

SYNTHESES OF A SERIES OF OCTAETHYLPORPHYRIN-BENZOQUINONE LINKED MOLECULES  
AS A MODEL FOR THE PRIMARY PROCESS OF PHOTOSYNTHESIS

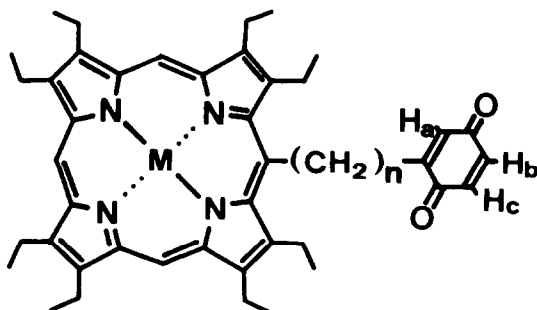
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**Abstract** To clarify the primary process of photosynthesis, a series of model compounds, in which an octaethylporphyrin and a benzoquinone ring are connected with different lengths of a polymethylene chain, were synthesized and their photophysical properties were investigated.

It is well known that in the early stage of the bacterial or green plant photosynthesis an electron is transferred from a photoexcited chlorophyll during the lifetime of its singlet state to a near located benzoquinone compound, i.e., ubiquinone or plastoquinone. The stable charge separation is attained after the electron transfer from the excited state in vivo, but never in artificial systems.<sup>1)</sup> The difference between them is thought to be mainly due to the special arrangement of the donor (chlorophyll) and the acceptor (quinone) in vivo.

Although some model compounds containing the two chromophores were prepared to examine the electron transfer,<sup>2)</sup> systematic study about the relative orientation of both chromophores has scarcely been carried out. Here we chose octaethylporphyrin (OEP) as a suitable donor porphyrin because the ring is substituted only with alkyl groups affecting little the electronic state.<sup>3)</sup> In this communication, we report on the synthesis and properties of compounds 1a-c and 2a-c bearing an OEP and a benzoquinone moieties whose relative orientations are more or less restricted by different lengths of a polymethylene chain.



1: M = H<sub>2</sub>

2: M = Zn

a: n = 2

b: n = 4

c: n = 6



204°C, MS m/e 786(M<sup>+</sup>), IR(KBr disk) 1661 cm<sup>-1</sup>]. Zinc complex of nonaethylporphyrin<sup>8</sup> (NEP), a spectral reference, was also prepared in a similar manner [Zn-NEP<sup>7</sup>]; reddish purple crystals from benzene-hexane, mp 270-272°C, MS m/e 624(M<sup>+</sup>)].

Chemical shifts of quinone protons in 1 and 2 are summarized together with those of toluquinone in Table 1. Upfield shifts were observed for all protons of the present polymethylene-bridged compounds as compared with the corresponding protons of toluquinone, showing clearly the location of quinone rings in the upfield shift region of the porphyrin ring. Electronic spectra of 1a-c and 2a-c are shown together with that of M-NEP in Figs. 1 and 2. All the spectra are very similar with that of M-NEP, indicating no appreciable interaction between the two chromophores in the ground state.

Table 1. Chemical Shifts( $\delta$ , ppm, CDCl<sub>3</sub>) of Quinone Protons of 1 and 2.

	Ha	Hb,Hc
Toluquinone	6.63	6.72-6.75
1a	6.37	6.62-6.64
1b	6.29	6.54
1c	6.39	6.62-6.64
2a	5.74	6.34-6.37
2b	5.96	6.30-6.37
2c	6.21	6.33-6.51

Relative fluorescence intensities of 1, 2, and M-NEP in three solvents with different polarity are summarized in Table 2. It is pointed out as the most characteristic respect that fluorescence intensities of all the quinone-linked compounds much decrease as compared with that of H<sub>2</sub>- or Zn-NEP. To estimate the efficiency of such an intramolecular quenching, relative quenching efficiencies

