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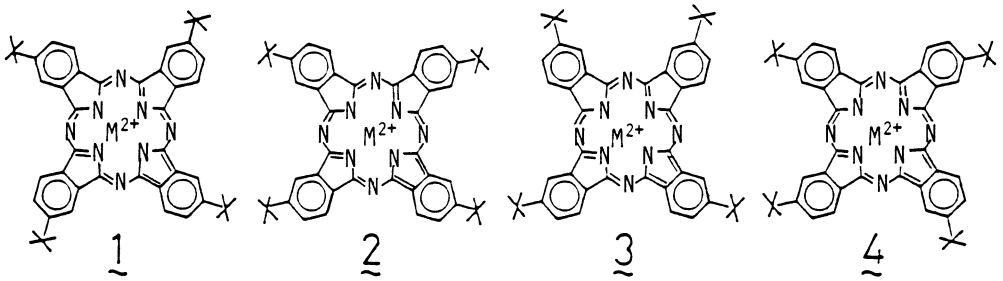
Synthesis and Spectroscopic Properties of Zn(II) Mono-2-(t-butyl)phthalocyanine

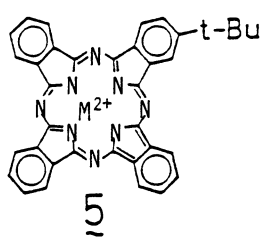
Hideo KONAMI* and Masahiro HATANO
Chemical Research Institute of Non-Aqueous Solutions,
Tohoku University, Katahira 2-1-1, Sendai 980

A simple method of synthesis which provides soluble mono-substituted phthalocyanine(Pc) complexes has been proposed. Concurrent measurements with non-, mono- and tetra-substituted Pc's enabled to assign ^{1}H NMR signals of ZnPc's, and suggested complicated structure of so-called Soret(B) band in the UV-region of electronic spectra.

Although many works have been reported on optical and electrical properties of thin film of phthalocyanines(Pc's),[1] poor solubility of Pc's has been a serious obstruction for the experiments. To avoid the experimental difficulty, synthetic techniques to introduce bulky substituents into Pc molecules have been applied.[2-4] Recently, 4-substituted phthalonitrile derivatives having t-butyl-group, alkoxy-group, etc. have become commercially available as starting materials. Soluble tetra-substituted Pc's can readily be synthesized from these reagents. However, the product may be a mixture of four isomers 1-4.[5]



Since one of the most important advantage of thin film or membrane preparations is based on the regularity of spatial arrangement of the molecules, the existence of isomers is quite unfavorable because it may increase randomness of the system. The synthetic method of pure mono- or di-substituted Pc's still remained a difficult problem.[6]



We wish to report here a simple method to obtain pure soluble mono-2-substituted Pc's 5, and to discuss the result of ^{1}H NMR and electronic spectra. As the present technique is based on a simple sto-

chastic principle, it can be easily extended to other substituents and other synthetic methods.

The essential point of the technique is to start with a mixture of phthalonitrile(PN, 2.48 g in this work) and substituted phthalonitrile (4-tert-butylphthalonitrile TBPN, 0.19 g) in regulated molar ratio. Starting with a mixture of PN and TBPN in which molar fraction of TBPN is w, a simple stochastic calculation gives;

$$p_1 = 4w(1-w)^3/[1-(1-w)^4], \quad (1)$$

$$f_1 = 4w(1-w)^3, \quad (2)$$

where p_1 and f_1 are the fraction of mono-substituted Pc among all the soluble Pc's and that among the total Pc's, respectively. The calculation gives also;

$$f_0 = (1-w)^4 \quad (3)$$

as the fraction of ZnPc among the total Pc's. When w is taken to 0.05 as in the present work, p_1, f_1, and f_0 are calculated as 0.924 (fraction of mono-substituted Pc in crude product), 0.171, and 0.815 respectively. Since mono-substituted Pc has fairly good solubility, it is easily separated from the reaction mixture.

