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SYNTHESIS OF QUINONE-CAPPED PORPHYRINS BY PORPHYRIN SELF-PHOTOSENSITIZED REACTION

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Quinone-capped porphyrins having formally perpendicular, coplanar, and orthogonal relative orientations were synthesized in one-pot by porphyrin self-photosensitization.

Because of considerable biochemical importance of electron-transfer reactions between porphyrins and quinones, a variety of porphyrins covalently linked to quinones have been synthesized.[1) In most cases, the synthesis of these compounds inevitably involved lengthy reaction sequences such as the preparation of protected quinone fragment, its coupling to the porphyrin macrocycle, deprotection, oxidation, and so on. One of the most recent advances in this field is the demonstration of the dependence of the rates of electron-transfer upon the distances between porphyrins and quinones. However, there is no discrete experimental evidence for how the rates of electron-transfer depend upon the relative orientation of porphyrins and quinones. For the purpose of this line, we will report here the short-cut synthesis of quinone-capped porphyrins with different relative orientations based on the porphyrin self-photosensitized reaction.[2)

The synthetic method involves just the irradiation of bis-phenol-linked porphyrin 1[3) (0.15×10^{-3} mol dm^{-3}) in the presence of 2,6-dichloro-1,4-benzoquinone 2 (0.25×10^{-3} mol dm^{-3}) in CH_2Cl_2 with light of wavelength longer than 590 nm under argon atmosphere. Separation by flash column chromatography (silica gel, CH_2Cl_2) gave quinone-capped porphyrin 3 in 34% yield. At a low conversion, mono-quinone-linked porphyrin 4 was obtained along with 3. Extended irradiation of 4 resulted in the formation of 3 without substantial side reactions. The structures of these photoproducts were fully established by their 400 MHz ^{1}H-NMR.$^{4)}$ Further, quinone-capped porphyrin 3 was quantitatively reduced to hydroquinone-capped porphyrin ($Na_2S_2O_4$, 15 min at 25 °C), which was transformed into diacetate (Ac_2O/pyridine, 2 h at 25 °C), in which two acetyl protons appeared at δ 1.40 and 1.43 ppm. The porphyrin 3 has an interesting structure in that the C=O bond axis of quinone moiety has formally a perpendicular orientation to the porphyrin macrocycle.

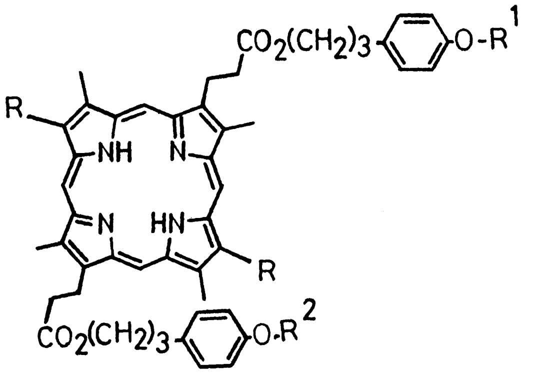
When 2,5-dichloro-1,4-benzoquinone 5 was employed instead of 2, we obtained coplanarly quinone-capped porphyrin 6 in 42% yield. Mono-quinone-linked porphyrin 7 was similarly isolated at a low conversion, and was confirmed to cyclize to 6 upon an extended irradiation. The corresponding diacetate derived from 6 showed acetyl protons at δ 1.40 ppm.

Finally, the porphyrin 1 was irradiated in the presence of 2,3-dichloro-1,4-naphthoquinone 8. Quinone-capped porphyrin 9 which has an orthogonal orientation of two chromophores was isolated in 8% yield along with bis-quinone-linked porphyrin 10 (14%).

As demonstrated above, this photochemical synthesis of quinone-capped porphyrins has versatile applicability and thus provides a direct access to three types of quinone-capped porphyrins with different relative orientations.

Although there are several examples of intramolecular photocyclization with the use of donor-acceptor intereactions by excitating either chromophore,$^{5)}$ the photo-induced capping process from 4 to 3 or from 7 to 6 constitutes a novel class of photocyclization in the sense that neither linking end of donor (phenol) or acceptor (quinone) is photoexcited but they are linked together by porphyrin self-photosensitization.

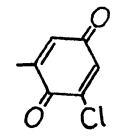
Studies on the detailed reaction mechanism and the photophysical properties of these model compounds will be presented elsewhere.



