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Synthesis of Non-Symmetrically Benzo-Substituted Phthalocyanines and Their Electronic Spectra

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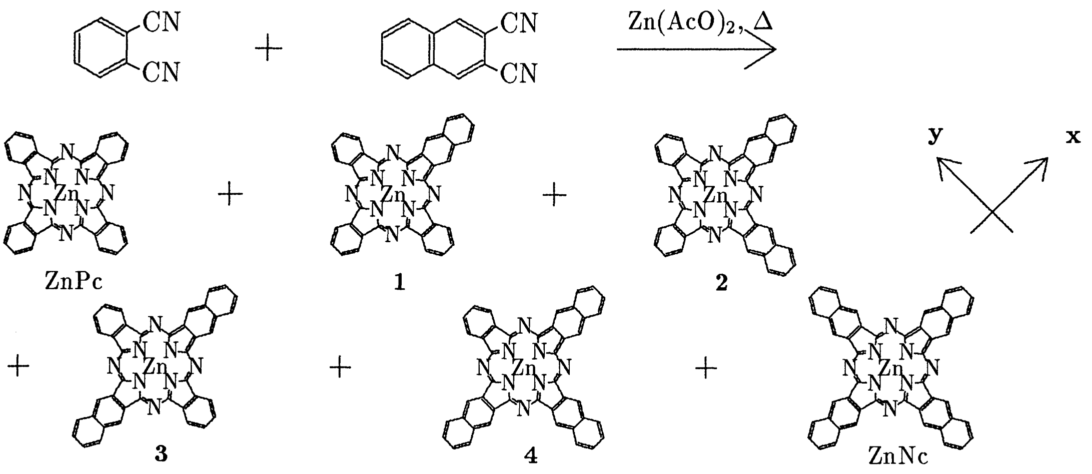
A series of benzo-substituted phthalocyanine-Zn complexes was isolated from a mixed product of two nitriles(*o*-phthalonitrile and 2,3-dicyanonaphthalene) and metal salt by chromatographic techniques. The UV-Visible absorption spectra of these compounds showed a schematic variation with the mode of substitution. The "D_{2h}" type complex showed strong anisotropy.

The chemistry of phthalocyanines is one of the most active fields in the material science because of the attractive physical properties and chemical stability of these compounds. Since the physical properties of phthalocyanines are mainly due to the π−framework of phthalocyanine molecules, it would be interesting to examine the influence of benzo-substitution on the peripheral benzene rings of a phthalocyanine molecule. Although investigations on naphthalocyanine(Nc)s which have more extended aromatic rings have been intensively developed by many authors,$^{1)}$ it would be also of special interest to investigate how the spectral properties would be modified when the symmetry is lowered by additional aromatic rings, because it is well known that the high symmetry of phthalocyanines plays an important role on the electronic states of these complexes.



Scheme 1.

However, well-controlled synthetic techniques to obtain such partially substituted phthalocyanines have not been established yet except for very few cases 2) unfortunately. In this article, we report a conventional method of separation from the mixed product of phthalocyaninatozinc (ZnPc) and naphthalocyaninatozinc (ZnNc), and four non-symmetrically benzo-substituted phthalocyanines, benzo[b]phthalocyaninatozinc (**1**), dibenzo[b,k]phthalocyaninatozinc (**2**), dibenzo[b,t]phthalocyaninatozinc (**3**), and tribenzo[b,k,t]phthalocyaninatozinc (**4**) (Scheme 1) using a gel permeation chromatography(GPC) and some spectral features of these complexes. Although such a GPC method has been used for purification of phthalocyanines and porphyrins,2,3) this seems to be the first success of the method to separate substituted phthalocyanines from mixture.

