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CIDNP STUDY ON PORPHYRIN-PHOTOSENSITIZED REACTIONS WITH PHENOL AND QUINONE

DIMERIZATION OF 4-METHOXYPHENOL AND CROSS COUPLING OF BENZOQUINONE TO PORPHYRINS COVALENTLY LINKED WITH PHENOL GROUP

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Abstract—Photoreactions of porphyrin (TPP) with phenol and/or quinone in non-polar benzene solution were studied mainly by the CIDNP technique. In the photoreaction of TPP with 4-methoxyphenol (1), CIDNP effects due to TPP$^{-\cdot}$ and 1$^{+\cdot}$ were observed, while the generation of considerable amounts of free 4-methoxyphenoxyl radical was indicated by ESR and CIDNP in the three-component system involving TPP, 1, and *p*-benzoquinone (Q). Based on these results, two new photoreactions leading to permanent products were developed: (1) photosensitized dimerization of 1 and (2) photo-induced cross coupling of Q to porphyrins covalently linked with phenol group. The unique role of phenol in the photo-induced electron transfer reaction of TPP and Q in a non-polar solvent was discussed in terms of its dual function as both the proton and electron donor.

Since Grossweiner and co-workers reported the flash photolysis study on the photosensitized reaction of eosin with phenol in 1959,[1] phenol compounds have been widely used as reductants in the photosensitized reaction of triplet dyes.[2] However, in most cases, oxygen has been used as the oxidant and there have usually been no observed chemical changes under deaerated conditions. A variety of techniques such as time-resolved optical spectroscopy,[2a,d,f] electron spin resonance (ESR),[3] and chemically induced dynamic nuclear polarization (CIDNP),[2c,4] have been extensively applied to disclose the detailed mechanism of the photosensitized reactions of dyes with phenols by virtue of the lack of permanent chemical changes under deaerated conditions. Among these studies, the photo-CIDNP technique has been applied in the photoreaction of reversible hydrogen atom abstraction from phenol by triplet xanthene dyes, triphenylmethane dyes and nitroaromatic compounds.[2c] Photo-CIDNP effects due to reversible photoreaction of flavins with amino acid residues such as tyrosine, histidine, and tryptophane have been successfully used for the study on the three-dimensional structure of proteins in solution.[5] However, it is rather surprising that porphyrin compounds, a class of the representative dyes, have not been employed in photoreactions with phenols with the exception of the oxygenation reaction by singlet oxygen.[2b]

On the other hand, considerable attention has recently been focused on the photo-induced reaction of porphyrins and/or chlorophylls with quinones under a variety of conditions as simple models for photosynthesis in natural plants.[6] As generally accepted, the primary electron transfer reaction of photosynthesis in natural plants takes place in the non-polar media such as the lipid membrane. However, most of the light energy absorbed by porphyrins and/or chlorophylls is consumed by rapid reverse electron transfer in the geminate radical ion pair in non-polar media *in vitro*. Consequently, irradiation of porphyrins and quinones in non-polar media such as benzene under deaerated conditions does not give any permanent products likewise with the porphyrin–phenol system.

In the course of our photo-CIDNP studies on the porphyrin sensitized reactions,[7] we have found that irradiation of three-component system of phenol–porphyrin–quinone in benzene results in two novel photochemical reactions: (1) oxidative dimerization of phenol and (2) cross coupling of quinones to porphyrins covalently linked with phenol group. We wish to emphasize that new photochemical reactions described in this paper have been found and developed on the basis of photo-CIDNP results.

RESULTS AND DISCUSSION

CIDNP study on photoreaction between porphyrin and phenol

At first, the photoreaction of 5,10,15,20-tetraphenylporphyrin (TPP) with phenol in benzene-d_6 was investigated by the CIDNP technique. When a benzene-d_6 solution of TPP was irradiated in the presence of 4-methoxyphenol (1) with light of wavelength longer than 490 nm under an argon atmosphere, the strong absorption CIDNP signal was observed in pyrrolic β-hydrogens of TPP at ambient temperature (Fig. 1). The intensity of this CIDNP signal increased in proportion to the phenol concentration in the range of 10–300 mM. At such high concentrations of 1, it was very difficult to observe the CIDNP signals due to 1. At low concentration of 1 (*ca* 5 mM), both *o*- and *m*-hydrogens of 1 were polarized in similar magnitudes as weak but distinct emission signals along with the weak polarization of TPP (Fig. 2). The CIDNP pattern observed for phenol 1 is quite different from those in the reversible hydrogen abstraction reactions of phenol with dyes, nitroaromatics and ketones.[2c] In the latter reactions, *o*- and *m*-hydrogens of phenol are polarized in opposite directions to each other and the magnitudes of polarization of *o*-hydrogens are usually larger than those