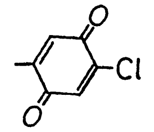
R=$C_{12}H_{25}$

1; $R^1=R^2=H$

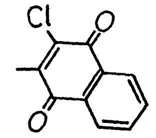
4; $R^1=H$, $R^2=$

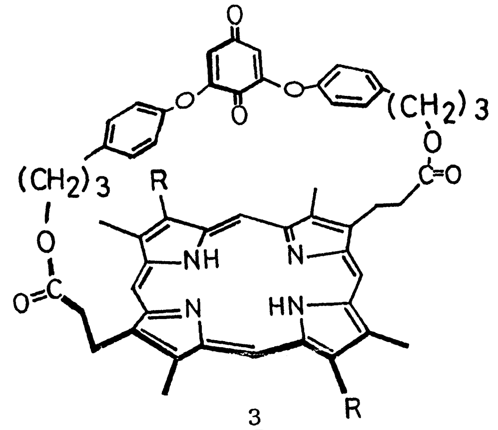


7; $R^1=H$, $R^2=$



10; $R^1=R^2=$





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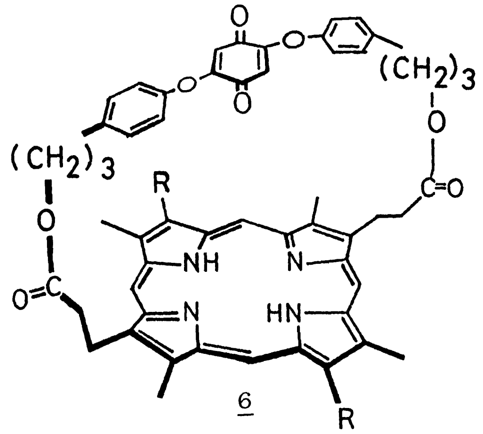

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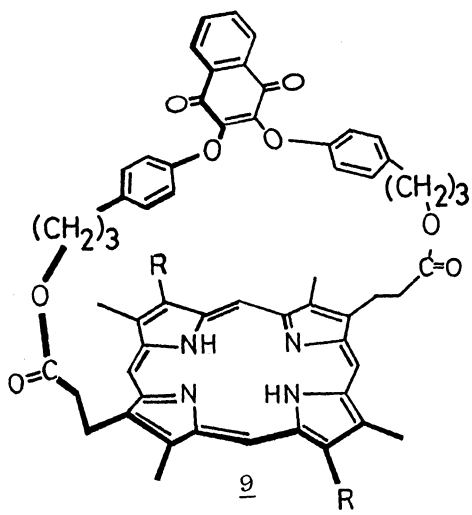

9

References

1) For a comprehensive list of recent references, See: A. D. Jordan, B. A. Leland, G. G. Geller, J. J. Hopfield, P. B. Dervan, J. Am. Chem. Soc., 106, 6090 (1984); M. R. Wasielewski and M. P. Niemczyk, ibid., 106, 5043 (1984); J. R. Bolton, T.-F. Ho, S. Liauw, A. Siemiarczuk, C. S. K. Wan, and A. C. Weedon, J. Chem. Soc., Chem. Commun., 1985, 559.

2) K. Maruyama, H. Furuta, and A. Osuka, submitted.

3) Didodecyl substituted porphyrin was prepared by the method of Chang's procedure. Condensation of the corresponding bis acid chloride with 3-(4-hydroxy)phenyl-1-propanol in CH_2Cl_2 afforded 1 in 84% yield.

4) ^{1}H-NMR Data of selective photoproducts follow: 3; 10.03(s, 2H), 9.96(s, 2H), 6.20(d, J=8.1 Hz, 4H), 5.58(d, J=8.1 Hz, 4H), 4.32(m, 2H), 4.22(m, 2H), 4.04(m, 4H), 3.90(quinone ring H, s, 2H), 3.66(s, 6H), 3.58(s, 6H), 3.23(m, 2H), 3.14(m, 2H), 2.34(m, 4H), 2.30(m, 4H), 1.76(m, 4H), 1.55(m, 4H), 1.4-1.2(m, 28H), 0.86(t, J=6.5 Hz, 6H): 4; 10.10(s, 1H), 10.07(s, 1H), 10.06(s, 1H), 10.04(s, 1H), 6.80(d. J=2.1 Hz, 1H), 6.27(d, J=8.5 Hz, 2H), 6.05(d, J=8.5 Hz, 2H), 6.03(d, J=8.2 Hz, 2H), 5.74(d, J=8.2 Hz, 2H), 5.15(d, J=2.1 Hz, 1H), 4.41(m, 4H), 4.05(m, 4H), 3.96(t, J=6.4 Hz, 4H), 3.65(s, 6H), 3.63(s, 3H), 3.61(s, 3H), 3.31(t, J=7.6 Hz, 2H), 3.24(t, J=7.6 HZ, 2H), 2.24(m, 4H), 2.07(t, J=7 Hz, 2H), 1.97(t, J=7 Hz, 2H), 1.71(m, 4H), 1.5-1.2(m, 32H), 0.85(t, J=6.5 Hz, 6H).

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