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Porphyrin-Quinone Compounds with a Spacer of Diacetylene Unit

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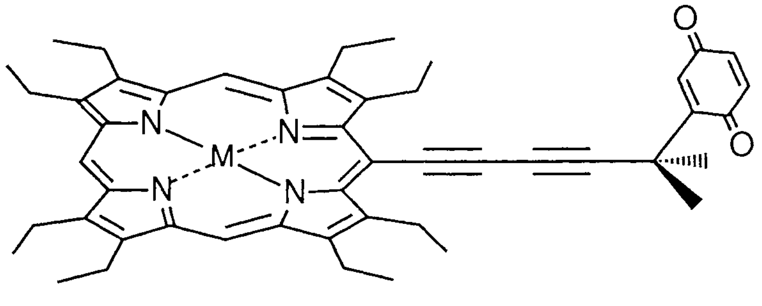
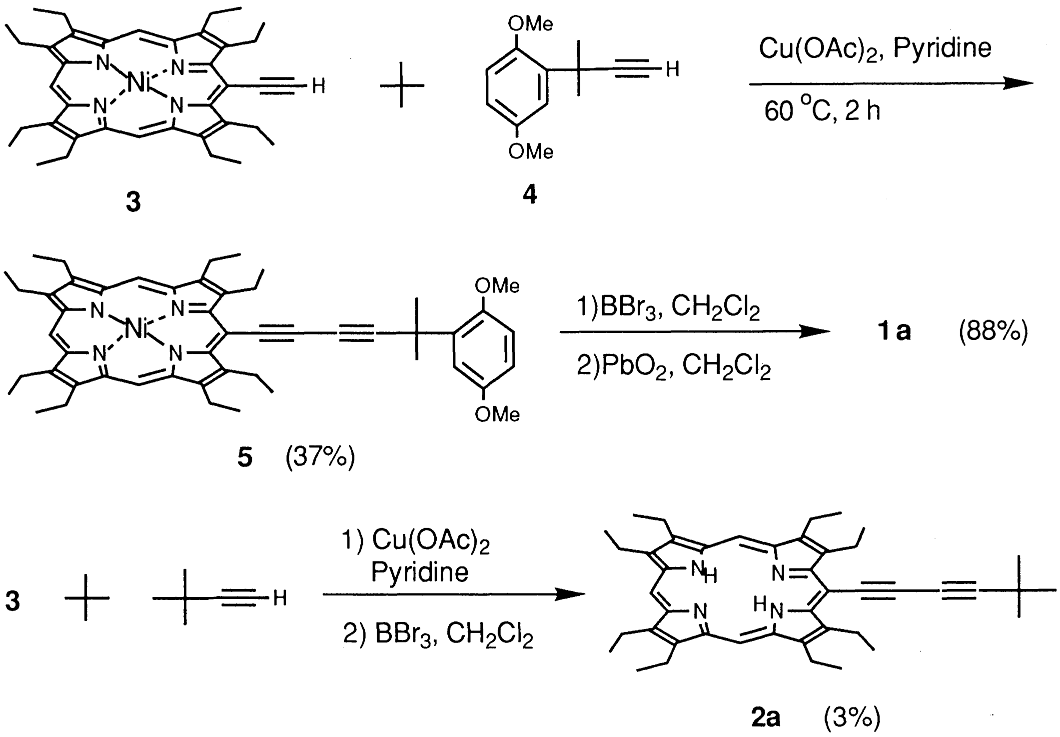
Porphyrin-quinone model compounds with a diacetylene spacer were synthesized. Electronic state of the porphyrin ring was found to be altered due to the direct introduction of the diacetylene group into the meso position, and very fast charge separation was observed in these model compounds.