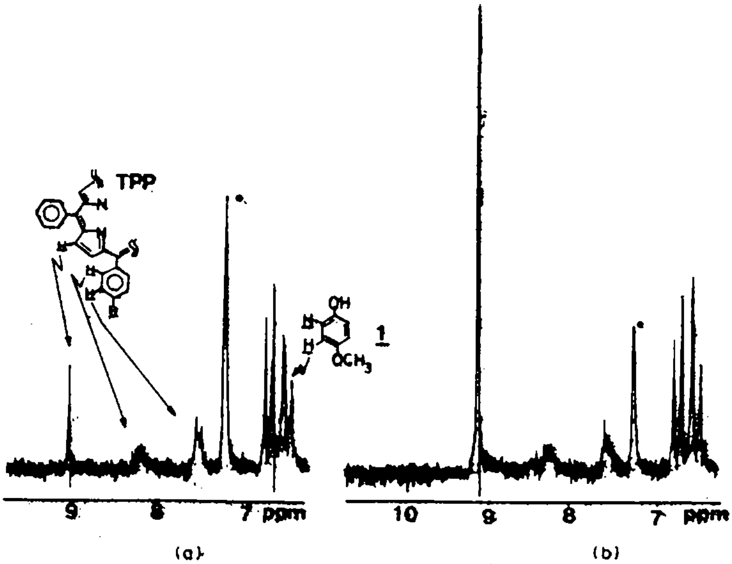

Fig. 1. CIDNP observed in the photoreaction of 1 and TPP in C_6D_6; (a) in the dark; (b) during irradiation (*, solvent).

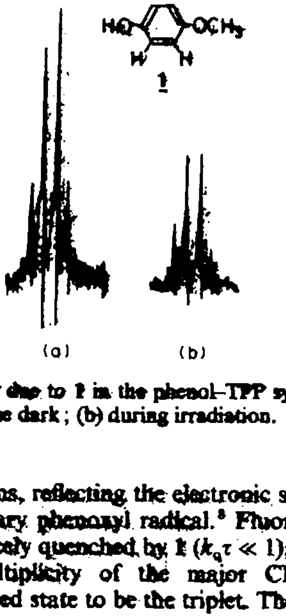

Fig. 2. CIDNP due to 1 in the phenol–TPP system; (a) in the dark; (b) during irradiation.

of *m*-hydrogens, reflecting the electronic structure of the intermediary phenoxyl radical.[8] Fluorescence of TPP was scarcely quenched by 1 ($k_q\tau \ll 1$); indicating the spin multiplicity of the major CIDNP-contributing excited state to be the triplet. The polarized signals of TPP and 1 can be explained on the basis of the radical pair theory of CIDNP by a mechanism of radical-ion-pair-induced polarization[9a,10] (Scheme 1). This mechanism involves electron transfer from 1 to the triplet excited state of TPP ($^3TPP^*$), generating the triplet pair of radical ions, $TPP^{\overline{\cdot}}$ ($g = 2.0027$)[11] and $1^{\dot{+}}$ ($g = 2.0035$)[12], and reverse electron transfer in this pair to generate the reactants in their singlet ground states ($\mu,\varepsilon > 0$).[10] Pyrrolic β-hydrogens, which are directly attached to the porphyrin macrocycle, may have negative hyperfine coupling constants in $TPP^{\overline{\cdot}}$ ($a^{\beta-H} < 0$).[13] Both the *o*- and *m*-hydrogens of the cation radical of 1 also have negative hyperfine coupling constants ($a^o, a^m < 0$).[14] Accordingly, polarized absorption is expected for the pyrrolic β-hydrogens of TPP and polarized emission for ring hydrogens of 1.†

Further evidence for the formation of the phenol cation radical was provided by the observation of photo-induced hydrolysis of 4-methoxy-2,3,6-trimethylphenol (2). In the CIDNP experiment with 2, the accumulation of trimethylhydroquinone (3) and methanol was observed. The photo-induced hydrolysis did not take place in the carefully dried solvent. When 2 (10 mM) and TPP (1 mM) in commercially available benzene-d_6 was irradiated for 5 min about 20% of 2 was hydrolyzed into 3 and methanol. Because one could not expect the demethylation from the corresponding phenoxyl radical,[15] the photo-induced hydrolysis of 2 is most reasonably explained by the mechanism involving cation radical A as the intermediate, which is trapped by the nucleophilic attack of adventitious water, resulting in the formation of 3 and methanol (Scheme 2). Usually, polarization of porphyrin compounds has not been observed in the reversible photo-induced electron transfer reactions in steady state because of their rapid and extensive electron exchange broadening.[9b] Accordingly, the time-resolved CIDNP technique[16] is required for the detection of polarization due to porphyrin compounds. Thus, it is interesting to note that this method is very simple and useful for the study on the electronic structure of photo-generated

$$^3TPP^* + \underline{1} \longrightarrow {}^3\overline{TPP^{\overline{\cdot}}\,\underline{1}^{\dot{+}}} \qquad (1)$$

$$^3\overline{TPP^{\overline{\cdot}}\,\underline{1}^{\dot{+}}} \longrightarrow {}^1\overline{TPP^{\overline{\cdot}}\,\underline{1}^{\dot{+}}} \qquad (2)$$

$$^3\overline{TPP^{\overline{\cdot}}\,\underline{1}^{\dot{+}}} \longrightarrow TPP^{\overline{\cdot}} + \underline{1}^{\dot{+}} \qquad (3)$$

$$^1\overline{TPP^{\overline{\cdot}}\,\underline{1}^{\dot{+}}} \longrightarrow TPP + \underline{1} \qquad (4)$$

Scheme 1.