In this work, the usual template reaction technique[7] is applied to prepare Zn(II) mono-2-(t-butyl)phthalocyanine (ZnMTPc). After the reaction, acetone (300 ml) was added to the product, and the suspension was refluxed for 2 h. The insoluble product which contains ZnPc was filtered off and washed several times with hot acetone. All the filtrate was evaporated to dryness. The crude product was purified by column chromatography of silica using diethylether as eluent. An elemental analysis as $C_{36}H_{24}N_4Zn$ was follows; Found: C,68.11; H,4.13; N,17.30; Zn,10.46%. Calcd: C,68.19; H,3.81; N, 17.67; Zn,10.33%. ZnPc was prepared from the precipitate by washing with acetone and 5% aqueous HCl solution. Zn(II) tetra-(t-butyl) phthalocyanine (ZnTTPc) was prepared in analogous way for comparison.

The value f_0/f_1 was estimated as 4.1 by computational optimization of absorption spectra of the reaction mixture containing ZnPc and ZnMTPc, being in agreement with the predicted value(4.7) from the above expression. This shows that the stochastic calculation is applicable to the present case. The product was soluble in various solvents, and Langmuir-Blodgett

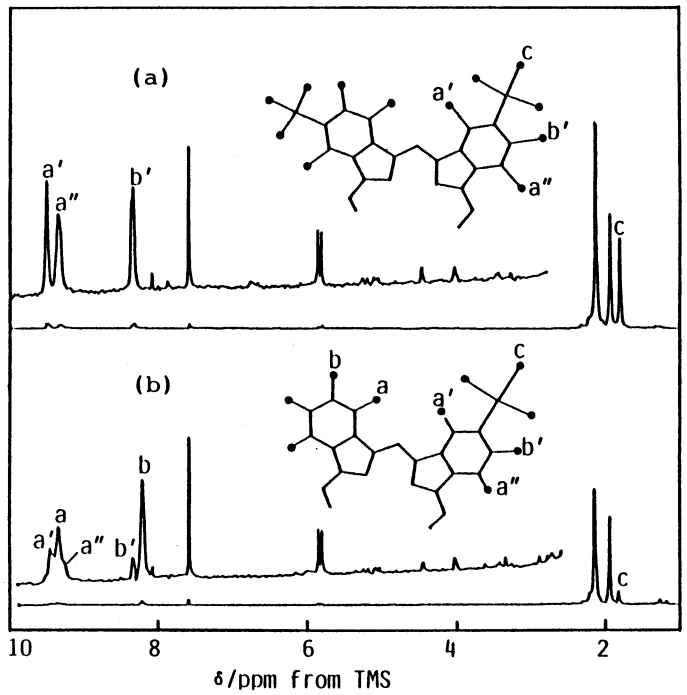


Fig.1. ^1H NMR Spectra of (a) ZnTTPc, (b) ZnMTPc. Peak positions: a;9.32ppm, a';9.44ppm, a";9.31ppm, b;8.32-8.33ppm, c;1.82ppm. Other peaks are assigned to the solvent(CD_3CN, 99.96%).

membrane formation is investigated by the authors and coworkers.

^{1}H NMR spectra of ZnTTPC and ZnMTPc are shown in Figs.1(a) and (b). Since ZnTTPc has only **a'** and **a"** α-protons, the peaks at 9.44ppm and 9.31ppm are assigned to either proton **a'** or proton **a"**, the peak at 9.32ppm overlapped with them is then assigned to the proton **a** on non-substituted phenyl rings of ZnMTPc. Hence, the peaks at 9.31ppm, 9.32ppm and 9.44ppm are assigned to the protons **a"**, **a** and **a'**, respectively. There are two kinds of outer protons **b** and **b'** for ZnMTPc, and ZnTTPc complex has almost equivalent four protons **b'**. Therefore, the peaks at 8.20ppm and 8.32-8.33ppm are clearly assigned to **b** and **b'**, respectively.

It is essentially unable to measure chemical shifts of protons of Pc's without substituents in solution due to its poor solubility, although they are of much importance. Present study suggests that if the chemical shifts of ZnPc were observable, they would appear at 9.32ppm and 8.20ppm for the inner and outer protons of ZnPc, respectively, and these values can be used to compare with the data of other soluble Pc's.

