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Laser Induced CIDNP Study of Photochemical Electron Transfer Reaction between Covalently Linked Porphyrin-Tryptophan Compounds and 1,4-Benzoquinone

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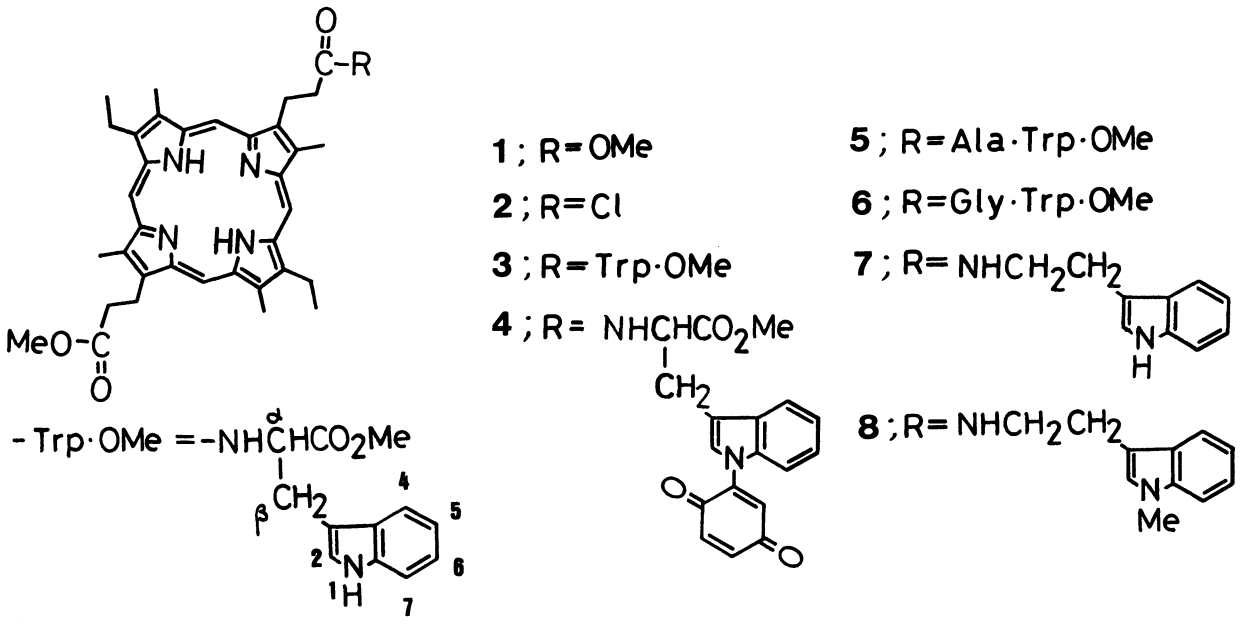
Argon ion laser excitation of covalently linked porphyrin-tryptophan compound in the presence of 1,4-benzoquinone in benzene-d_6 resulted in strong ^{1}H-NMR polarizations of tryptophan moiety. These CIDNP effects are reasonably explained by the mechanism involving the secondary electron transfer from tryptophan moiety to porphyrin cation radical as the key step.

Intensive study over the past decade or so has led to a general acceptance that the primary photochemical step in photosynthesis involves one-electron transfer from an photoexcited porphyrin chromophore to an appropriate acceptor to generate a transient radical ion pair.[1] In the natural reaction center protein complex, photogenerated radical ions are surprisingly so stabilized that the subsequent charge separation is achieved with high efficiency. It is tempting to speculate that very selective interactions such as protonation, deprotonation, and electrostatic repulsion and attraction, by amino acid side chains in the protein may play a key role in stabilizing the transient radical ion intermediates.[2] As part of a research program to elucidate the roles of amino acid residues in biological electron transfer reactions involving porphyrin compounds,[3] we have synthesized a series of covalently linked porphyrin-tryptophan compounds and investigated their photoreactions with 1,4-benzoquinone (**BQ**).