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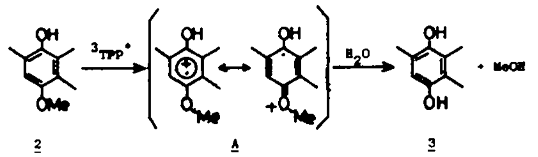
†Absorption signals of methyl-Hs were observed in the case of alkyl-substituted phenols.



Scheme 2.

porphyrin anion radicals,† because it will provide signs and relative magnitudes of hyperfine coupling constants of the precursor radicals. Quantitative studies of CIDNP effects due to a variety of porphyrins involving face-to-face porphyrin dimers are currently in progress.

Similar CIDNP signals were observed when TPP was subjected to the photo-induced reaction with a variety of phenols, such as 4-methylphenol, 4-t-butylphenol, 2,6- and 3,5-dimethylphenol, and 2,4,6-trimethylphenol. The magnitude of CIDNP due to porphyrin increased as the oxidation potential of phenols decreased and no CIDNP signals were observed with phenols with oxidation potentials higher than 0.60 V (SCE),[17] such as phenol, 4-bromophenol, 4-chlorophenol, or 4-nitrophenol. The dependence of CIDNP intensities upon concentration of phenols is shown in Fig. 3. Among the phenols with lower oxidation potentials, 4-methoxyphenol (1) gave the strongest CIDNP signal due to TPP presumably because the methoxyl group could stabilize the phenol cation radical by virtue of its electron donating property. We believe that observation of CIDNP signals according to $TPP^{\cdot-}$ strongly rests on the stability of phenol cation radical counterparts.

CIDNP study on photoreaction between porphyrin and quinone

No CIDNP signal was observed in the TPP–*p*-benzoquinone (Q) system in benzene-d_6, although the polarized quinone signals in protic media (CD_3OD) had been reported in the presence of acid[18] and/or Mg^{2+}, as well as lowering the temperature of the system.[7e] Lack of CIDNP effects in non-polar solvent such as benzene-d_6 may be interpreted on the basis of the very rapid decay of the ion radical pair $^xTPP^{\cdot+}Q^{\cdot-}$ (x = 1 or 3) by the reverse electron transfer.[19]

TPP-sensitized dimerization of 1 *in the presence of quinone*

When *p*-benzoquinone (Q, 10 mM) was added to a benzene-d_6 solution of TPP and 1, the CIDNP signal according to TPP disappeared and the ring hydrogens of 1 showed substantial broadening (Fig. 4). Free 4-methoxyphenoxyl radical was clearly detected at ambient temperature by ESR ($g = 2.0052$, $a^o = 5.51$ G and $a^m = 0.75$ G),[20] indicating the generation of a high concentration of free 4-methoxyphenoxyl radical in the reaction mixture. However, the most significant finding in this three-component system is *the accumulation of permanent product* derived from 1.

Thus, irradiation of a benzene solution of TPP (0.5 mM), 1 (100 mM) and Q (10 mM) under an argon atmosphere ($\lambda > 590$ nm), gave rise to the formation of dimer, 2-hydroxy-4′,5-dimethoxydiphenyl ether (5) (49%) along with hydroquinone (H_2Q) at 50% conversion of Q. TPP remained unchanged at this stage of the reaction. The regioselective coupling at position 2 of 1 was strictly confirmed by 400 MHz ^1H-NMR analysis. As the reaction proceeded, its rate decreased markedly probably because of the accumulation of H_2Q which seemed to act as a radical scavenger.[21] When H_2Q (10 mM) was added to the standard solution prior to irradiation, the dimerization of 1 did not occur at all. This scavenging effect of H_2Q indicates that the dimerization takes place via free radical processes, which is consistent with ESR measurement. Thus, we have examined the thermal reaction of 1 with di-t-butylperoxide (DBPO) at high temperature, which was reported to give the free phenoxyl radical.[22] When 1 and DBPO in chlorobenzene were heated at 140° for 20 h, the same dimer 5 was formed in a moderate yield of 76%.

The quantum yield (Φ_d) for the formation of dimer 5 was dependent upon the concentrations of both 1 and Q (Figs 5 and 6). Φ_d increased as the concentration

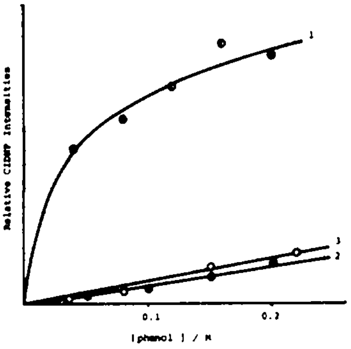


Fig. 3. Dependence of CIDNP intensities upon concentration of phenols: 1, 4-methoxyphenol ⊙; 2, 4-methylphenol ●; 3, 2,6-dimethylphenol ○.

