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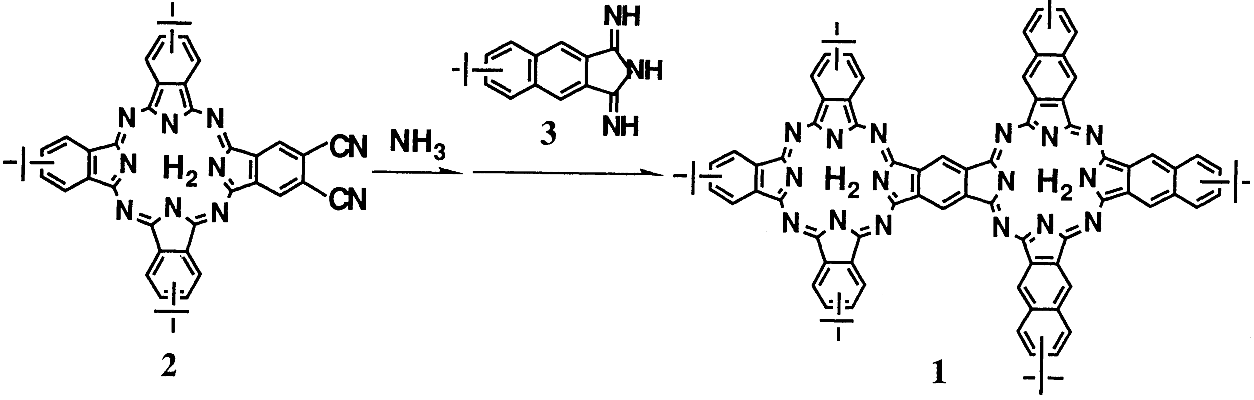
A Planar Phthalocyaninylnaphthalocyanine as a Broad Near-Infrared Absorber

Nagao KOBAYASHI,* Yasuhiro HIGASHI, and Tetsuo OSA*
Pharmaceutical Institute, Tohoku University, 980-77

A planar heterodinuclear phthalocyaninylnaphthalocyanine (**1**) in which a phthalocyanine (Pc) and naphthalocyanine (Nc) share a common benzene ring has been synthesized for the first time and its electronic absorption, magnetic circular dichroism (MCD), and fluorescence data are reported. **1** and its deprotonated species show broad Q bands in the near-IR region.

Macrocycles having intense absorptions in the near-IR region are required in many fields using lasers, such as optical discs and photodynamic cancer therapy.1) Pcs and Ncs are promising candidates, however their absorption bands are often too sharp and do not coincide well with the wavelengths of laser light. In this respect, planar phthalocyaninyl-naphthalocyanines (PcNc) are attractive, since the Q_{0-0} bands of most Pcs and Ncs generally lie at *ca.* 660-730 and 750-830 nm, respectively.2) In this communication, we report the synthesis and some spectroscopic properties of the first planar PcNc, *i.e.* **1**. Although, there have been some reports on planar homodimers,3) planar heterodimers consisting of a similar type of mononuclear unit but with different sizes have not been reported to date.



$2^2,7^2,12^2$-Tri(*tert*-butyl)benzo[*b,g,l*]-dicyanobenzo[*q*]-5,10,15,20-tetraazaporphine (**2**) (390 mg, 0.534 mmol), obtained from 4-*tert*-butyldiiminoisoindoline and 4,5-dicyanodi-iminoisoindoline by mixed condensation,4) was treated with ammonia gas in the presence of sodium methoxide in dry dioxane-methanol (4:1 v/v, 50 ml).5) The resultant diiminoisoindoline derivative and 6-*tert*-butyl-1,3-diiminobenz[*f*]isoindoline (**3**) (1600 mg, 6.32 mmol) were mixed well and heated to 230-250 °C under a nitrogen atomospere. The crude product was imposed on a basic alumina column using methylene chloride (CH_2Cl_2)/hexane (1:1 v/v) as the eluting solvent followed by gradually increasing the CH_2Cl_2 content to 100%, and subsequently the green fraction was further purified by gel-permeation columns of Bio-beads SX2 (Bio-rad), eluting with tetrahydrofuran (THF) or CH_2Cl_2 (repeated several times). The front running heterodinuclear fraction was collected and recrystallized from CH_2Cl_2-hexane to give **1** as a greenish powder (92 mg, 12%), which gave the desired parent ion peak at *m*/*z* = 1432 (M^+-4H(pyrrole protons)) in the mass spectrum using FAB technique. Elemental analysis and ^1H NMR data were satisfactory.6)