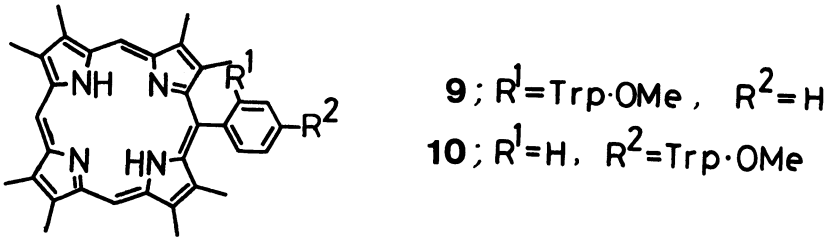
Tryptophan-linked porphyrin **3** was prepared by the reaction of the corresponding acid chloride **2** with tryptophan methyl ester in CH_2Cl_2 in 94% yield.[4] Other tryptophan- or tryptamine-linked porphyrins **5**, **6**, **7**, and **8** were prepared in the same fashion in over 90% yields. In nonpolar benzene-d_6 solution, protons due to the tryptophan moiety of **3** are shielded and appear at δ 2.46 (m, 2H, C-β H), 3.20 (s, C-2 H), 3.65 (s, N-1 H), 5.56 (d, C-7 H), 6.52 (t, C-5 H), 6.60 (t, C-6 H), and 6.80 (d, C-4 H), indicating a folded conformation of the tryptophan moiety above the porphyrin macrocycle. Hydrogen-bonding between tryptophan N-H bond and porphyrin imine nitrogen seems to be a main driving force to induce the folding of the tryptophan moiety. Thus, the aromatic tryptophan protons were shifted to lower field upon addition of hydrogen-bonding donor or acceptor such as methanol-d_4, acetonitrile-d_3, and acetone-d_6. The folding of tryptophan and tryptamine moieties was similarly observed in alanyltryptophan- and glycyltryptophan-linked porphyrin **5** and **6** and tryptamine-linked porphyrin **7**.

When a benzene-d_6 solution of **3** and **BQ** in the probe of 400 MHz ^{1}H-NMR



spectrometer was irradiated under argon atmosphere with 0.3 s pulses from an argon ion laser at 514 nm, strong CIDNP effects due to the tryptophan protons (b, C-4 H; c, C-6 H; d, C-5 H; n, C-β H) were observed along with enhanced emission of **BQ** ring proton (g) and enhanced absorption of $\mathbf{BQH_2}$ ring proton (f) (Fig. 1).[5] Polarized signals a, e, h, i, k, and l were not due to either **3**, **BQ**, nor $\mathbf{BQH_2}$ and thus were assigned to cross-coupling product of **4**. Indeed, prolonged irradiation of **3** and **BQ** in a degassed benzene solution followed by flash column chromatography led to the isolation of **4** in 8% yield. Polarized signals f, g, j, k, and l disappeared in the photoreaction with $\mathbf{BQ}$-d_4. Similar CIDNP spectra were observed in the photoreactions of **5**, **6**, and **7** with **BQ** in benzene-d_6. In marked contrast, irradiation of a benzene-d_6 solution of N-methyltryptamine linked porphyrin **8** and **BQ** did not give any CIDNP effects due to the tryptamine moiety, indicating the involvement of indole N-H bond in the indole protons polarization.

We interpret these CIDNP effects according to the photochemical electron transfer mechanism depicted in Scheme 1. The ground state absorption spectra, fluorescence emission spectra, and lifetimes of the porphyrins are not perturbed by the presence of the appended tryptophan, in spite of its folded conformation. Further, the triplet-triplet absorption spectrum of **3** was quite similar (λ_{max}= 453 nm) with that of mesoporphyrin-II dimethyl ester **1** and its decay in degassed benzene was satisfactorily fitted by a single exponential curve with a lifetime of 1.17 ms; the lifetime of triplet state of **1** was 1.12 ms. Therefore,



