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Isoporphyrins. Near-Infrared Dyes with Noticeable Photochemical and Redox Properties

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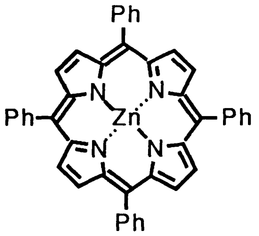
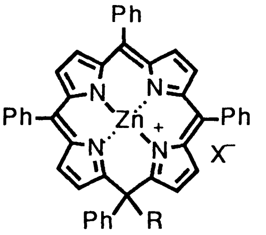
An isoporphyrin prepared by the action of dibenzoyl peroxide on 5,10,15,20-tetraphenylporphinatozinc(II) (ZnTPP) shows absorption bands in the near-infrared region, is photolyzed to afford ZnTPP, and is facilely reduced by amines to ZnTPP.

With recent development of semiconductor lasers emitting near-infrared radiation, much effort has been done to search near-infrared dyes. Porphyrins exhibit strong absorptions around 400 nm (Soret band) and at 500–600 nm (Q band); however, partial saturation of their conjugated ring system in the pyrrole 3,4-bond as seen in chlorins and chlorophylls extends the absorption to longer wavelengths.$^{1)}$ Oxidation of the porphyrins through electron removal has actively been investigated from biological interest.$^{2)}$ However, little attention has been paid to isoporphyrins, the porphyrin cations with a saturated meso-carbon atom, except the standpoint of biochemical interest in oxidation of porphyrins,$^{3)}$ though first described in 1970 for (5-methoxy-5,10,15,20-tetraphenyl-5*H*-porphinato)zinc(II) perchlorate [zinc(II) tetraphenylmethoxyisoporphyrin perchlorate, **1**].$^{4)}$



ZnTPP



1 : R = OCH_3, X = ClO_4
2 : R = OCOPh, X = OCOPh

During the course of an investigation on organic peroxides, we have found that (5-benzoyloxy-5,10,15,20-tetraphenyl-5*H*-porphinato)zinc(II) benzoate (zinc tetraphenylbenzoyloxyisoporphyrin benzoate, **2**), obtained by the action of dibenzoyl peroxide (BPO) on 5,10,15,20-tetraphenylporphinatozinc(II) (ZnTPP),$^{5)}$ is photolyzed and exhibits remarkable redox properties.

In a typical run, a solution of BPO (0.39 g, 1.6 mmol) in dichloromethane (0.1 dm^3) was added to a solution of ZnTPP (1.0 g, 1.5 mmol) in the same solvent (0.1 dm^3), and the mixture was kept at room temperature for 12 h. The solution gradually turned from red purple due to ZnTPP to green due to the product. In the absorption spectrum, the bands of ZnTPP were gradually decreased accompanying a concurrent growth of the characteristic absorption of **2** with isosbestic points (Fig. 1). Evaporation of the solvent and subsequent precipitation from chloroform-hexane afforded **2** (0.7 g, 0.76 mmol) as a pale green solid.

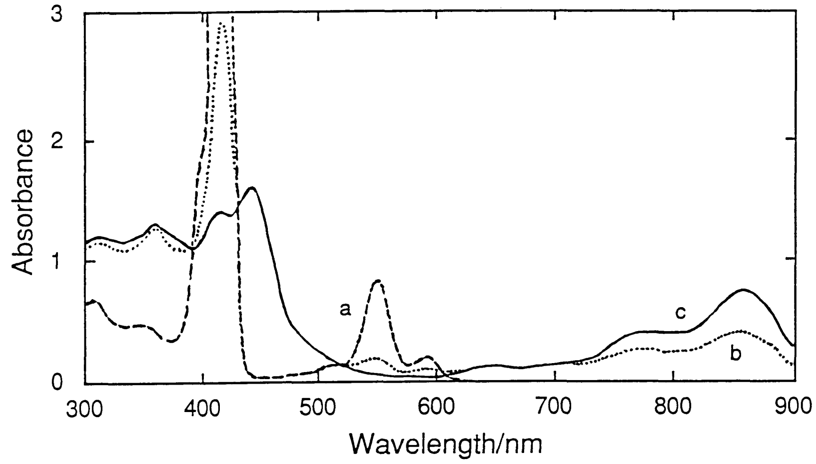
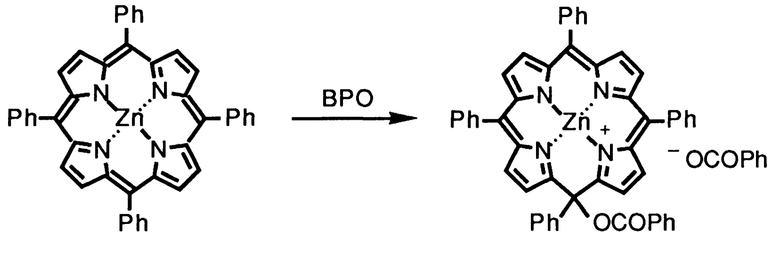


Fig. 1. Spectral change during reaction of BPO with ZnTPP in CH_2Cl_2. a) ZnTPP, 3×10^{-5} M (----); b) immediately after addition of a solution of BPO in CH_2Cl_2, [ZnTPP] = 3×10^{-5} M, [BPO] = 8×10^{-3} M (····); c) after 24 h (—).