Figure 1 shows the electronic absorption and MCD spectra of **1** and its deprotonated species. The most characteristic feature is the broadness of the Q band, which stretches from *ca.* 500 to 1100 nm. This is not a simple superimposition of the Q band of mononuclear *tert*-butylated Pc and Nc, but rather appears to be caused by interacting dipoles in the Pc and Nc moieties.3b,c) In contrast, the Soret band region does not differ greatly from that of general Pcs and Ncs.7) When the central four pyrrole protons are deprotonated8) by adding Bu_4NOH, two strong peaks appear in the Q band. Although their positions are close to the Q_{0-0} bands of Pcs and Ncs, the MCD spectrum (especially the Faraday *B*-term associated with the absorption peak at 820 nm) is typical of that of a compound having no degenerate state, indicating again that the spectrum is not a simple addition of those of a Pc and Nc with D_{4h} symmetry.

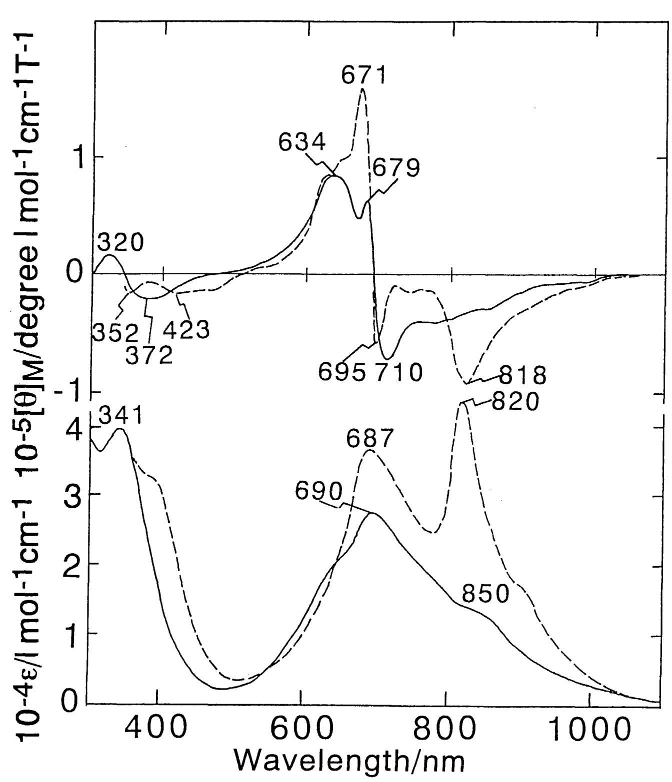


Fig. 1. Electronic absorption (bottom) and MCD (top) spectra of **1** (solid lines) and de-protonated **1** (broken lines) in THF.