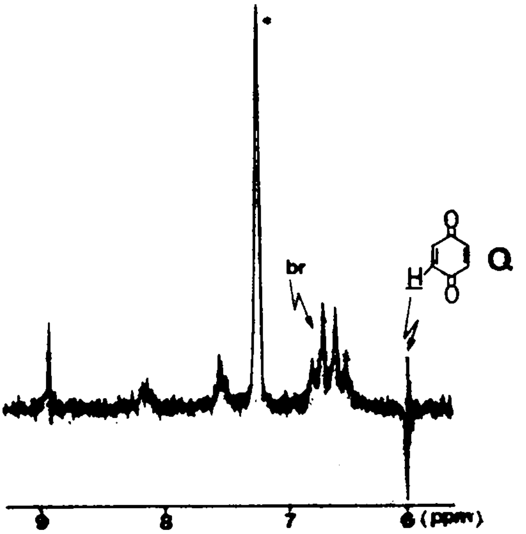


Fig. 4. Photo-CIDNP observed in the phenol–porphyrin–quinone system (br, broadening; •, solvent).

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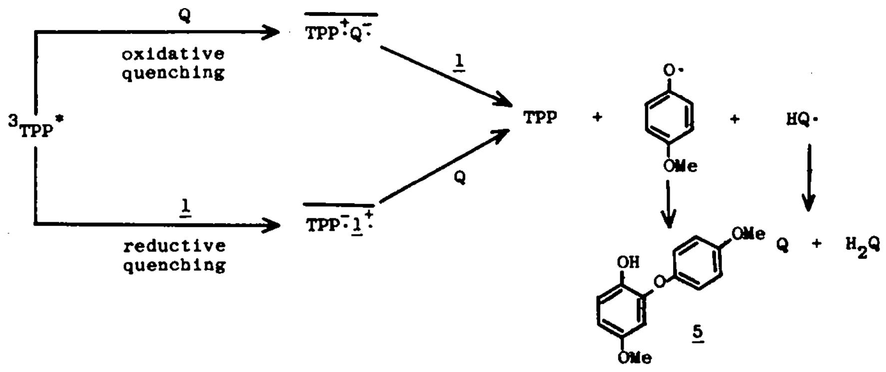
† Enhanced absorption due to meso-protons of substituted meso-porphyrin dimethyl ester were also detected under similar conditions.



Scheme 3.

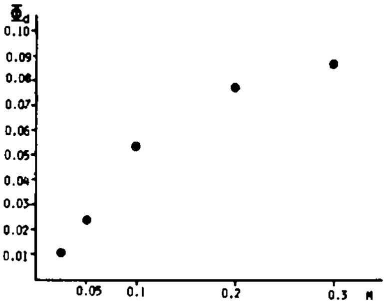


Fig. 5. Dependence of quantum yield (Φ_d) for formation of photo-induced coupling dimer 5 upon concentration of 4-methoxyphenol 1.

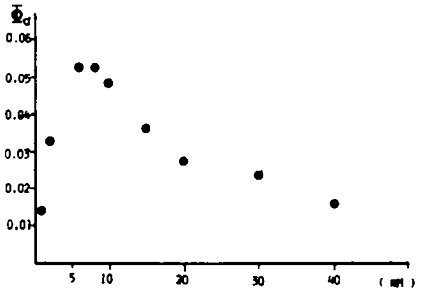


Fig. 6. Dependence of quantum yield (Φ_d) for formation of photo-induced coupling dimer 5 upon benzoquinone concentration.

of 1 increased, while Φ_d reached maximum at [Q] = 5 mM and then decreased markedly as the concentration of Q increased. The profile of Φ_d dependence upon the concentration of Q in Fig. 6 coincides well with that of the porphyrin triplet yield calculated using porphyrin fluorescence quenching data,† clearly indicating that phenol coupling takes place via the porphyrin triplet state. A variety of benzoquinone derivatives other than Q were employed as oxidants in this photo-induced dimerization of 1. As shown in Fig. 7, Φ_d was greatly dependent upon the reduction potentials of quinones. Larger Φ_d values were observed with halogenoquinones having lower reduction potentials, while the dimerization did not occur in the case of alkylsubstituted benzoquinones.‡

Possible mechanisms for the dimerization can be depicted as shown in Scheme 3. Oxidative quenching of $^3TPP^*$ by Q may lead to the radical ion pair, $TPP^{+\cdot}Q^{-\cdot}$ which seems to decay by reverse electron transfer to regenerate the starting materials in the absence of 1. However, in the presence of 1, the radical ion pair will react with 1 to give the 4-methoxyphenoxyl radical and the semiquinone radical HQ·. The former radical decays by recombination to give 5, while the latter decays mainly by disproportionation. An alternative mechanism involving reductive quenching of $^3TPP^*$ by 1 followed by electron transfer from $TPP^{-\cdot}$ to Q may be conceivable. However, under our conditions with [1] = 100 mM and [Q] = 10 mM, about 95% of $^3TPP^*$ is estimated to be quenched by Q on the basis of their quenching rates of $^3TPP^*$.§ Therefore, it may be safely considered

