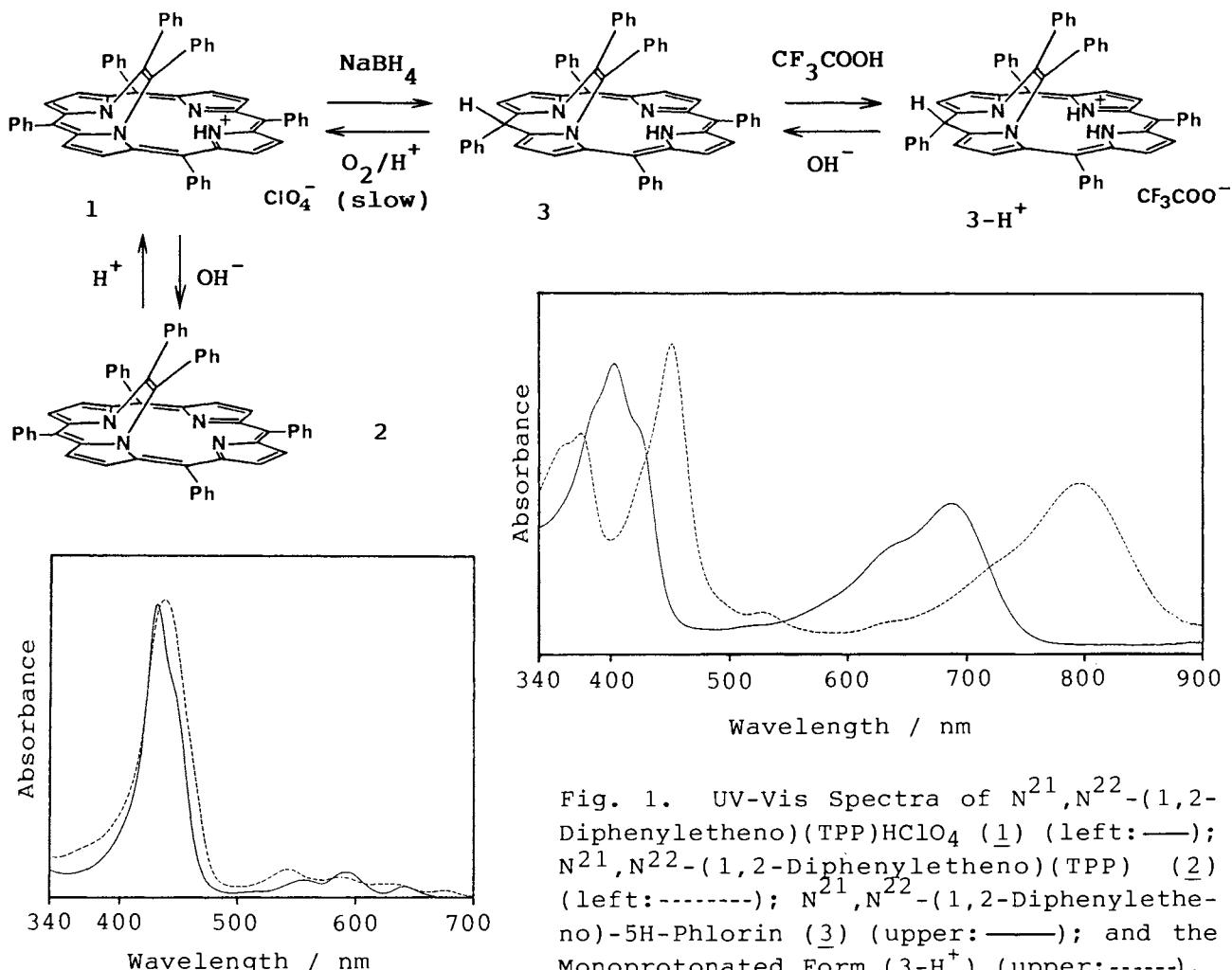


Fig. 1. UV-Vis Spectra of N²¹,N²²-(1,2-Diphenyletheno)(TPP)HClO₄ (1) (left:—); N²¹,N²²-(1,2-Diphenyletheno)(TPP) (2) (left:-----); N²¹,N²²-(1,2-Diphenyletheno)-5H-Phlorin (3) (upper:—); and the Monoprotonated Form (3-H⁺) (upper:-----).

