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Benzene or Naphthalene Ring-fused Mono-Substituted Type Tetraazaoctaphenylporphyrin Zinc Complexes

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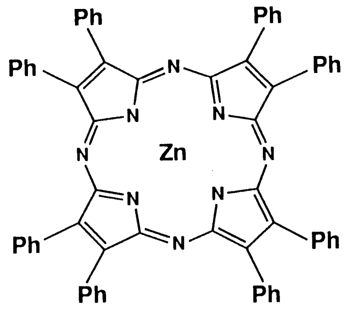
A zinc tetraazaoctaphenylporphyrin (ZnTAP) and benzene or naphthalene ring-fused unsymmetrcal ZnTAPs are synthesized and characterized by UV-visible absorption, emission, excitation, and magnetic circular dichroism (MCD) spectroscopy together with cyclic and differential pulse voltammetry. With lowering of the molecular symmetry, both the energy differences, between the Soret and Q bands and the splitting of the $Q_{0\text{-}0}$ band increase while the quantum yield (ϕ_F) of the fluorescence decreases.

Tetraazaporphyrins (TAPs) are structural intermediates between porphyrins and phthalocyanines (Pcs) in that they possess four *meso*-nitrogens but lack four fused benzene rings. In order to examine the spectroscopic changes due to lowering of the molecular symmetry of porphyrins, TAPs are convenient candidates for the following reasons. i) The effect of substituent groups (ESG) appears more prominently in the Q band than the Soret band, and the Q band of TAPs is much more intense than that of common porphyrins.1) ii) The ESG is larger for smaller porphyrins rather than larger Pcs.2) iii) Preparation of mono-substituted-type TAPs is simple, as shown below. In spite of these attractive features, however, no systematical preparation of such TAPs has yet been carried out. In this communication, we report some intriguing spectroscopic and electrochemical properties of ZnTAPs with lower symmetry. Although, the ESG for general alkyl groups has been reported in several publications,1,2) that caused by one fused ring of different size to TAPs or common porphyrins has not been reported to date.

Compound **1** was obtained by fusing diphenylmaleonitrile in the presence of zinc salts at 250-260 °C,3) while **2** and **3** were prepared similarly by mixed condensation between diphenylmaleonitrile3) and 3,6-diphenylphthalonitrile4) or 1,4-diphenyl-2,3-dicyanonaphthalene.5) After the reaction was completed, **2** and **3** were purified through alumina column and gel-permeation chromatography using Bio-beads SX-8 (Bio-rad). The yields of **2** and **3** were *ca*. 6-9% depending on the trial and they showed the desired parent ion peaks at 1036 (M^+) (*m*-nitrobenzyl-



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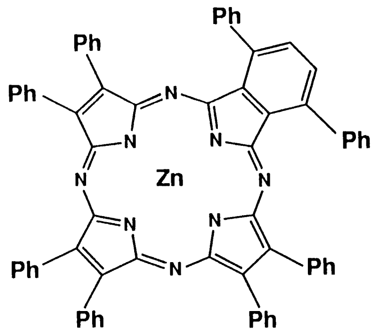

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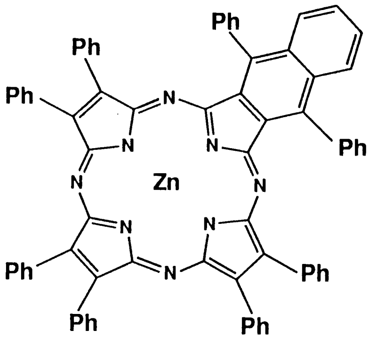

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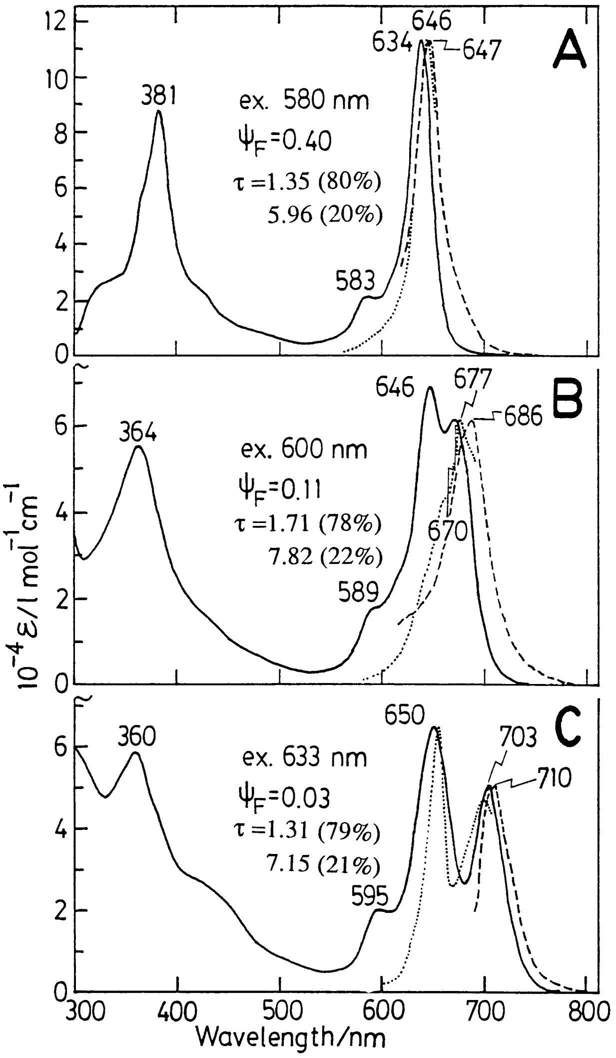