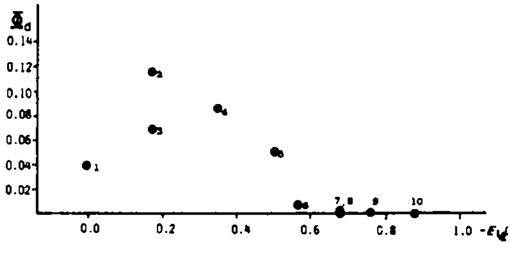


Fig. 7. Dependence of Φ_d on the reduction potential of quinones. Quinones used are: 1—chloranil (−0.01); 2—2,5-dichloroquinone (0.18); 3—2,6-dichloroquinone (0.18); 4—chlorobenzoquinone (0.34); 5—*p*-benzoquinone (0.51); 6—toluquinone (0.58); 7—2,5-dimethylbenzoquinone (0.67); 8—2,6-dimethylbenzoquinone (0.68); 9—trimethylbenzoquinone (0.75); 10—duroquinone (0.84). In parentheses are indicated the reduction potentials vs SCE from Ref. 31.

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†$K_q\tau$ was estimated to be 150 from the fluorescence quenching experiment.

‡When octaethylporphyrin was used in place of TPP, dimer 5 was obtained even with alkyl-substituted benzoquinones. The effects of porphyrin structure in this dimerization reaction will be discussed fully elsewhere.

§Preliminary flash photolysis measurements have shown that the quenching rate constant for the reaction of 1 with $^3TPP^*$ is *ca* 1×10^6 M^{-1} s^{-1}. As the rate constant for the reaction of Q with TPP, we used the value of 2.1×10^9 M^{-1} s^{-1} (in toluene).[19]

that the oxidative mechanism is responsible for the major reaction course.

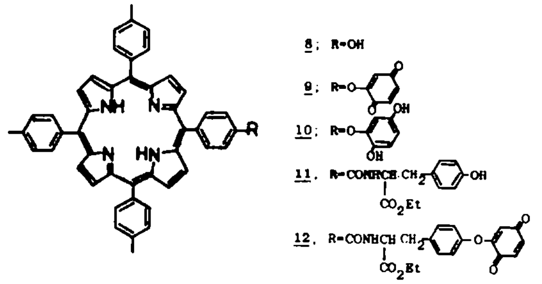
The disappearance of CIDNP due to TPP in Fig. 4 could be explained by the radical pair substitution mechanism, that is, initially forming a short-lived radical ion pair, $\mathrm{TPP}^{+\cdot}\mathrm{Q}^{-\cdot}$, immediately turning into a CIDNP-contributing triplet neutral radical pair, 4-methoxyphenoxyl radical and a HQ· pair. The emission signal due to Q could be derived by the in-cage disproportionation.†

Photosensitized cross coupling of quinone to "phenolic porphyrin"

In place of TPP, "phenolic porphyrins" which contain phenoxyl group in their own were subjected to the photo-induced reaction with quinone in non-polar benzene solution. First, 5-(4-hydroxyphenyl)-10,15,20-tris(*p*-tolyl)porphyrin (**8**) as a "phenolic porphyrin" (2 mM) was irradiated in the presence of Q (10 mM) with light of wavelength longer than 590 nm under an argon atmosphere. Surprisingly, a single porphyrin product **9** was produced with concurrent formation of hydroquinone. No other products, except the unreacted starting materials **8** and Q were detected by TLC or 400 MHz ^{1}H-NMR analysis. Benzoquinone ends in **9** appear at δ 6.87 (d, J = 10.3 Hz), 6.79 (dd, J = 10.3 and 2.2 Hz), 6.22 (d, J = 2.2 Hz) in its 400 MHz ^{1}H-NMR spectrum ($CDCl_3$). The benzoquinone adduct (**9**) was quantitatively reduced to hydroquinone adduct **10** ($Na_2S_2O_4$, 10 min at 25°). Hydroquinone ends in **10** appear at δ 6.87 (d, J = 8.9 Hz), 6.63 (d, J = 2.8 Hz), 6.43 (dd, J = 8.9 and 2.8 Hz). When the hydroquinone adduct was irradiated in the presence of Q in deaerated benzene solution, **10** was found to convert immediately into the benzoquinone adduct **9** with concurrent formation of H_2Q. This result strongly suggests that hydroquinone adduct **10** was the primary coupling product, which was readily oxidized to quinone adduct **9** by further irradiation in the presence of excess Q, although the formation of **10** was not detected even at low conversions of **9**.

The quantum yield (Φ_c)‡ for the formation of the cross coupling adduct was dependent upon the concentration of Q. Increasing the concentration of Q markedly decreased Φ_c, indicating that these photo-coupling reactions take place via the porphyrin triplet state, likewise with the photo-induced dimerization of **1**.