A mixed product was prepared by the well-known condensation reaction4) from a mixture of two nitriles and a metal salt. A mixture of *o*-phthalonitrile (0.72 g), 2,3-dicyanonaphthalene(1.00 g), and zinc acetate(0.68 g) was heated for 5 min. at 270 ℃ and allowed to cool. The crude product was crushed and dissolved into THF(400 ml), then insoluble part was filtered off. The solution was passed through an alumina column to remove impurities (where, large part of ZnNc was adsorbed on alumina) and dried on an evaporator. The dried product was dissolved into minimum amount of THF, and left for four days at 0 °C to precipitate a mixture of **3** and less amount of ZnNc. The precipitate was collected by filtration and further purified by recrystallization from THF solution. The filtrate was applied on a BIO-BEADS SX-8(BIO-RAD) column(L=120 cm) and passed with THF. This column operation was repeated several times to obtain pure components of **1**,**2**, and **4**. The order of the solubilities in THF was found as ZnPc + **1** > **2** > **4** > ZnNc > **3**.5) (We found here that poor solubility of ZnPc is highly improved by the co-existence of **1**.)

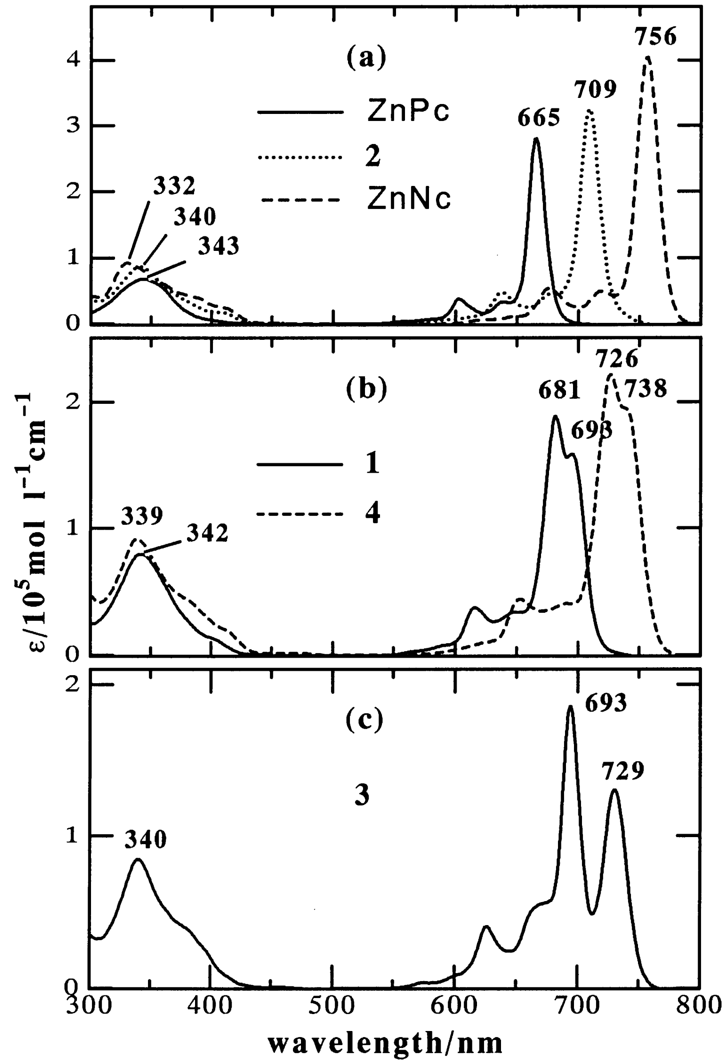


Fig.1. Absorption spectra of **1-4**, ZnPc, and ZnNc in THF solution.

