

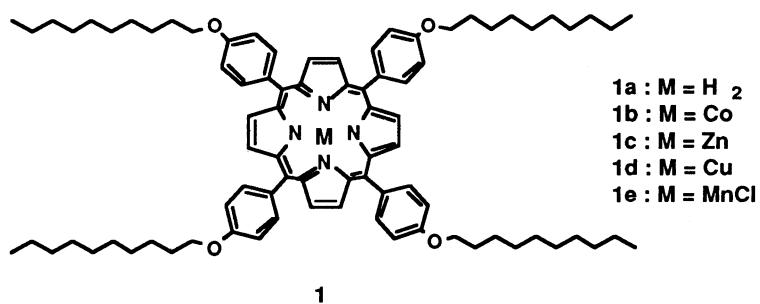
Optical Properties of Tetrakis(p-n-decyloxyphenyl)porphyrin and the Corresponding
Metal Complexes by Casting Method

Shin-ichi KUGIMIYA* and Motoko TAKEMURA

College of General Education, University of Tokushima, Josanjima, Tokushima 770

Optical properties of tetrakis(p-n-decyloxyphenyl)porphyrin and its metal complexes (Co^{II}, Zn^{II}, Cu^{II}, and Mn^{III}Cl) have been investigated in the casting film (stacking state). Type of stacking of the titled porphyrins in the film has been controlled by changing the number of the porphyrin molecules used for the film preparation.

Heme-heme interactions in organized assembly have been studied extensively in last two decades.¹⁾ For understanding the mechanisms of energy or electron transfer in photosynthetic systems, investigations of photophysical and photochemical properties of hemes and chlorophylls in both self-organized assemblies^{2,3)} (such as monolayer, bilayer, or liquid crystal^{4,5)} and covalently linked multiheme systems^{6,7)} are important. Recently, we have reported liquid crystalline properties of the titled porphyrins.⁸⁾ Here, we report that types of stacking of the titled porphyrin and the corresponding metal complexes in the casting film (stacking state) depend upon changing the concentration of the porphyrin solution during the preparation of the film.



Porphyrins used here were prepared and purified by the procedure described in elsewhere. Casting films of the porphyrins on a cover glass (24 x 32 mm) were obtained by a procedure described as follows; in a typical condition, 1-50 μ L of CH_2Cl_2 solution ([porphyrin] = 1×10^{-4} M) of the porphyrins was added into 300 μ L of petroleum ether on the glass and then the solvent was evaporated in the air at

room temperature. It took about 1 h for drying. Absorption spectra of the porphyrin films thus obtained were recorded from 350 to 750 nm at room temperature. The spectral data of **1** films are given in Table 1 and Fig. 1.

Table 1. Absorption maxima of Soret band of the titled porphyrins^{a)}

| Porphyrin (M =) | 1a (H ₂) | 1b (Co) | 1c (Zn) | 1d (Cu) | 1e (MnCl) |
|---|-----------------------------|----------------|----------------|----------------|------------------------|
| λ_{max} /nm in CH ₂ Cl ₂ | 421 [24] ^{b)} | 425 [21] | 428 [13] | 432 [15] | 487 ^{c)} [18] |
| λ_{max} /nm in film ^{d)} | 445 [20] | 468 [36] | 456 [10] | 448 [28] | 514 ^{c)} [26] |

a) 30 μ l of the porphyrin solutions were used for the preparation of the film. b) Halfwidth (nm) of Soret band in bracket. c) The largest peak of Soret bands. d) The largest peak of two split Soret bands.