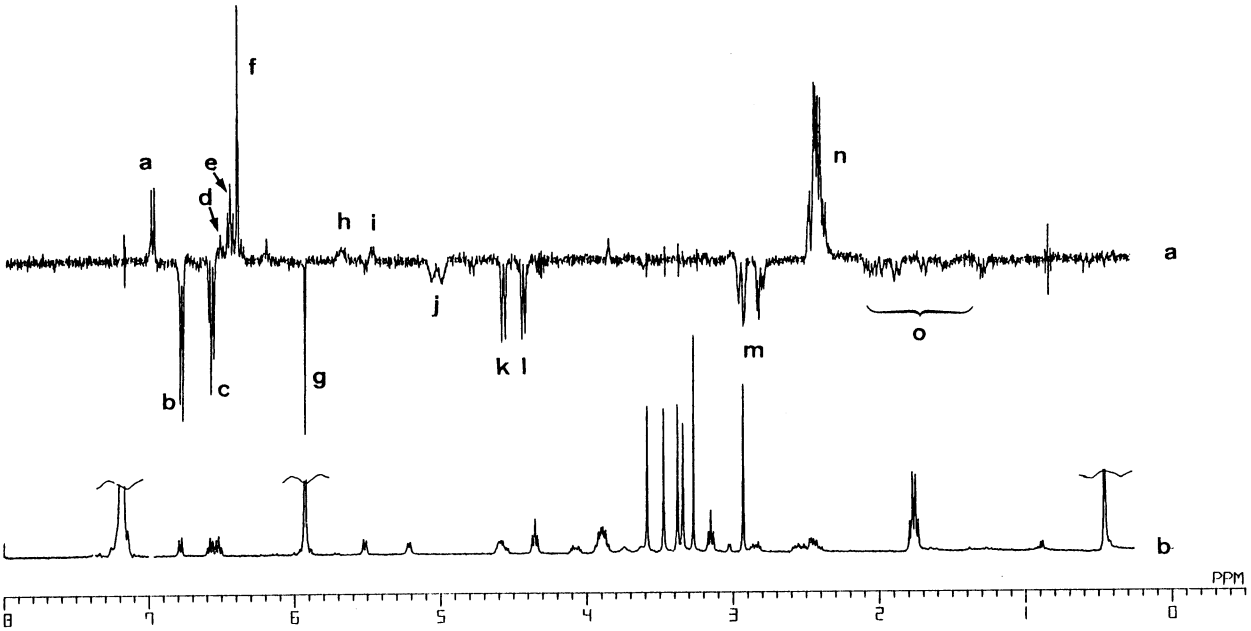
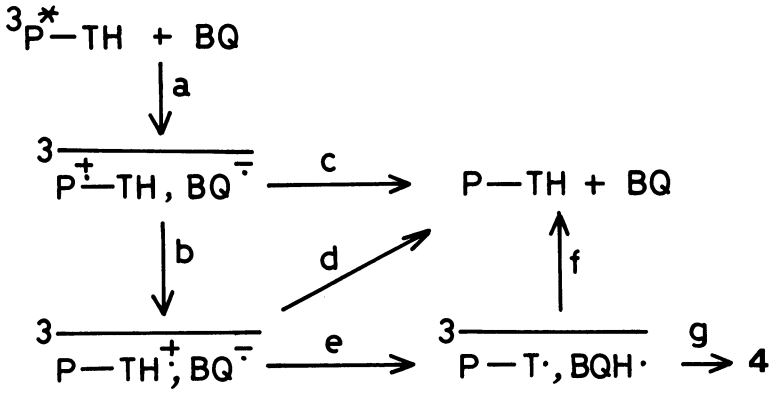


Fig. 1. a, 400 MHz photo-CIDNP difference (light-dark) spectrum of 3 (2 mM) and **BQ** (10 mM) in benzene-d_6, 32 scans; b, dark spectrum.

it may be concluded that the linked tryptophan moiety interacts with neither the singlet nor the triplet excited state of porphyrins in benzene. However, once the porphyrin cation radical is generated (path a in Scheme 1) by the photoreaction with **BQ**, an electron is transferred from the tryptophan moiety (TH) to the porphyrin cation radical (path b). Subsequent proton transfer (path e) from the tryptophan cation radical to **BQ** anion radical leads to the formation of neutral radical pair composed of indolyl radical and **BQH** , which will disproportionate to regenerate **3** and **BQ** (path f) with nuclear polarization or couple to produce the cross adduct **4** (path g).



Scheme 1. P, porphyrin; TH, tryptophan BQ, 1,4-benzoquinone.

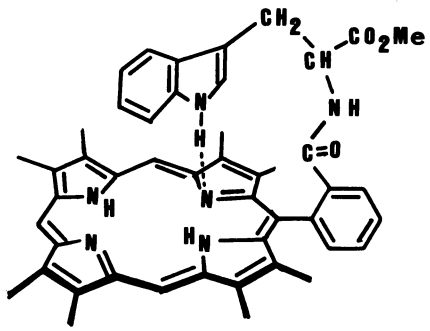


Fig. 2. Folded conformation of **9**.