The absorption spectra are depicted in Fig.1 with the spectra of ZnPc and ZnNc for comparison. Although some theoretical calculations should be performed to interpret these results, it would be useful to extract some spectroscopic properties from the observations. It should be noted that the spectra of these zinc-phthalocyanine derivatives can be classified into three groups by the splitting mode in the Q-bands; — (a) is a "degenerate" group in which each Q-band has only one sharp peak, here each peak appears at regular energy intervals of *ca.* 900 cm^{-1}, (b) is a "narrow-split" group in which the Q-bands show slightly split(energy separation = *ca.* 250 cm^{-1}) profiles, and (c) "large-split" one(energy separation = *ca.* 700 cm^{-1}). In the group (a), it is well-known that both ZnPc and ZnNc give rise to single Q-bands due to the degeneracy of LUMO(e_g) of Pcs in the D_{4h} symmetry of the molecules,6) however, it is notable that **2** also shows almost the same peak-shape in spite of the lowered symmetry (C_{2v}) which could give rise to no degenerate electronic states. This means that the degeneracy of the LUMO is little dissolved by the perturbation of the substituents. Complexes in the group (b) have similar geometrical arrangements of aromatic rings with C_{2v} symmetry (*N.B.* Symmetry axis and planes are taken differently from the case of **2**.), and the degeneracy is lifted in approximately same amount. The remarkably large splitting of the Q-band of **3** is readily understood considering the completely anisotropic structure (D_{2h} symmetry) of this compound, however, such a property is quite unusual among the family of metal-Pcs. Further investigation on non-linear optical properties of a thin film of this novel complex is in progress by the authors, and some new features have been observed.7)

The spectra in the UV-visible region(350–430 nm) also show some noticeable change; it is noted that new bands appear as shoulders in the lower energy side of the Soret-bands(300–380 nm). Since the total intensity of these bands of each complex increases in proportion to the number of substituents, these would be reasonably assigned to some local excitations on naphthalene rings. Ohno *et al* assigned similar bands seen in the spectra of Ncs to the excitation on the outer rings,8) and our results are in compromise with their results. The Soret bands are expected to show similar manner in the peak splittings because the transition is also associated with the LUMO, but no distinguishable peaks were observed due to the broad band-width. In conclusion, the present work demonstrated that it would be worthy to investigate more efficient reaction path to synthesize the "D_{2h}" type Pcs because those optical properties are quite unique among other phthalocyanines.

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5) The results of elementary analyses are as follows. **1**: Found: C, 69.06; H, 3.08; N, 17.30%. Calcd for $C_{34}H_{18}N_8Zn$: C, 68.85; H, 2.89; N, 17.84%. **2**: Found: C, 69.96; H, 3.05; N, 15.89%. Calcd for $C_{40}H_{20}N_8Zn$: C. 70.86; H, 2.97; N, 16.53%. **3**: Found: C, 69.96; H, 3.32; N, 15.65%. Calcd for $C_{40}H_{20}N_8Zn$: C, 70.86; H, 2.97; N, 16.53%. **4**: Found: C, 73.50; H, 3.16; N, 15.33%. Calcd for $C_{44}H_{22}N_8Zn$: C, 72.58; H, 3.05; N, 15.39%. The FAB-MASS spectral data are as follows. Each peak

showed typical shape due to the natural isotopic abundance of Zn. **1:** M/Z = 626, **2:** M/Z = 676, **3:** Peak was not observed due to very low solubility. **4:** M/Z = 726. The 300 MHz ^{1}H NMR data in DMSO-d_6 are as follows. **1:** 6.98(s 2H), 6.60-6.68(m 6H), 6.09-6.06 (4 br 2H), 5.61-5.66(m 6H), 5.39-5.42(4 br 2H). **2:** 6.96(s 2H), 6.93(s 2H), 6.60-6.64(4 br 4H), 6.03-6.09(5 br, s at 6.06, 4H), 5.57-5.63(m, s at 5.59 and 5.61 4H), 5.36-5.41(m 4H). **3:** 7.44(s 4H), 6.92-6.95(4 br 4H), 6.23-6.26(4 br 4H), 5.76-5.79(4 br 4H), 5.43-5.46(4 br 4H). **4:** 6.93-6.95(2 br 4H), 6.87(s 2H), 6.55-6.57(4 br 2H), 6.00-6.99(m 6H), 5.51-5.54(4 br 2H), 5.32-5.38(m 6H).

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