ZnTPP

2

It is noticeable that **2** exhibits the characteristic absorptions in 700–900 and 300–500 nm regions (Fig. 1) [λ_{max}/nm (ε/10 mol^{-1} dm^2): 417 (32000), 444 (33000), 775 (8900), and 857 (15100)], which make **2** green like chlorophylls. These absorptions and ^1H NMR (Fig. 2) [δ=6.2–6.8 (m, protons of the pyrrole rings), 7.3–7.9 (m, protons of the phenyl groups), 8.3 (m, protons of the benzoyl group) for **2** are similar to those of **1**.[1]

Isoporphyrin **2** is, however, not very sensitive to near-infrared and long-wavelength visible light, and therefore, **2** can be handled under room light. However, irradiation of **2** (0.01 mol^{-1} dm^3) in dichloromethane under argon with unfiltered light (longer than 300 nm) from a 500 W xenon lamp led to its decomposition to ZnTPP (Fig. 3).[6]

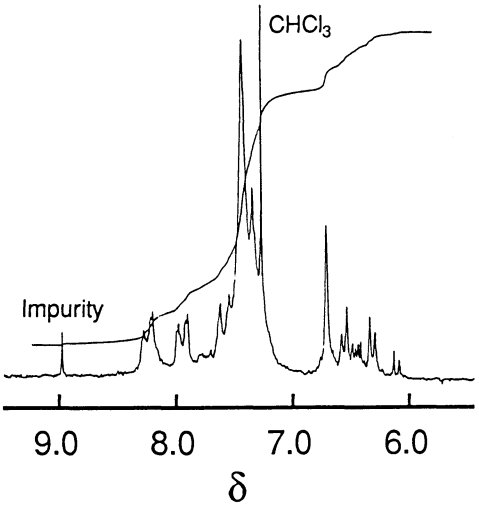


Fig. 2. 100 MHz ^1H NMR spectrum of isoporphyrin **2** in $CDCl_3$.

The irradiation in dichloromethane or benzene showed an ESR signal reasonably assigned to the radical cation of ZnTPP ($ZnTPP^{+\cdot}$, g=2.0027). This signal was decreased by interruption of the irradiation and recovered by reillumination (Fig. 4).

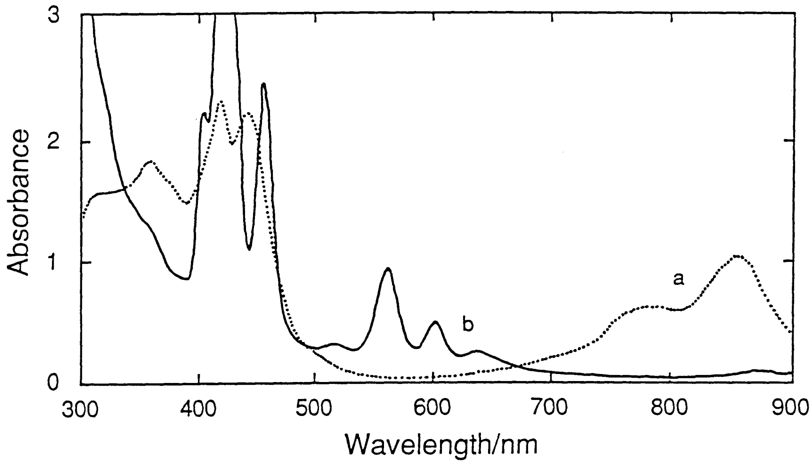
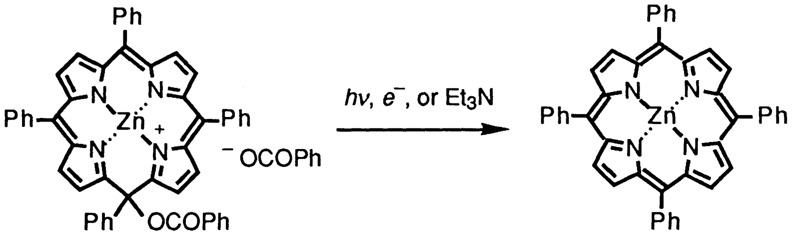


Fig. 3. Spectral change on irradiation of isoporphyrin **2** with UV light in CH_2Cl_2. a) Before irradiation (····); b) after irradiation for 12 h with a xenon lamp (>300 nm)(—).