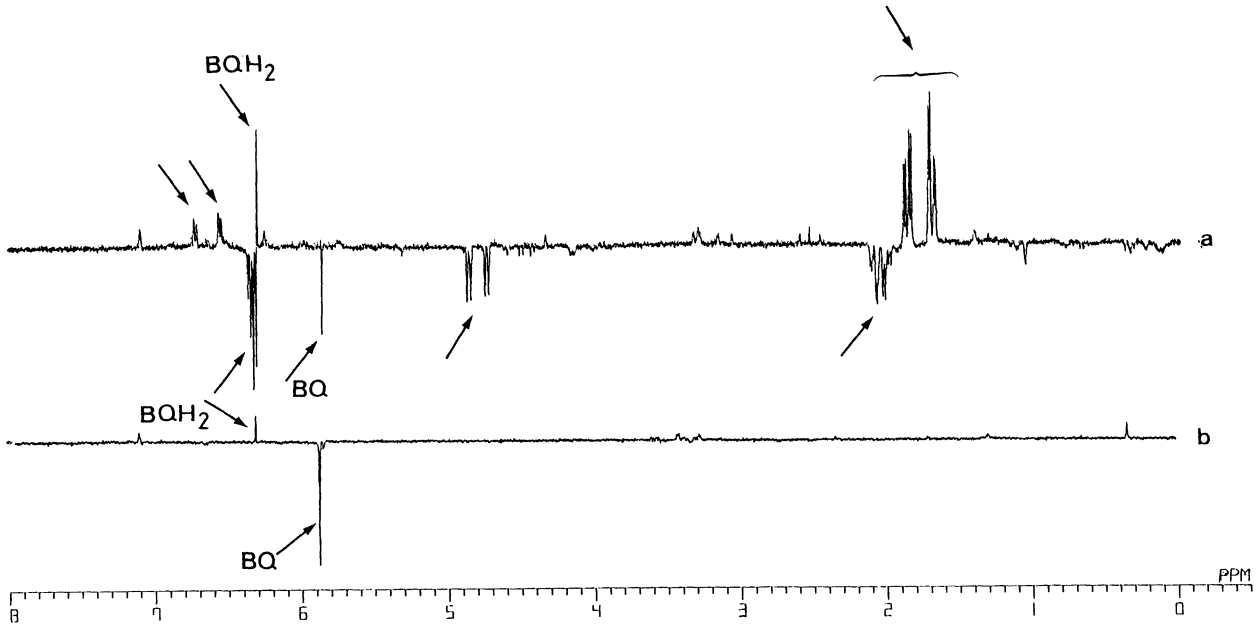


Fig. 3. a, 400 MHz photo-^{1}H-CIDNP difference spectrum of **9** (2 mM) and **BQ** (10 mM) in benzene-d_6. b, Photo-^{1}H-CIDNP difference spectrum of **10** (2 mM) and **BQ** (10 mM).

Next we examined the photoreactions of tryptophan-linked porphyrin **9** and **10** with **BQ** by CIDNP technique. The tryptophan moiety of **9** is forced to have a folded conformation, as depicted in Fig. 2. Consistent with this structure, three meso protons of **9** appear at different chemical shifts, δ 10.15, 10.11, and 10.09 ppm and the aromatic tryptophan protons are strongly shieled.[6] On the other hand, the tryptophan moiety of **10** cannot have a folded conformation.[7] Fig. 3a and 3b show the results obtained with **9** and **10**, respectively. In sharp contrast to the prominent CIDNP effects due to the tryptophan moiety of **9**, only polarized signals due to **BQ** and **BQH$_2$** were observed in the photoreaction of **10** with **BQ**. The contrasting results of **9** and **10** clearly show that the secondary electron transfer (path b) can only occur from the tryptophan moiety placed at a close proximity of the porphyrin macrocycle.

References

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2) S. G. Boxer, Biochim. Biophys. Acta, 726, 265 (1983).
3) K. Maruyama, H. Furuta, and A. Osuka, Chem. Lett., 1986, 475. A. Osuka, H. Furuta, and K. Maruyama, ibid., 1986, 479.
4) All new compounds in this paper have satisfactory spectroscopic data.
5) The 400 MHz photo-^{1}H-NMR system was described in the following paper, K. Maruyama and H. Furuta, Chem. Lett., 1986, 645.
6) 400 MHz ^{1}H-NMR data of **9** (benzene-d_6); δ 6.29 (d, C-4), 6.25 (m, C-5 and 6), 4.56 (d, C-7), 1.11 (broad, NH), 0.68 (s, C-2).
7) 400 MHz ^{1}H-NMR data of **10** (benzene-d_6); δ 10.26 (meso NH, 2H), 10.04 (meso NH, 1H), 7.62 (d, C-4), 7.3-7.4 (m, C-5, 6, and 7, 3H), 6.75 (s, NH), 6.60(s, C-2).

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