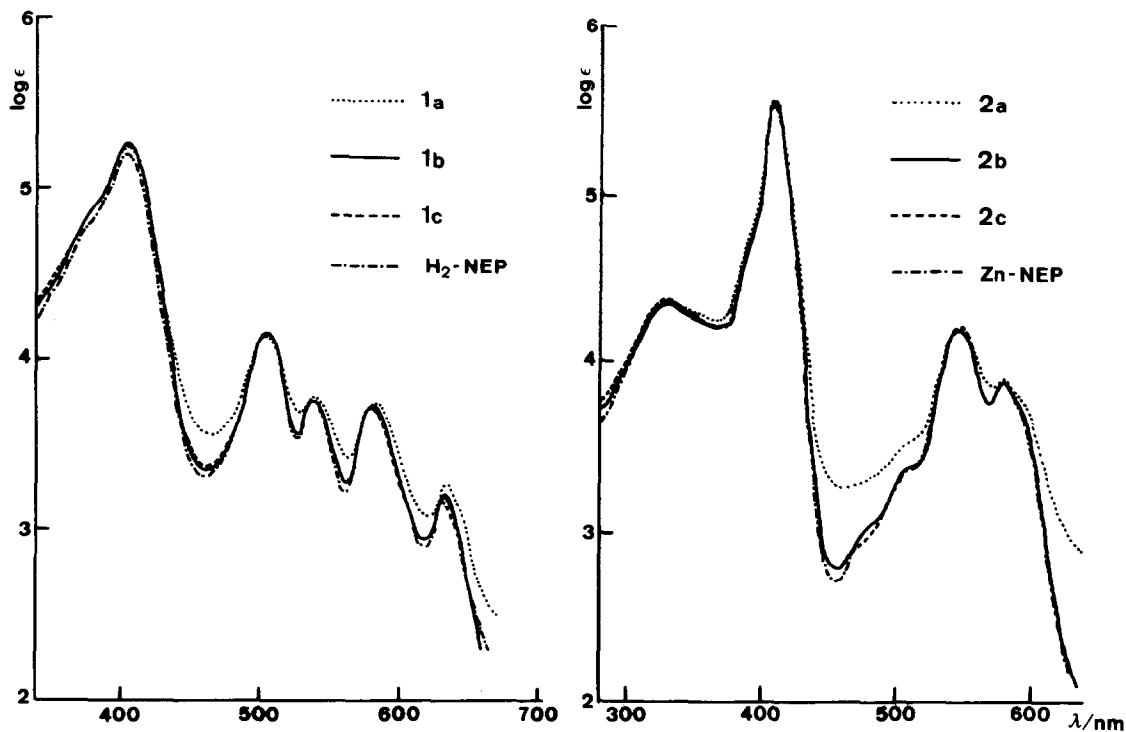
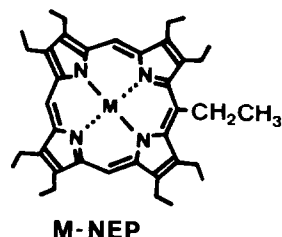


Fig. 1. Electronic spectra of 1 in THF. Fig. 2. Electronic spectra of 2 in THF

Table 2. Relative Fluorescence Intensities of 1, 2, and M-NEP.

	CH*	THF	PrCN		CH*	THF	PrCN
H <sub>2</sub> -NEP	385	397	336	Zn-NEP	541	487	351
1a	171	2	1	2a	12	3	2
1b	21	5	4	2b	9	2	1
1c	46	30	24	2c	23	11	8

\* cyclohexane



were calculated by applying to the present intramolecular systems the values of quenching constant ( $k_{\text{f}}\tau_{\text{f}}$ ), which were evaluated by the Stern-Volmer plot for fluorescence intensities of H<sub>2</sub>- or Zn-NEP and toluquinone mixtures [relative quenching efficiency, 1a:  $1.0 \times 10^4$ ; 1b:  $3.9 \times 10^3$ ; 1c:  $6.7 \times 10^2$ ; 2a:  $3.9 \times 10^4$ ; 2b:  $5.2 \times 10^4$ ; 2c:  $1.0 \times 10^4$ ]. These data clearly show that the electron transfer occurs very efficiently in the intramolecular systems where both chromophores are closely situated and that the coordinated metal as well as the shortening of polymethylene chain make the quenching efficiency larger. Picosecond laser photolysis<sup>9)</sup> of 1a-c demonstrated the first example of model compounds for the singlet state ion pair generated from inter- and intra-molecular porphyrin-quinone systems in solution. The detail will be reported elsewhere.

## References and Notes

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