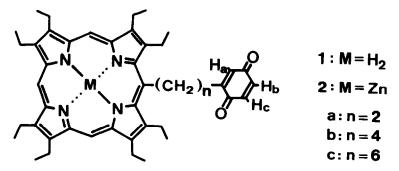
SYNTHESES OF A SERIES OF OCTAETHYLPORPHYRIN-BENZOQUINONE LINKED MOLECULES AS A MODEL FOR THE PRIMARY PROCESS OF PHOTOSYNTHESIS

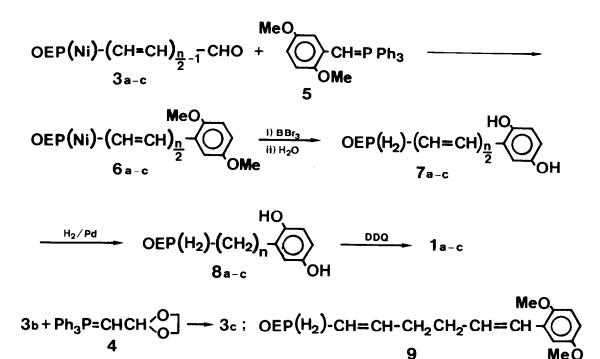
Shinji Nishitani, Nobuyuki Kurata, Yoshiteru Sakata*, and Soichi Misumi The Institute of Scientific and Industrial Research, Osaka University Suita, Osaka 565, Japan Masahito Migita, Tadashi Okada, and Noboru Mataga Department of Chemistry, Faculty of Engineering Science, Osaka University Toyonaka, Osaka 560, Japan

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.¹⁾ 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,²⁾ systematic study about the relative orientation of both chromophores has scarcely been carried out. Here we chose octaethyporphyrin(OEP) as a suitable donor porphyrin because the ring is substituted only with alkyl groups affecting little the electronic state.³⁾ In this communication, we report on the synthesis and properties of compounds la-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.





Starting compounds $3a^{4}$ and $3b^{5}$ were prepared according to the references. Unknown aldehyde 3c was prepared by treatment of 3b with 4, derived from 1,3dioxan-2-ylmethyltriphenylphosphonium bromide⁶⁾ and lithium methoxide $[3c^{7}]$: 88% yield, deep green prisms from benzene-hexane, mp 230.0-230.5°C]. The Wittig reaction of 3a-c with triphenylphosphoran 5, prepared from the corresponding phosphonium salt and BuLi in THF, was carried out at room temperature to give 6 [6a⁷]: 84%, dark red purple plates from benzene-methanol, mp 204-205°C; 6b⁷):95%, fine dark purple prisms from chloroform-methanol, mp 177.5-179.0°C; 6c⁷⁾: 82%, dark brown prisms from chloroform-methanol, mp 111.5-113.0°C]. Hydrogenation of 6a and 6b was failed due to steric hindrance around the double bonds. On the other hand, compounds 7 obtained by treatment with BBr, in CH2C1, at -20°C were smoothly hydrogenated with 10% Pd-C in benzene to afford 8. Oxidation of 8 with DDQ in benzene gave the desired compounds 1. In the case of 6c, dihydro compound 9 obtained by partial reduction with Pd-C was similarly worked up as described for 6a,b to give 1c [1a^{7]}: 21% yield from 6a, dark violet crystals from benzenemethanol, dec > 198°C, MS m/e 668(M⁺), IR(KBr disk) 1659 cm⁻¹; $1b^{7}$: 20% from 6b, dark violet crystals from benzene-methanol, dec> 180°C, MS m/e 696(M⁺), IR(KBr disk) 1661 cm⁻¹; 1c⁷⁾: 36% from 6c, dark violet prisms from benzene-hexane, dec > 166.5°C, MS m/e 724 (M⁺), IR(KBr disk) 1659 cm⁻¹]. Treatment of 1 with $Zn(OAc)_2 \cdot 2H_2O$ in CHCl₃ under reflux for ca. 10 min yielded zinc complexes 2 [$2a^{7}$]: violet prisms from benzene-hexane, mp 211-212°C, MS m/e 730(M⁺), IR(KBr disk) 1651, 1659 cm⁻¹; 2b⁷): violet prisms from benzene-hexane, mp 214-216°C, MS m/e 758(M⁺), IR(KBr disk) 1659 cm⁻¹; 2c⁷⁾: violet prisms from benzene-hexane, mp 202204°C, MS m/e 786(M⁺), IR(KBr disk) 1661 cm⁻¹]. Zinc complex of nonaethylporphyrin⁸⁾(NEP), a spectral reference, was also prepared in a similar manner [Zn-NEP⁷): reddish purple crystals from benzene-hexane, mp 270-272°C, MS m/e 624(M⁺)].

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 la-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.

of Quinone	Protons	of 1 and 2.
	Ha	Hb,Hc
Toluquinone	6.63	6.72-6.75
la	6.37	6.62-6.64
lb	6.29	6.54
lc	6.39	6.62-6.64
2 a	5.74	6.34-6.37
2 b	5.96	6.30-6.37
2 c	6.21	6.33-6.51

Table 1. Chemical Shifts (δ , ppm, CDCl₂)

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_2^- or Zn-NEP. To estimate the efficiency of such an intramolecular quenching, relative quenching efficiencies

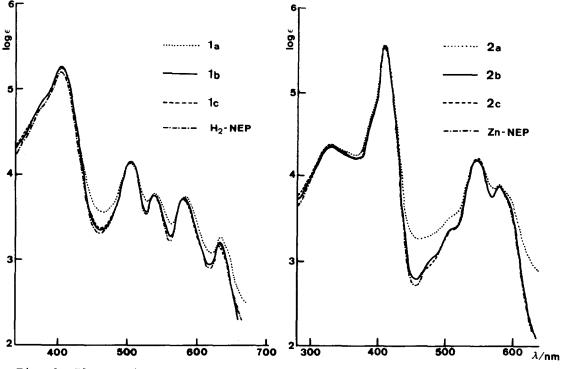


Fig. 1. Electronic spectra of 1 in THF. Fig. 2. Electronic spectra of 2 in THF

	and M-NEP.								
••••••••••••••••••••••••••••••••••••••	CH*	THF	PrCN		CH*	THF	PrCN		
H ₂ -NEP	385	397	336	Zn-NEP	541	487	351		
la	171	2	1	2a`	12	3	2		
lb	21	5	4	2 b	9	2	1		
lc	46	30	24	2c	23	11	8		
* cyclol	202220			· · · · · · · · · · · · · · · · · · ·					

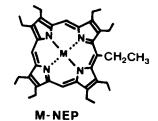


Table 2. Relative Fluorescence Intensities of 1, 2,

* cyclohexane

were calculated by applying to the present intramolecular systems the values of quenching constant($k_{f}\tau_{f}$), which were evaluated by the Stern-Volmer plot for fluorescence intensities of H₂- or Zn-NEP and toluquinone mixtures [relative quenching efficiency, la: 1.0×10^{4} ; lb: 3.9×10^{3} ; lc: 6.7×10^{2} ; 2a: 3.9×10^{4} ; 2b: 5.2×10^{4} ; 2c: 1.0×10^{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 photolysis⁹ of la-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.

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