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 C₈ 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.

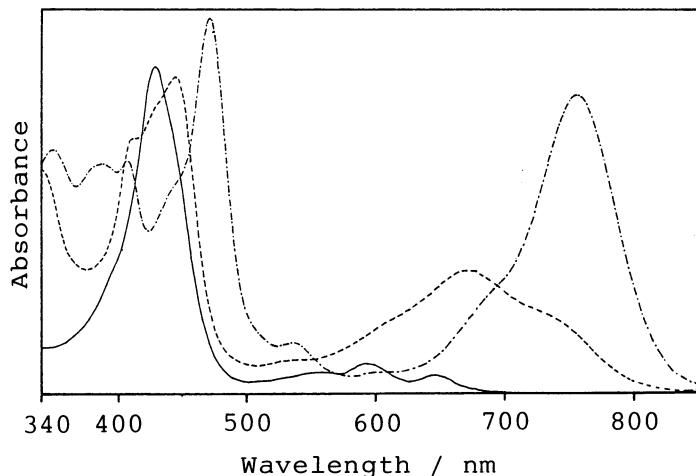
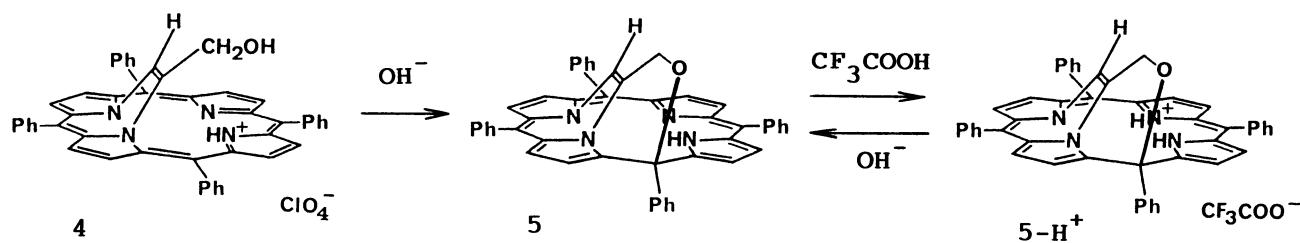


Fig. 2. UV-Vis Spectra of N²¹,N²²-(Hydroxymethyl-etheno)(TPP)HClO₄ (4) (—); the 10H-Phlorin (5) (-----); and its monoprotonated form (5-H⁺) (----).

phore similar to 3 (see Table 1). While the bridge O-methylene protons (δ -1.08 and -1.71, $J_{\text{gem}} = 14.0$ 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, $J_{\text{gem}} = 13.0$ Hz). This indicates that the bridge hydroxy group is deprotonated

Table 1. Selected ¹H NMR Chemical Shifts of N²¹,N²²-Etheno-Bridged Porphyrins (1,2,4) and Phlorins (3,5) (δ -value in CDCl₃)

| | <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 8.84 8.90 8.96 | 9.00 9.02 9.04 9.05 |
| Bridge | 2.65(o) 5.93(m) 6.34(p) | ~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) $J_{\text{gem}} = 14.0$ Hz, $J_{\text{vic}} = 4.0$ Hz. b) $J_{\text{vic}} = 9.2$ Hz. c) $J_{\text{gem}} = 13.0$ Hz.

N²¹,N²²-(hydroxymethyl-etheno)(TPP)HClO₄ (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 CH₂Cl₂ - 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 chromo-

under basic conditions and the resulting alkoxide anion adds to the 10-meso position which is only accessible 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, N^{21},N^{22} -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) $\lambda_{\max}(\log \epsilon)$ 441 (5.01), 544 (4.02), 585 (3.81), 628 (3.75), 677 (3.55).
- 6) 3: MS 793 (M+1). UV-Vis(CH₂Cl₂) $\lambda_{\max}(\log \epsilon)$ 405 (4.63), 426 (4.51), 690 (4.30).
- 7) 5: MS 669 (M+1). UV-Vis(CH₂Cl₂) $\lambda_{\max}(\log \epsilon)$ 446 (4.56), 672 (4.15).

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