Next, we have examined the photoreaction of the tyrosine-linked porphyrin (**11**) with Q. Under similar conditions, irradiation of **11** and Q resulted in the predominant formation of the coupling product **12** and H_2Q. It should be stressed here that this photo-coupling reaction is very useful for the synthesis of quinone-linked porphyrin compounds,[23] since it needs no quinone protection and involves a simple one-pot photochemical procedure. The fluorescence property of **9** was characteristic of quinone-linked porphyrins in that the relative fluorescence quantum yield of **9** was much less (< 0.02) than that of TPP (0.13).[24]



To clarify the mechanistic details, we have investigated the CIDNP signals of these photo-coupling reactions. When a benzene-d_6 solution of **8** (0.5 mM) was irradiated in the presence of Q (5 mM), the CIDNP signal due to Q was observed as a weak emission signal. More distinct CIDNP signals were observed in the photo-coupling reactions of **11** with Q (Fig. 8). Polarized signals due to the coupling product **12** as well as the starting materials **11** and Q, whose assignments are indicated by arrows, were observed in this case. CIDNP effects due to the coupling product **12** clearly indicate that the photo-induced coupling of quinone to "phenolic porphyrin" takes place via the triplet neutral radical pair.§ Quenching of the porphyrin triplet by Q probably results in the triplet radical ion pair, where the phenol group works as the proton and electron donor giving rise to the phenoxyl radical and the semiquinone radical.

Photoexcitation of TPP in the presence of either **1** or Q alone in non-polar benzene solution results in the formation of ion radical pair, $1^{+\cdot}\mathrm{TPP}^{-\cdot}$ or $\mathrm{TPP}^{+\cdot}\mathrm{Q}^{-\cdot}$, respectively. Both of these intermediates seem to decay by the rapid reverse electron transfer

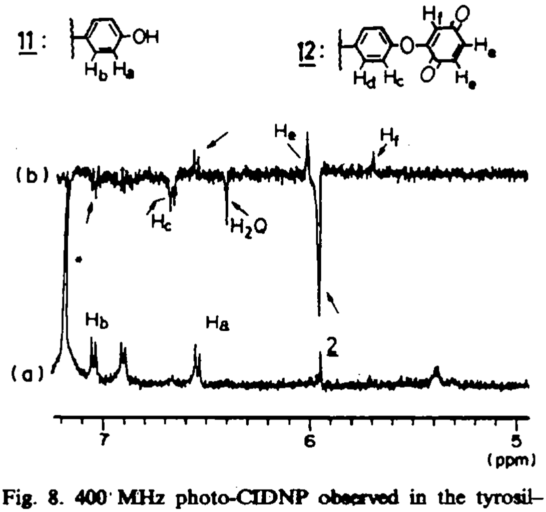


Fig. 8. 400 MHz photo-CIDNP observed in the tyrosil-porphyrin **11** and benzoquinone (Q) system (*, C_6H_4): (a) dark; (b) difference spectra (light–dark).

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†Because both are phenoxyl type radicals in neutral radical pair, Δg is presumably small. In fact, we have observed the multiplet effect (*E*/*A*) with methyl-Hs when 2,5-dimethylbenzoquinone was subjected to this photoreaction in place of Q.

‡Φ_c was estimated to be 0.01.

§For the *o*-hydrogen of the phenoxyl group, $\Delta g > 0$, $a_H < 0$, $\varepsilon > 0$, $\Gamma_{[illegible]} < 0$, see also Ref. 10. Thus, in-cage recombination of the geminate radical pair will lead to the formation of **12**. The polarized absorption due to the *o*-hydrogen of the phenol group in **11** and the polarized emission for the hydrogen of Q appear to be derived from out-of-cage processes.

reaction and do not lead to the permanent photoproducts as described above. However, irradiation of TPP in the presence of both 1 and Q led to the generation of a sufficient concentration of the 4-methoxyphenoxyl radical enough for its dimerization. In the reaction of "phenolic porphyrin", it has also been shown that the coupling product is formed via an in-cage recombination process of the neutral radical pair. Therefore, it seems likely that conversion of ion radical pair such as $\overline{1^{\dot{+}}\mathrm{TPP}^{\dot{-}}}$ or $\overline{\mathrm{TPP}^{\dot{+}}\mathrm{Q}^{\dot{-}}}$ into neutral radical pairs is critical for the accumulation of permanent products. In this regard, the role of phenol in the photo-induced electron transfer reaction of TPP and Q is very interesting in the sense that it apparently acts as the proton donor to $\mathrm{Q}^{\dot{-}}$ as well as the electron donor to $\mathrm{TPP}^{\dot{+}}$, finally giving rise to the formation of the neutral radical pair composed of the phenoxyl radical, the semiquinone radical and TPP in the ground state.

In summary, photoreaction of porphyrin (TPP) with phenols and/or quinones in benzene have been studied mainly by the CIDNP technique. In the photoreaction of TPP with 1, CIDNP effects due to $\mathrm{TPP}^{\dot{-}}$ and $1^{\dot{+}}$ were observed, while the addition of Q to the reaction mixture led to the disappearance of CIDNP signals due to TPP and the substantial broadening of 1. In the latter conditions, free phenoxyl radical was detected by ESR. Based on these results, we have developed two new photoreactions by using the three-component system involving sensitizer (TPP), electron donor (phenol), and electron acceptor (quinone): (i) photosensitized dimerization of 4-methoxyphenol and (ii) photo-induced cross coupling of quinone to "phenolic porphyrin". The unique role of phenol in the photo-induced electron transfer reaction of TPP and Q was discussed in terms of its dual function as both the proton and electron donor.