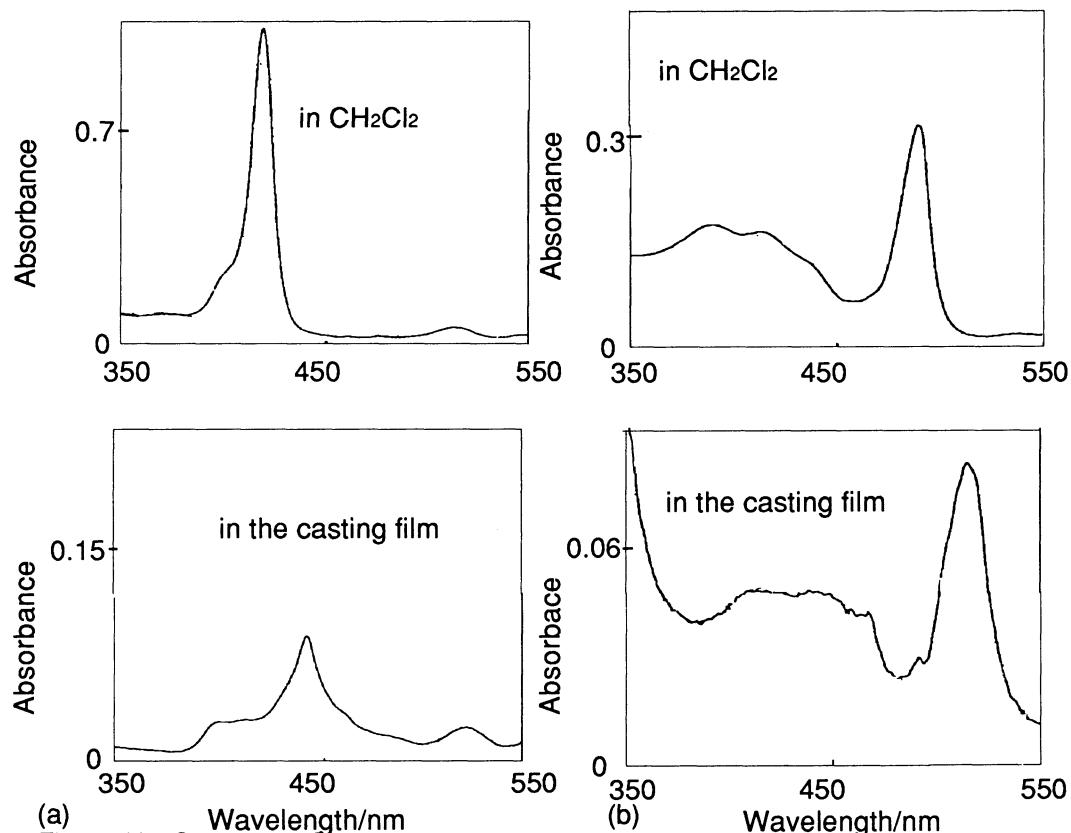


Fig. 1. UV Spectra of Soret band region of the casting films, a) **1a**. b) **1e**. The conditions were written in Table 1. UV Spectra of the casting films of **1b**, **1c**, and **1d** are not shown.

The Soret band in the absorption spectra of **1a** film (prepared without any host assembly) are split into red-shifted (445 nm, large) and blue-shifted (400 nm, small) relative to that (421 nm) of **1a** in the CH₂Cl₂ solution.^{2,4)} The Soret band of the corresponding metal complexes (including redox active manganese (III) chloride complex **1e**: see Fig. 1b) are similar to that of **1a** under the conditions described in Table 1. Half-width of the Soret band of **1** film were close to that of **1** in CH₂Cl₂ solution (see Table 1) using petroleum ether as a solvent. Half-widths of the Soret band is a good indicator of the

degree of order of the stacking of the porphyrin chromophores.⁴⁾ The porphyrin films (half-width = 10 nm, for **1c**) described here are well ordered as comparison with octaalkylporphyrin derivative film (halfwidth = 31 nm, for alkyl: n-octoxyethyl and metal: zinc) reported by Bard, et al.⁴⁾ When we used other solvents, such as benzene, THF, EtOH, CHCl₃, or pyridine etc., Soret band of the porphyrin film is broadened (the half-width of **1c** film prepared from benzene solution is 56 nm, for an example). This indicates that solubility of alkyl chains of **1** in the solvent determines the degree of alignment of **1** between the neighboring other chromophores in the casting film.