2

A very remarkable feature of the isoporphyrin is its capability to accept electrons. This arises probably from the electronic structure of the nucleus corresponding to the two-electron oxidized form of ZnTPP, $ZnTPP^{2+}$, bonded with an benzoate anion at the meso-carbon. In cyclic voltammetry, **2** showed an irreversible cathodic current peak at −0.4 V vs. SCE in dichloromethane in the presence of tetrabutylammonium perchlorate (0.1 mol dm^{-3}). Cathodic reduction of **2** at −0.5 V under nitrogen afforded ZnTPP in a nearly quantitative yield.

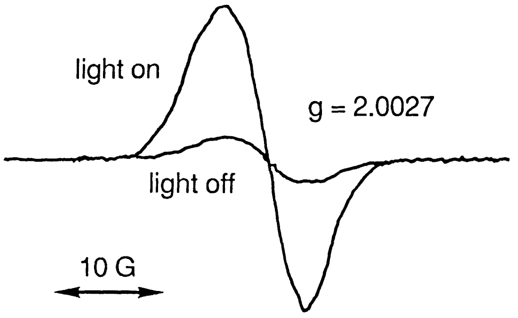


Fig. 4. ESR spectra during and after irradiation with UV light.

Likewise, chemical reductions of **2** proceeded very facilely. Amines like diazabicyclo[2.2.2]octane (DABCO) and triethylamine reduced **2** very readily to ZnTPP in a nearly quantitative yield in dichloromethane at room temperature in the dark. The reaction proceeded with isosbestic points in the absorption spectrum (Fig. 5).

Finally, it is to be noted that the isoporphyrins, which have not been well investigated, could not only be a new class of near-infrared dyes of moderate photosensitivity but also exhibit unique redox behavior among porphyrin derivatives.

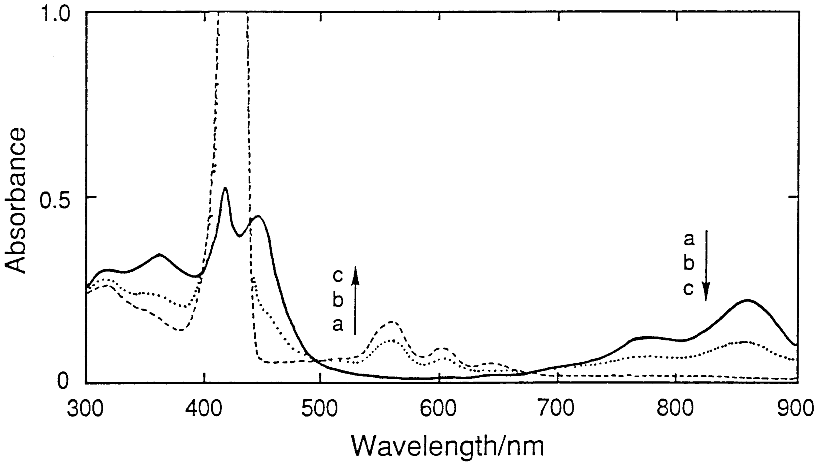


Fig. 5. Spectral change during reaction of isoporphyrin **2** with triethylamine in CH_2Cl_2. a) Isoporphyrin **2**, 5×10^{-5} M (—); b) immediately after addition of Et_3N into a CH_2Cl_2 solution of isoporphyrin **2**, [**2**] = 5×10^{-5} M and [Et_3N] = 5 M (---); c) after 50 min (····).

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References

1) G. D. Dorough and F. M. Huennekens, *J. Am. Chem. Soc.*, **74**, 3974 (1952).
2) H. Fisher and K. Herrle, *Ann. Chem.*, **527**, 138 (1937); H. J. Shine, A. G. Padilla, and S.-M. Wu, *J. Org. Chem.*, **44**, 4069 (1979); W. A. Lee and T. C. Bruice, *Inorg. Chem.*, **25**, 131 (1986); J. A. Guzinski and R. H. Felton, *J. Chem. Soc., Chem. Commun.*, **1973**, 715; A. Gold, W. Ivey, G. E. Toney, and R. Sangaiah, *Inorg. Chem.*, **23**, 2932 (1983); M. Kohno, *Bull. Chem. Soc. Jpn.*, **61**, 1509 (1988).
3) D. Dolphin and R. H. Felton, *Acc. Chem. Res.*, **7**, 26 (1974).
4) D. Dolphin, R. H. Felton, D. C. Borg, and J. Fajer, *J. Am. Chem. Soc.*, **92**, 743 (1970).
5) D. Dolphin, Z. Muljiani, K. Rousseau, D. C. Borg, J. Fajer, and R. H. Felton, *Ann. N. Y. Acad. Sci.*, **206**, 177 (1973). They very briefly mentioned about this reaction relating to biological oxidation of porphyrins without describing any procedure of the reaction and properties of the resulting compounds.
6) Contamination with a small amount of ZnTPP in **2** accelerated the photolysis.

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