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EFFICIENT INTRAMOLECULAR QUENCHING AND ELECTRON TRANSFER IN TETRAPHENYLPORPHYRIN ATTACHED WITH BENZOQUINONE OR HYDROQUINONE AS A PHOTOSYSTEM MODEL

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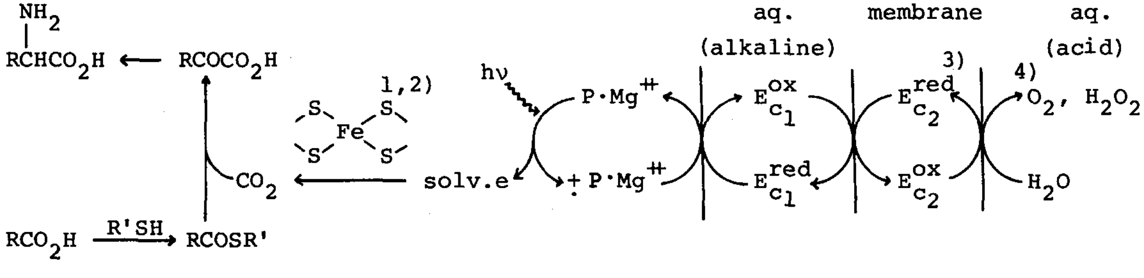
In our current attempts to model *photosynthesis*[1–4] by use of completely artificial compounds (Scheme 1), there still remain serious difficulties unsolved. Among them, one of the most important problems seems to be the fact that simple irradiation of a porphyrin (or chlorophyll)$\cdot Mg^{++}$ complex (hereafter it is abbreviated as $P\cdot Mg^{++}$) can not lead to the effective separation of *oxidizing element* ($\dot{+}P\cdot Mg^{++}$ or any other species of the high oxidation potential) from *reducing element* (solvated electron or any other species of high reduction potential).[5] As a possible approach to the problem, the authors have been trying to prepare a porphyrin appropriately attached to a suitable electron acceptor



EC: Electron carrier where ox and red correspondes to oxidized and reduced form.

Scheme 1.

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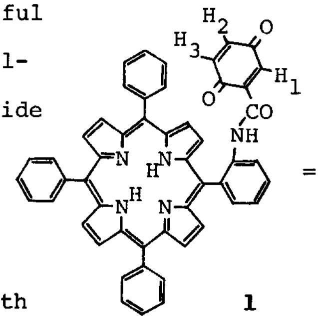
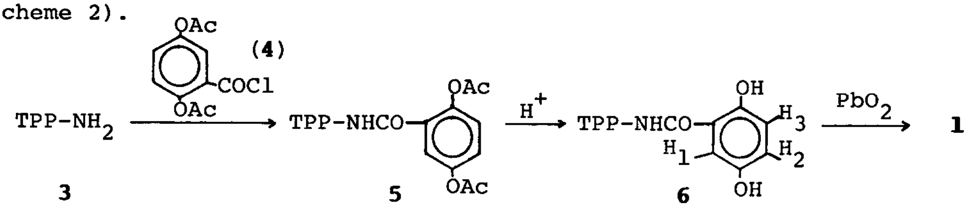


= TPP-NHCO-Q

The authors now wish to report the successful preparation and unique properties of tetraphenylporphyrin attached to benzoquinone via the peptide linkage (**1**) as a first example of this type.

Mono-o-nitrotetraphenylporphyrin (**2**), prepared from the mixed condensation of 3 eq of benzaldehyde and 1 eq of o-nitrobenzaldehyde with 4 eq of pyrrole was reduced to the corresponding monoamino derivative (**3**) with stannous chloride in conc. HCl[6] (3.0 % overall yield based on benzaldehyde) (Scheme 2).



Scheme 2.