Fig. 1. Absorption (solid lines), emission (broken lines), and excitation spectra (dotted lines) of (A) **1** in pyridine-*o*-dichlorobenzene (DCB) (2:1 v/v), (B) **2** in DCB, and (C) **3** in DCB. Excitation wavelengths and ϕ_F and τ values (in ns) are also shown.

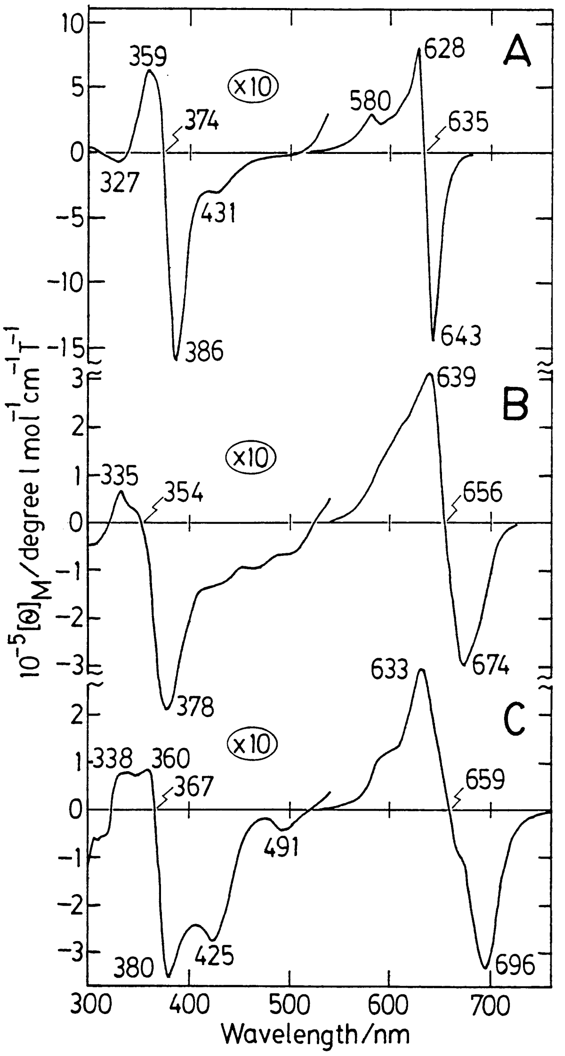

Fig. 2. MCD spectra of (A) **1** in pyridine-DCB (2:1 v/v), (B) **2** in DCB, and (C) **3** in DCB. Magnetic field/T = 1.09.

alcohol matrix; $C_{68}H_{42}N_8Zn$ requires 1035.7430) and 1086 (M^+) ($C_{72}H_{44}N_8Zn$ requires 1085.7586) in the mass spectra using the FAB technique.

Figure 1 shows the absorption, emission, and excitation spectra of **1**-**3**. In the order of **1** to **3**, *i.e.* with enlargement of the π-system and departure of the symmetry from D_{4h}, the Soret band shifts to shorter wavelength while the Q band moves to longer wavelength and the splitting of the Q_{0-0} band increases. Thus, the attachment of one fused benzene unit shifts the longest-wavelength Q band by *ca.* 700-850 cm^{-1} and increases the Q_{0-0} splitting by *ca.* 550-580 cm^{-1}.6) Interestingly, the splitting of the Soret band seems small, if any, and of the two split Q_{0-0} bands in **2** and **3**, the intensity of the lower energy bands is weaker. The absorption coefficients decrease with lowering of the symmetry. Thus, those of **2** and **3** are much smaller than those of **1**. However the actual absorption intensity (oscillator strength, **f**) in the Q band does not differ greatly among **1**-**3**. The relative ratio of **f** in the 530-800 nm is 1:1.05 :1.17 for **1**:**2**:**3**.