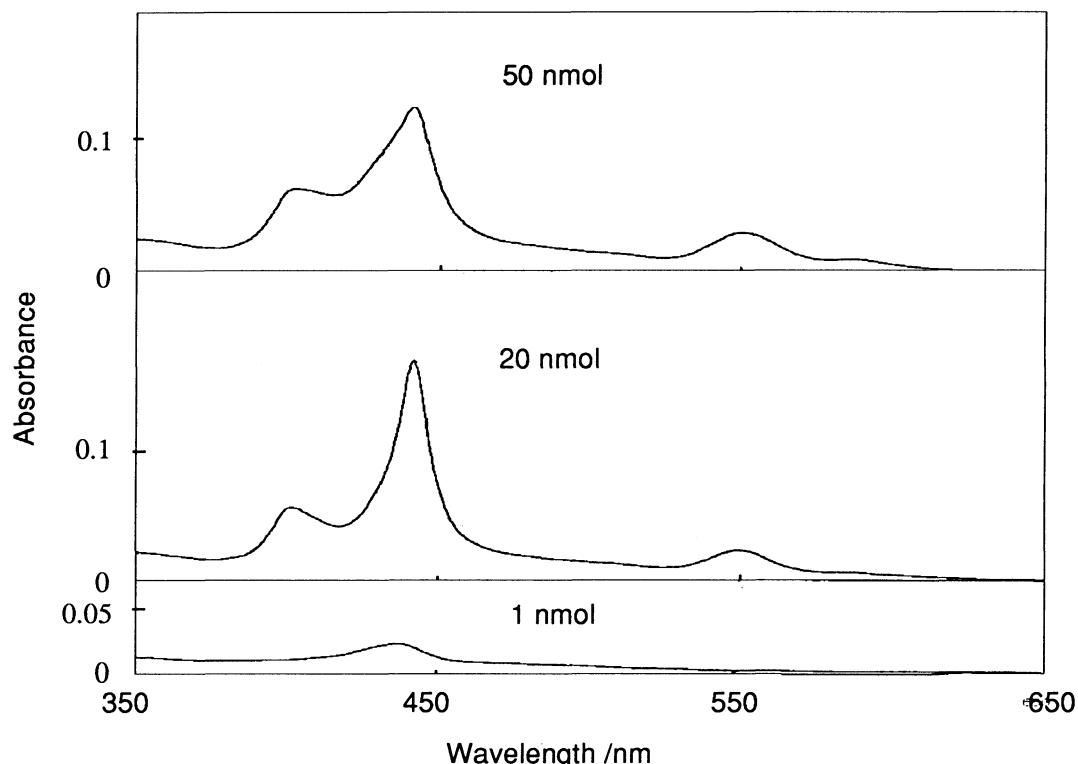


Fig. 2. Spectral features depends on the amount of the porphyrin used for the film preparation. The films were prepared by the method described in the text.

When we changed the amount of the porphyrin used during the film preparation, the characteristic absorption features of the porphyrin in the casting film were changed (see Fig. 2). In Fig. 3, the relative hight of the split Soret bands (the hight of Q(1,0) band was used as a standard (1.00)) are shown as a function of the amount of the porphyrin used for the film preparation. The hight of the red-shifted Soret band, a major peak, is narrower and larger, when the amount of **1c** used is smaller (see Fig. 3 (b)). The blue-shifted Soret band was observed when we used more than 20 μ L of **1c** solution. But the blue-shifted Soret band was disappeared when we used 1 μ L of **1c** solution (see Fig. 3 (a)). These results imply that the orientation of porphyrin chromophore in **1c** film may change depending on the amount of the porphyrin used for the film preparation.

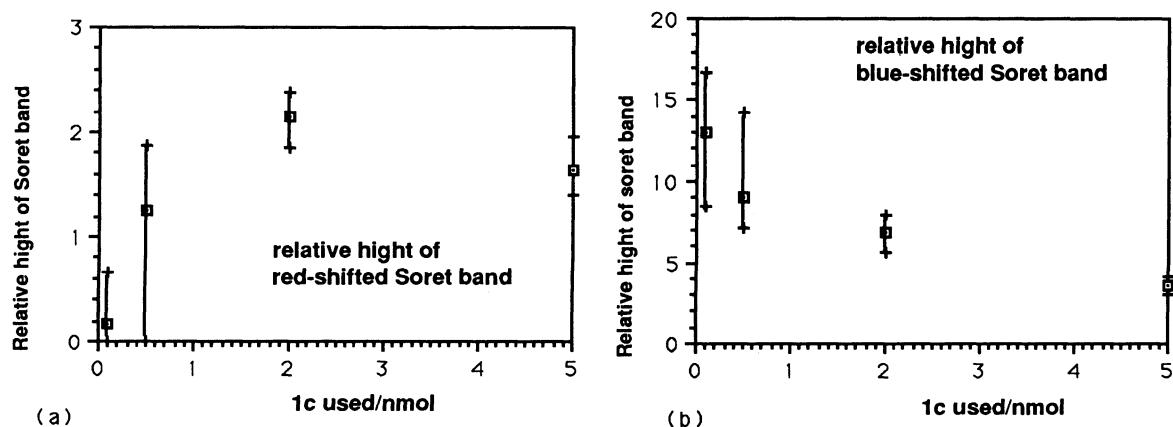


Fig. 3. Photophysical properties of **1c** film depend on amount of **1c** used. Relative height of peaks were calculated using the height of Q (0,1) band as a standard (1.00). The Soret band of **1b** film was split into two peaks, a blue-shifted (at 400 nm: (a)) and a red-shifted (at 456 nm: (b)) peaks.

In summary, stacking types of the titled porphyrin, a liquid crystalline porphyrin, in the casting film has been changed by the porphyrin molecule used for the film preparation.

References

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(Received May 1, 1990)