Treatment of **3** with 10 eq of 2-chlorocarbonyl-1,4-diacetoxybenzene (**4**) prepared from the corresponding carboxylic acid[7] and thionyl chloride afforded **5** in 76 % yield. Selective hydrolysis of **5** in methanol HCl (apparent pH was 1), followed by the PbO_2 oxidation in benzene at room temperature[8] gave **1** in 75 % yield. Spectral characteristics of **1**—**6** are summerized in Table I. Among the spectral properties listed, the most interesting to note is that the quinone protons are experiencing rather abnormal shielding effect in H-nmr spectra; H_1 by 2.9, H_2 1.4, and H_3 1.6 ppm more shielded for **6** compared with 2-phenylaminocarbonyl-1,4-dihydroxybenzene and H_1 by 0.1, H_2 2.0, and H_3 3.0 ppm for **1** compared with 2-phenylaminocarbonyl-p-benzoquinone. This remarkable shielding effect clearly demonstrates that both of quinone and hydroquinone moieties are located in close proximity to the porphyrin plane, although hydroquinone and quinone are in quite different orientation (most probably H_1 of **6** takes the nearest position to the porphyrin plane while H_3 of **1** in the nearest position). These situation of close proximity is especially favorable for the interaction between two functional groups, porphyrin and hydroquinone or quinone.

Typical examples of favorable interaction are seen in the energy transfer

Table I.

Compound	Visible spectra in $CHCl_3$ (nm)	Mass spectra (m/e)	NMR spectra in $CDCl_3$ (ppm)
1	421, 518, 554, 594, 649	765 (41 %) 763 (2) 629 (100)	4.75 (d, 1H); 5.52 (q, 1H); 6.84 (d, 1H); 7.36—8.40 (m, 19H); 8.60—9.20 (m, 8H); 9.84 (S, 1H)
3	420, 516, 551, 591, 649	629 (100)	3.10 (broad, 2H); 6.98—8.40 (m, 19H); 8.80—8.90 (m, 8H)
5	421, 518, 553, 593, 649	807 (9) 765 (7) 671 (100) 629 (53)	0.80 (S, 3H); 2.30 (S, 3H); 6.22 (d, 1H); 6.26 (d, 1H); 6.56 (q, 1H); 7.40—8.30 (m, 19H); 8.66—8.96 (m, 8H)
6	420, 517, 552, 592, 648	765 (10) 629 (100)	4.04 (d, 1H); 5.95 (q, 1H); 6.17 (d, 1H); 7.40—8.30 (m, 19H); 8.76—9.00 (m, 8H)

and the electron transfer. When tetraphenylporphyrin (TPP, 6.65×10^{-7}M) was irradiated in the presence of p-benzoquinone in chloroform, quenching of TPP (6.65×10^{-7}M) fluorescence was observed depending on the concentration of quinone.[9] Fluorescence of **1** (6.65×10^{-7}M) was also observed at very low intensity, demonstrating that the remarkable quenching is taking place. Intrapolating the quinone concentration-fluorescence intensity relationship observed for the TPP-quinone mixture to the fluorescence intensity of **1**, "effective concentration" of quinone in **1** to quench TPP fluorescence intramolecularly was estimated to be 4.2×10^{-2}M, indicating much more favorable interaction than that expected from the free intermolecular interaction.

Another example was seen for the efficient electron transfer from the hydroquinone moiety to ferric ion of TPP$\cdot$Fe^{+++} complex. The electron transfer from hydroquinone to P$\cdot$Fe^{+++} was reported in pyridine for octaethylporphyrin, mesoporphyrin and deuteroporphyrin.[10] The rate of the electron transfer reaction measured by us by using a stopped-flow rapid scanning electronic spectrum demonstrated that it was proportional both to 1st order of TPP$\cdot$Fe^{+++} and 1st order of hydroquinone concentration. The rate of the electron transfer in **6**$\cdot$Fe^{+++}complex

(1.33×10^{-5}M), prepared from **6** and ferrous acetate in acetic acid and chloroform,[11] follows 1st order kinetics ($k = 3.50 \times 10^{-1} sec^{-1}$), where similar intrapolation of the observed second order rate of the HQ-TPP·Fe^{+++} reaction ($k = 1.6 \times 10^{1} sec^{-1}M^{-1}$) to above again afforded 2.1×10^{-2}M as an "effective concentration" of HQ around Fe^{+++}, in an excellent agreement with that for the fluorescence quenching.

The present finding of a very effective (energy or electron transfer) donor-acceptor type combination and its possible extension seem to be significant for better understanding of the reaction mechanism in such a highly organized molecular assembly as chloroplast, and also it is an important principle to be applied to a wider range of electron and/or energy transfer systems.

References and Note

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