Elucidation of photosynthesis is one of the crucial subjects in recent chemistry and biology.[1] A number of quinone-linked porphyrins with different redox potentials have so far been prepared to understand the factor of free energy gap which controls photosynthetic electron transfer.[2,3] In these synthetic models, however, modifications of chromophores to change redox properties were carried out mainly at quinone rings and not at porphyrin rings, because of the difficulty in changing redox properties of porphyrins. To obtain a wide variety of free energy gap in model compounds, it is requested to change the redox potentials of porphyrin rings as often seen in natural systems. When a π system such as phenyl or ethylenic chromophore is introduced into porphyrin at meso position, which has high electron density in HOMO level, no conjugation takes place between the two chromophores due to the large steric hindrance for the planar conformation. Acetylene unit is a promising candidate for a substituent at meso position because of its high symmetrical and well-defined linear geometry as well as small steric demand. Moreover, diacetylene unit is expected to act as "molecular wire" in electron transfer and also conjugated acetylenes seem to be hopeful for molecular devices such as non-linear optics and electronic conductors.[4] Bearing these in mind we designed compounds **1**, where one end of diacetylene is directly connected to the meso position of octaethylporphyrin and the other end is linked to benzoquinone with one intervening saturated carbon atom.[5,6] To prevent isomerization of the diacetylene bond, two methyl groups are introduced at the carbon atom between the diacetylene and the quinone.



1 (**a**: M=H_2; **b**: M=Zn)



Scheme 1.

The synthesis of **1a** and the corresponding reference **2a** was carried out as shown in Scheme 1. The coupling reaction of **3**[6,7] and **4**[8] in the presence of copper acetate in pyridine and purification by flash column chromatography (SiO_2/ 25% $CHCl_3$-hexane) afforded diacetylene compound **5** in 37% yield. Demethylation and demetallation of **5** with BBr_3 followed by oxidation with PbO_2 and purification by flash column chromatography (SiO_2/ CH_2Cl_2) gave **1a** in 88% yield. Reference compound **2a** was prepared, with

Table 1. UV-Vis Spectral Data and Oxidation Potentials in CH_2Cl_2

Compound	λmax/nm					
	Soret	Q-bands				$E_{1/2}^{ox}$/mV a)
OEP	397	496	531	564	618	892
1a	425	523	561	593	648	____b)
2a	426	522	559	593	648	728
OEP(Zn)	400	530		567		680
1b	428	562		602		____b)
2b	429	561		600		628

a) Oxidation potentials (mV vs. Ag/Ag^+) were measured by differential pulse voltammetry at a Pt electrode, in CH_2C_2 containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate at 20 °C.

b) Complicated spectra were obtained due to decomposition of **1a** and **1b**.

similar manner to that for **1a**, by the coupling reaction of **3** and 3,3-dimethyl-1-butyne in low yield. Preparation of zinc complexes **1b** and **2b** was carried out by treatment of **1a** and **2a** with zinc acetate in $CHCl_3$, respectively. Structures of all new compounds were confirmed by spectroscopic analyses.[9)]

Electronic spectra of **1** and **2** in CH_2Cl_2 show that there is no appreciable interaction in the ground state between the two composite chromophores; porphyrin and quinone (Table 1). However, λmax of Soret and Q bands of **1** and **2** are red-shifted by about 30 nm compared with those of octaethylporphyrin (OEP) and zinc octaethylporphyrin (OEP(Zn)) due to an introduction of diacetylene group into the porphyrin ring. Measurement of oxidation potentials showed that the ability to release an electron from **2a** and **2b** is higher than that of OEP and OEP(Zn) (Table 1). These data clearly indicate that the introduction of acetylene group changes electronic state of the porphyrin ring.

Table 2. Relative Fluorescence Intensities, Lifetime of the Excited Singlet States, and Electron Transfer Rate

Compound	$\phi_{f,rel}$[a)]	τ/ps	k_{et}[b)]/s^{-1}
1a	<0.01	20	5.0×10^{10}
1b	<0.01	____[c)]	
2a		5600[d)]	

a) Relative fluorescence intensity of Q(0,0) band with respect to the reference compounds, **2a** and **2b**, excited at Soret band.

b) Electron transfer rate constant was calculated using the equation $k_{et}=1/\tau - 1/\tau_{ref}$.

c) Lifetime was shorter than the time resolution of our picosecond dye laser system, ca. 10 ps.

d) Fluorescence lifetime measured by a time correlated single photon counting.