Fluorescence and excitation spectra show a mirror-image relationship with very small Stokes shift, but emission occurs only from the lowest energy Q band, as seen in the figure. More importantly, the quantum yield (ϕ_F) of the emission decreases with lowering of the molecular symmetry, *i.e.* in the order **1** to **3** (see Fig. 1 for values). This means that the singlet excited state is less stable the lower the symmetry of the porphyrins. The lifetimes (τ) were smaller than those of general porphyrins and Pcs. Although the reason for the decrement of ϕ_F and τ is not clear at present, such phenomena have not been shown previously in porphyrin or Pc chemistry. Thus, these data suggest that the molecular symmetry of porphyrins has to be intentionally heightened in order to obtain a higher quantum yield.

Figure 2 shows MCD spectra of **1**-**3**. The spectrum of **1** is that of typical metalloporphyrins and Pcs, in that it reveals two intense Faraday *A*-terms in both the Q and Soret regions. However, judging from the spectroscopic pattern, the true Soret band may be at *ca.* 410-440 nm, as suggested for MgTAP7) and proved for ZnPc and some MtPcs.8) Spectra of **2** and **3** have, at least theoretically, a contribution of Faraday *B*-terms. Because of the lowering of the symmetry, a few bands are detected between the Soret and Q bands more clearly than in the absorption spectroscopy.

Figure 3 shows the cyclic and differential pulse voltammetric curves of **2** and **3** in DCB (those of **1** could not be recorded because of its low solubility). Four redox couples are seen at 1.23, 0.72, -1.06, and -1.39 V for **2** and 1.20, 0.69, -1.05, and -1.38 V for **3**, respectively. Thus, the 1st and 2nd reduction potentials differ only slightly between **2** and **3**, but the oxidation potentials shift cathodically by about 30 mV as a result of the enlargement of π-system by one benzene unit. This means that unsymmetrical expansion of π-systems heightens the energy level of the HOMO orbital rather than lowering the level of the LUMO orbital. The potential differences (1.78 V for **2** and 1.74 V for **3**) between the 1st oxidation and reduction potentials are much smaller (roughly 500 mV) than those in general porphyrins (roughly 2.25 V).[9]

In summary, we have found that the fusion of one benzene or naphthalene ring to a MtTAP skeleton produces the following changes. i) Splitting of the $Q_{0\text{-}0}$ band. ii) Increase of the energy difference between the Soret and Q band. iii) Reduction of the quantum yields in the fluorescence emission. iv) Elevation of the energy level of the HOMO orbital rather than stabilization of LUMO orbital.

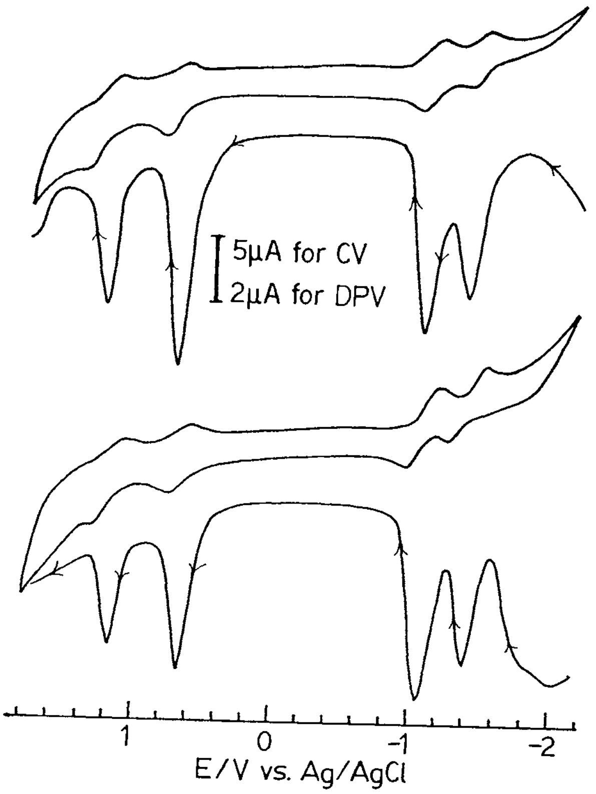

Fig. 3. Cyclic (CV) and differential-pulse (DPV) voltammograms of **2** (top) and **3** (bottom) in DCB containing 0.3 M of tetrabutylammonium perchlorate. Sweep rates /mV s^{-1} = 50 for CV and 5 for DPV. [**2**]/M = [**3**]/M = 10^{-3}.

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6) In the case of aromatic ring-fused H_2Pc, the Soret band shifts to longer wavelength only slightly with the increase of the size of attached aromatic ring. The red-shift of the Q band is *ca.* 420-530 cm^{-1} per benzene unit (N. Kobayashi, R. Kondo, S. i. Nakajima, and T. Osa, *J. Am. Chem. Soc.*, **112**, 9640 (1990)).
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8) Some Pcs are known to show Faraday *A*-terms in the longer wavelength region of the hitherto accepted Soret band. See for example, M. Stillman and T. Nyokong, "Phthalocyanines-Properties and Applications," ed by C. C. Leznoff and A. B. P. Lever, VCH, New York, Weinheim, Cambridge, Chap. 3 (1989).

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