EXPERIMENTAL

^{1}H-NMR spectra were recorded with JEOL-PS-100 and JEOL-GX-400 spectrometers with TMS as internal standard and chemical shifts are reported in δ-values. Fluorescence spectra were taken on a Shimadzu spectrofluorometer RF-502A. An Ushio tungsten–halogen lamp (500 W) was used as a source of red (>590 nm) or yellow light (>490 nm) in combination with Toshiba VO-59 or VO-49 glass color filters, respectively. ESR measurements were undertaken on a JEOL-JES-FE1XG spectrometer.

100 MHz ^{1}H-CIDNP spectra were measured by using a JEOL-PS-100 spectrometer equipped with a modified NMR probe for the photo-irradiation. The detailed device used for CIDNP measurements during irradiation is described elsewhere.[25] 400 MHz ^{1}H-CIDNP spectra were taken by using a JEOL-GX-400 spectrometer equipped with a modified NMR probe for the photo-irradiation. 514.5 nm of laser light (1 W, NEC Argon Laser GLG 3300) was guided directly through a suprasil quartz rod to the sample. A computer-controlled mechanical shutter was interposed in front of the laser apparatus.

Flash column chromatography was performed by Kiesegel 60H (Merck). GLC analysis was carried out using JEOL JGC-1100 (silicon DCC 550 column).

Benzene (Wako Tokyo, Japan) was distilled under N_2 and stored with sodium. Benzene-d_6 (CEA-France) was purified by passing through a column of active aluminum oxide (Wako) immediately before preparing the sample soln, if necessary. *p*-Benzoquinone (Q), 2,5- and 2,6-dichlorobenzoquinone, and chloranil (Tokyo Kasei, Tokyo, Japan) were purified by vacuum sublimation after passing through a column of silica gel (Wako) with benzene. Toluquinone and 2,3,5-trimethylbenzoquinone were synthesized by oxidation of the corresponding hydroquinone with $FeCl_3$. 2,5-Dimethylbenzoquinone and 2,6-dimethylbenzoquinone were synthesized by oxidation of the corresponding phenols with Fremy's salt.[26] Duroquinone was synthesized from durene.[27] All the quinones were purified by vacuum sublimation before use. 4-Methoxy-2,3,6-trimethylphenol (2) was synthesized from the corresponding hydroquinone with dimethyl sulfate. 4-Methoxyphenol (1) and other phenols used were commercially available (Tokyo Kasei) and were recrystallized twice from benzene. Tetraphenylporphyrin (TPP) was synthesized according to the method of Adler *et al.*[28] (5 - (4 - Hydroxyphenyl) - 10,15,20 - tris(*p* - tolyl)porphyrin (8) was prepared by the similar method of Anton and co-workers.[29] Tyrosine-linked porphyrin 11 was synthesized in a manner as described below.

CIDNP measurements

General procedures. A sample soln containing a porphyrin and a phenol (and/or quinone) was deoxygenated in the NMR sample tube by bubbling the soln with argon gas (99.99%) for 3 min immediately before irradiation. Then, the sample was placed in the NMR probe and was irradiated by the tungsten–halogen lamp or argon laser. CIDNP spectra were recorded before, during and after irradiation. The steady state photolysis time was 15 s for 100 MHz ^{1}H-CIDNP measurements. Two-pulse sequence, light (t: irradiation time)–τ–$\pi/4$, was employed with the mechanical shutter interfaced with the computer for 400 MHz ^{1}H-CIDNP.

Photosensitized dimerization of 1

A mixture of TPP (3.1 mg, 0.5 mM), 1 (124 mg, 100 mM) and Q (10.8 mg, 10 mM) dissolved in benzene (10 ml) was bubbled with argon for 15 min and was irradiated with the tungsten–halogen lamp through the glass filter (VO-59) and water for cooling. After 30 min, the solvent was evaporated and the residue was subjected to flash column chromatography with benzene as eluent, giving dimer 5 (12 mg, 49% yield based on Q) and hydroquinone. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.98 (2H, d, J = 9.2 Hz), 6.93 (1H, d, J = 8.8 Hz), 6.88 (2H, d, J = 9.2 Hz), 6.53 (1H, dd, J = 2.8 and 8.8 Hz), 5.28 (1H, br), 3.80 (3H, s), 3.67 (3H, s); *m/e* 246 (M^+100).

Photosensitized cross coupling between "phenolic porphyrin"

Coupling reaction of 5-(4-hydroxyphenyl)-10,15,20-tris(p-tolyl)porphyrin (8) *with* Q. Compound 8 (13 mg, 2 mM) and Q (10.8 mg, 10 mM) were dissolved in 10 ml of benzene–acetonitrile (50:1), and were irradiated as described in the dimerization of 1.