Figure 2 shows UV-visible absorption spectra of dimethylsufoxide solutions of ZnPc, ZnMTPc and ZnTTPc. Each spectrum is normalized at the maximum in the visible region. So-called Soret(B) bands (ca. 340 nm) and Q bands (ca. 670 nm) shifts to a lower energy side with the increase of the substituents. The shifts in Q bands for ZnMTPc and ZnTTPc are 33 cm^{-1} and 139 cm^{-1}, respectively, and those in Soret bands are 250 cm^{-1} and 690 cm^{-1}. It is noted that the number of substituents and the energy shifts show good linear dependence in Q bands, while not in Soret bands.

It has been traditionally believed that the strongest absorption peak near 340 nm is associated with the B band ($2a_{2u}(\pi) \dashrightarrow 1e_g(\pi^*)$) of Gouterman's four orbital model.[9] However, Nyokong[10] et al. showed recently that the band of

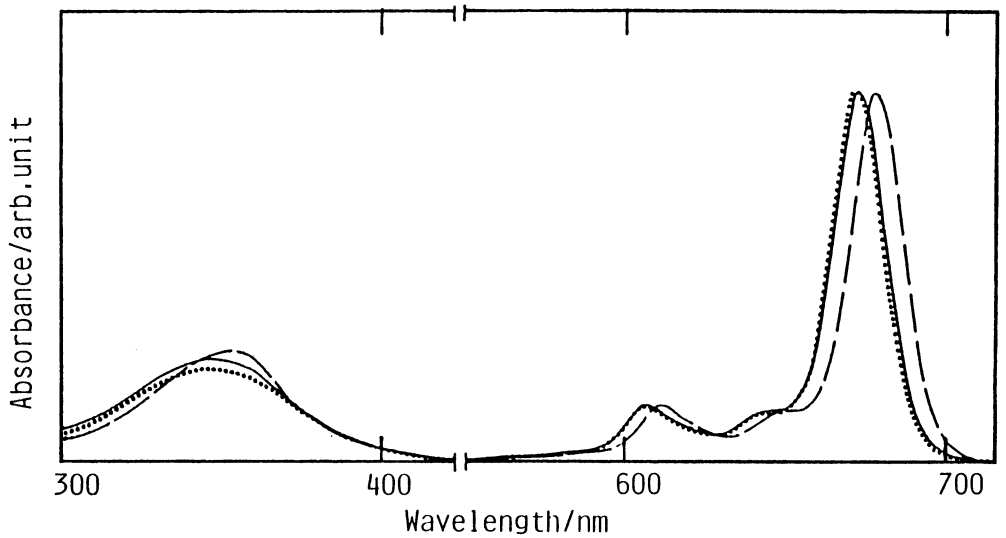


Fig.2. Absorption spectra of Zn(II) phthalocyanine(·····), Zn(II) mono-2-(tert-butyl)phthalocyanine(———), and Zn(II) tetra(tert-butyl)phthalocyanine(— ——). The intensities are normallized at the peak of visible reagion.

ZnPc-cyanide and -imidazole complexes in the UV region can be deconvoluted into several bands including at least three degenerate transitions which may be assigned to different π --> π^* transitions. They also showed that one strong transition ($2a_{1u}(\pi)$--> $1e_g(\pi^*)$) dominates the envelope in the Q region. This result is consistent with our observation on the linearity of the band energy shifts. It is obvious that the energy shift of each π --> π^* transition depends linearly on the number of substituents in the present case, because the effect can be regarded as a small perturbation. Since Q band is composed of one transition, the linearity must be conserved. In the Soret region which contains several transitions, linearity can no longer exist, because the shape of the envelope will be changed even if each band shifts proportionally to the number of substituents with individual coefficient.

In conclusion, the procedure described in this paper provides a potentially general synthesis of soluble mono-substituted Pc's in controlled purity. It has been demonstrated that the concurrent measurement with other derivatives can offer useful information on the spectroscopic properties.

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