The fluorescence spectrum of **1** was record-

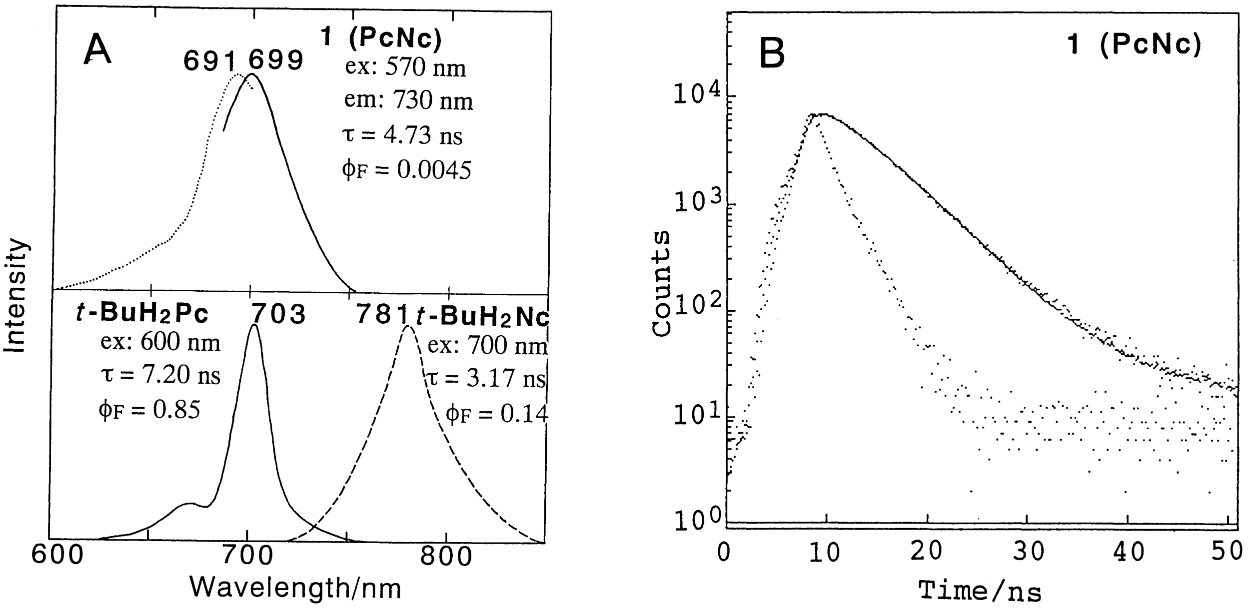


Fig. 2. (A) Fluorescence emission (and excitation) spectra of **1** (top) and tetra-*tert*-butylated metal-free Pc and Nc (bottom) in THF. Excitation wavelengths, a wavelength used to record the excitation spectrum, and ϕ_F and τ values are shown. There is no intensity relationship between the emission of the Pc and Nc. ϕ_F Values were determined by the use of tetra-*tert*-butylated tetrabenzoporphyrin in chloroform (ϕ_F = 0.57)3c) and 1,3,3,1',3',-3'-hexamethylindotricarbocyanine in dimethylsulfoxide (ϕ_F = 0.28) 11) as standards. (B) Fluorescence decay of **1** in degassed THF and its typical monoexponential fit (τ = 4.73 ns).

ed by exciting at 570 nm (Fig. 2). Values of 0.0045 and 4.73 ns, respectively, were obtained for the quantum yield (ϕ_F) and lifetime (τ) of the S_1 emission. Those values for non-metallated tetra-*tert*-butylated Pc and Nc, sub-macrocycles of **1**, were 0.85 and 7.20 ns and 0.14 and 3.17 ns, respectively, in the same solvent. Thus, the ϕ_F value of **1** is two orders of magnitude smaller and the τ value is also much smaller than the values for general metal-free Pcs (very roughly ϕ_F = *ca.* 0.2-0.8 and τ = *ca.* 5-10 ns). Possible causes for these smaller values are the occurrence of charge-transfer between the Pc and Nc moieties,9) and the larger π-size and lower molecular symmetry10) of **1** compared to usual Pcs. In particular, intense charge-transfer is conjectured from the fact that the ϕ_F value of **1** is one order of magnitude smaller than that of a metal-free planar homodinuclear Pc and tetrabenzoporphyrin sharing a common benzene ring (0.0373d) and 0.052,3c) respectively, in chloroform).

Thus the present study has shown that planar assembly of similar type of macrocycles but with different sizes is useful for the broadening of the absorption band. If one of the two constituting molecules has bands in the near-IR region, as in the present study, the resultant compound would show broad bands in the near-IR region.

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6) Elemental analysis. Found: C, 78.10: H, 5.92; N, 15.86%. Calcd for $C_{94}H_{84}N_{16}$: C, 78.52; H, 5.89; N, 15.59%. 500 MHz ^{1}H NMR ($CDCl_3$) δ: 6.3-10.0(br m, 26H, aromatic), 1.0-1.7(br m, 54H, aliphatic). Due plausibly to a very high tendency toward aggregation,[3b] the position of pyrrole proton resonance could not be determined at high concentrations used in NMR spectroscopy (>10^{-4} mol/l). One referee asked us to measure ^{13}C NMR spectra of **1**. Approximately 6 mg of **1** could be dissolved in 0.6 ml of deuterated $CHCl_3$ and accummulation was continued 81500 times. However, a signal/noise ratio was not high enough to read all signals without uncertainty. Many weak peaks with different intensity appeared. This phenomenon could be attributable to a high tendency toward cofacial type aggregation,[3b] and the presence of great number of isomers (note that there are two places for each *tert*-butyl group to attach). Accordingly, we could not but give up the assignment of signals. However, aromatic carbon signals appeared at 178, 168, and 120 - 133 ppm while those of aliphatic carbons were observed at 11 - 39 ppm.

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