After 3 h irradiation, the mixture was chromatographed ($CHCl_3$–CH_3OH), yielding 9 (9 mg, 60%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.90 (2H, d, J = 5.1 Hz), 8.85 (4H, d, J = 5.1 Hz), 8.77 (2H, d, J = 5.1 Hz), 8.29 (2H, d, J = 8.1 Hz), 8.09 (6H, dd, J = 2.6 and 7.9 Hz), 7.55 (6H, dd, J = 2.6 and 7.9 Hz), 7.49 (2H, d, J = 8.55 Hz), 7.19 (2H, d, J = 8.55 Hz), 6.92 (1H, d, J = 10.3 Hz), 6.84 (1H, dd, J = 2.2 and 10.3 Hz), 6.23 (1H, d, J = 2.2 Hz), 2.70 (9H, s), −2.78 (2H, s).

Coupling reaction of tyrosine-linked porphyrin 11 *with* Q. Compound 11 was synthesized from 13[30] and L-tyrosine ethylester hydrochloride. The acid chloride of 13 was prepared by dissolving 13 (100 mg, 0.14 mmol) in a mixture of benzene (10 ml) and oxalylchloride (0.8 ml). The soln was stirred at room temp for 3 h and the solvent was then removed under reduced pressure. To remove excess oxalylchloride, acid chloride was resolved in 10 ml of benzene and the volatile fraction was removed under reduced pressure. To a CH_2Cl_2 soln of L-tyrosine ethylester hydrochloride (65 mg, 0.26 mmol) and Et_3N (0.1 ml), acid chloride dissolved was added dropwise. After stirring for 2 h at room temp, the solvent was evaporated and the residue was chromatographed with $CHCl_3$–CH_3OH. Compound 11 was obtained as purple crystals (43 mg, 32%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.88 (2H, d, J = 5.1 Hz), 8.87 (4H, s), 8.78 (2H, d, J = 5.1 Hz), 8.29 (2H, d, J = 7.7 Hz), 8.13 (2H, d, J = 8.0 Hz), 8.08 (6H, d, J = 7.3 Hz), 7.56 (2H, d, J = 8.1 Hz), 7.53 (4H, d, J = 7.7 Hz), 7.13 (2H, d, J = 8.1 Hz), 6.97 (1H, d, J = 7.7 Hz), 6.78 (2H, d, J = 8.1 Hz), 5.62 (1H, br), 5.23 (1H, dd, J = 12.8 and 9.2 Hz), 4.29 (2H, q, J = 7.3 Hz), 3.36 (1H, dd, J = 6.0 and 14.5 Hz), 3.27 (1H, dd, J = 6.0 and 14.5 Hz), 1.34 (3H, t, J = 7.3 Hz), −2.75 (2H, br).

Compound 11 (18 mg, 2 mM) was similarly photoirradiated with Q as described in the dimerization of 1. After evaporation and column chromatography, quinone-linked 12 was obtained as purple crystals (12 mg, 60%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.87 (2H, d, J = 4.7 Hz), 8.85 (4H, s), 8.76 (2H, d, J = 4.7 Hz), 8.30 (2H, d, J = 8.1 Hz), 8.13 (2H, d, J = 8.1 Hz), 8.08 (6H, d, J = 6.8 Hz), 7.54 (6H, d, J = 7.7 Hz), 7.38 (2H, d, J = 8.5 Hz), 7.10 (2H, d, J = 8.5 Hz), 6.78 (1H, d, J = 9.8 Hz), 6.69 (1H, dd, J = 2.1 and 10.3 Hz), 5.24 (1H, dd, J = 12.8 and 7.3 Hz), 4.29 (2H, q, J = 7.3 Hz), 3.48 (1H, dd, J = 5.9 and 14.5 Hz), 3.37 (1H, dd, J = 5.9 and 14.5 Hz), 1.34 (3H, t, J = 7.3 Hz), −2.80 (2H, s).

Thermal dimerization of 1 *with DBPO.*[22] A chlorobenzene soln (50 ml) of 1 (6.2 g, 50 mmol) was heated to 100° under a flow of N_2. DBPO (730 mg, 5 mmol) was added and the temp raised to 140°. The mixture was then stirred and heated at this temp for 20 h. After distillation of solvent, the residue was chromatographed on a silica gel column using $CHCl_3$–C_6H_6 as eluents, giving a colorless oil of 5 (0.46 g, 76%).

Quantum yield measurements. Quantum yields were measured in a benzene soln of a known amount of Q or 1 and 0.1 mM of TPP by using an argon laser. Flux of 514.5 nm light was estimated to be 4.30×10^{-7} Einsteins s^{-1} from the power meter value (0.1 W). A sample soln (4 ml) was bubbled with argon for 10 min and was irradiated in a quartz cell (1 cm light pathlength) with stirring for 5 min. The amounts of dimer (5) were determined by GLC using *m*-terphenyl as internal standard.

Fluorescence quenching. A benzene soln of TPP or 8 ($10^{-6} \sim 10^{-5}$ M) with a known amount of Q or 1 was excited at 515 nm and the emission spectra were recorded at 651 nm. In the range of 10–500 mM, the quenching effect due to 1 was not observed at all. From the Stern–Volmer plot, $k_q\tau$ with Q was evaluated to be 150 for both Q and 8.

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