

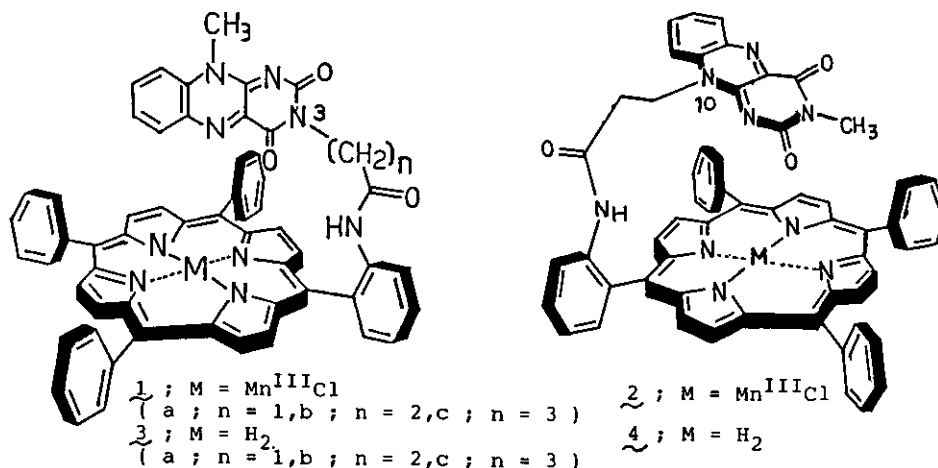
SYNTHESIS AND PROPERTIES OF NOVEL FLAVIN-LINKED PORPHYRIN

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Flavin coenzymes can undergo facile one-electron transfer to produce semiquinone species as well as two-electron transfer, so that flavin serves as "2e⁻/1e⁻ transfer carrier" between 2e⁻ donor such as NAD(P)H and 1e⁻ acceptor such as metallohemoprotein.

In order to understand the flavin-heme electron transfer and its transient nature, we have studied N³-flavin-linked porphyrin (1)¹⁾. We report here the synthesis, spectral properties and the intramolecular electron transfer reactions of N¹⁰-flavin-linked porphyrin (2). ¹H-NMR spectrum of freebase (4) showed upfield shift of internal pyrrole NH about 1 ppm. This value was similar to (3b), but aromatic protons of flavin were not seen in 4-7 ppm region in the case of (4). Kinetic studies of electron transfer reaction with NADH model compound were performed using (1a-c) and (2). Rate enhancements by intramolecular effect were followed; $k_{\text{intra}}/k_{\text{inter}} = 8.0$ (1a), 3.9 (1b), 2.1 (1c) and 1.7 (2). These results suggested that $k_{\text{intra}}/k_{\text{inter}}$ values were affected by methylene spacer length and linked-position of flavin and porphyrin. We proposed that the small rate enhancement of (2) was due to the difference in the conformation of transient ternary complex.



1) J.Takeda, S.Ohta and M.Hirobe, Tetrahedron Lett. in press.