Fluorescence intensities of the quinone-linked porphyrin **1a** and **1b** in CH_2Cl_2 were extremely quenched as compared with those of the corresponding reference compounds **2a** and **2b** as shown in Table 2. This indicates that very fast forward electron transfer occurs between the porphyrin and the quinone. The lifetime of the excited singlet state of **1a** in CH_2Cl_2 was determined by analyzing the time dependence of the transient $S_n \leftarrow S_1$ absorbance excited with a picosecond dye laser system at 590 nm.[10,11)] The sample solution was circulated rapidly in order to avoid the degradation of the compound **1a**. The decay curve of $S_n \leftarrow S_1$ absorbance fit well to single exponential one. The lifetimes of **1a** and **2a** were used to calculate photoinduced electron transfer rate in **1a** as indicated in Table 2. Quite large electron transfer rate was obtained in this case. Since π system of the porphyrin chromophore is extended by the introduction of diacetylene group, there is only two saturated bonds between the donor and the acceptor. Direct overlap across the space between the two π systems is possible, and this may be responsible for the very fast electron transfer in **1a**.[12)] This is one of the examples in which the fastest charge separation was observed, although the mechanism of electron transfer, "through bond" or "through space", is ambiguous.

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References

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2) M. R. Wasielewski, "Photoinduced electron transfer," ed by M. A. Fox and M. Chanon, Elsevier, Amsterdam (1988), Part A, p 161.
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4) J. M. Lehn, *Angew. Chem. Int. Ed. Engl.*, **27**, 89 (1988).
5) Similar polyyne porphyrins were reported by Maruyama et al. However, no direct conjugation between porphyrin and polyyne occurs, because there is an orthogonal phenyl spacer between polyyne and porphyrin: K. Maruyama and S. Kawabata, *Bull. Chem. Soc. Jpn.*, **63**, 170 (1990).
6) *meso*-Ethynyl porphyrin and the corresponding 1,3-butadiyne dimer have already reported by Arnold et al: D. P. Arnold, A.W. Johnson, and M. Mahendran, *J. Chem. Soc., Perkin Trans 1*, **1978**, 366. Extensive interaction between the chromophores was indicated in the dimer because of the conjugation between the porphyrins through diacetylene group.7)
7) D. P. Arnold and L. J. Nitschinsk, *Tetrahedron*, **48**, 8781 (1992).
8) Coupling reaction of 2,5-dimethoxyphenylmagnesium bromide with methoxyallene following successive dimethylation with ethyllithium and methyliodide gave **4**. Synthesis of **4** will be reported elsewhere in detail.
9) **1a:** ^{1}H NMR (270 MHz, $CDCl_3$) δ=–2.70 (2H, br.s), 1.88 (6H, s), 1.8-2.0 (24H, m), 4.0-4.2 (12H, m), 4.29 (4H, q, J=7.3 Hz), 6.82 (2H, s), 7.26 (1H, s), 9.91 (1H, s), 10.08 (2H, S). MS (FAB) 733 $(M+2)^+$.
1b : ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.87 (6H, s), 1.8–2.0 (24H, m), 4.0–4.2 (12H, m), 4.32 (4H, q, J=7.6 Hz), 6.82 (2H, s), 7.29 (1H, s), 9.89 (1H, s), 9.97 (2H, s). MS (FAB) 795 $(M+1)^+$.
2a: ^{1}H NMR (270 MHz, $CDCl_3$) δ=–2.70 (2H, br.s), 1.48 (9H, s), 1.8-2.0 (24H, m), 4.0-4.2 (12H, m), 4.28 (4H, q, J=7.3 Hz), 9.90 (1H, s), 10.07 (2H, s). MS (FAB) 639 $(M)^+$.
2b: ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.48 (9H, s), 1.8-2.0 (24H, m), 4.0-4.2 (12H, m), 4.33 (4H, q, J=7.3 Hz), 9.97 (1H, s), 10.05 (2H, s). MS (FAB) 700 $(M+2)^+$.
10) Y. Hirata, T. Okada, N. Mataga, and T. Nomoto, *J. Phys. Chem.*, **96**, 6559 (1992).
11) Back electron transfer rate in THF could not be determined probably due to ultrafast recombination of charged species.
12) Antolovich et al. reported porphyrin-quinone compound with norbornyl-based hydrocarbon spacer in which there is two saturated bonds between donor and acceptor. In this model compound similar very fast forward electron transfer (ket=3.3×10^{10} s^{-1} in CH_2Cl_2) was observed . M. Antolovich, P. J. Keyte, A. M. Oliver, M. N. Paddon-Row, J. Kroon, J. W. Verhoeven, S. A. Jonker, and J. M. Warman, *J. Phys. Chem.*, **95**, 1933 (1991).

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