CHEMISTRY LETTERS, pp. 2031-2034, 1992.

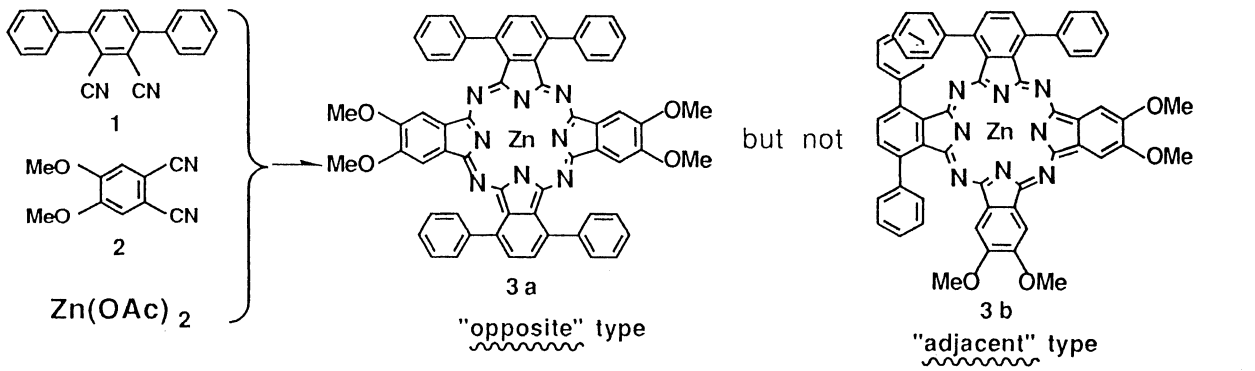
Synthesis, Spectroscopy, Electrochemistry, and Spectroelectrochemistry of a Zinc Phthalocyanine with D_{2h} Symmetry

Nagao KOBAYASHI,* Tohru ASHIDA, and Tetsuo OSA*
Pharmaceutical Institute, Tohoku University, Aobayama, Aoba, Sendai 980

An efficient method is reported for the preparation of metallophthalocyanines (MtPcs) with D_{2h} symmetry (di-substituted type). A ZnPc with D_{2h} symmetry thus obtained has been characterized by NMR, absorption, fluorescence emission and excitation and magnetic circular dichroism (MCD) spectroscopy, together with differential pulse voltammetry.

Metallophthalocynanines (MtPcs) are generally obtained by template reactions using metal salts and aromatic *ortho*-dinitriles or -dicarboxylic anhydrides.[1] When two kinds (A and B) of nitriles or anhydrides are employed in the mixed condensation reaction, at least six kinds of MtPcs are obtained (A and B now stand for isoindoline units in Pcs): Pcs consisting of four A's or B's, three A's and one B, three B's and one A, and two A's and two B's (two isomers, "*adjacent*" and "*opposite*" types). However, the separations of these Pc derivatives are extremely difficult. Although mono-substituted type Pcs have been obtained by the mixed condensation method,[2] a polymer support method,[3] or *via* the so-called subphthalocynines,[4] well-defined Pcs containing two A and B units have not been reported.[5] Indeed even if it can be confirmed that two A and B units are included in a Pc molecule by NMR and mass spectrometry, separation and identification of the "*adjacent*" and "*opposite*" type Pcs are of paramount difficulty. In this communication, we describe a simple and efficient method for the preparation of "*opposite*" type Pcs. In order to achieve a structure-directed synthesis, we have intentionally utilized 3,6-diphenylphthalonitrile, **1**, (Scheme 1) as one of the two starting dinitriles. Since two phenyl groups are protruding from the 3 and 6 positions of phthalonitrile, the possibility of obtaining an "*adjacent*" type Pc should be quite small because of the steric hindrance between two phenyl groups belonging to different **1** molecules. This is indeed substantiated as shown below.

Zinc acetate (1 equiv.), 4,5-dimethoxyphthalonitrile, **2** (1 equiv.),[6] and **1** (3 equiv.)[7] were mixed well and heated at 250-270 °C for *ca.* 20 minutes. After being cooled, the reaction mixture was washed with water and ethanol, and chromatographed on basic alumina with chloroform as eluent. The first band was collected and further separated by gel permeation chromatography using a Bio-beads SX-8 (Bio-rad) column and tetrahydrofuran as eluent. The first band was a ZnPc originating from three **1** and one **2** but it was in only a trace amount (less than 0.01%!). The compound in the second green band (yield 9% after two crystallizations from toluene) showed a desired parent ion peak of 1001 ($C_{60}H_{40}N_8O_4Zn$ requires 1001.714) in its mass spectrum using a fast atom bombardment (FAB) technique and the ratio of aromatic and aliphatic protons was also desired 28:12 in its NMR spectrum.[8] Figure 1 shows the 500 MHz ^1H NMR spectrum of this compound in the aromatic region. Although two structures, **3a** and **3b** (Scheme), are conceivable for the above mass datum, the simplicity of this



Scheme 1.

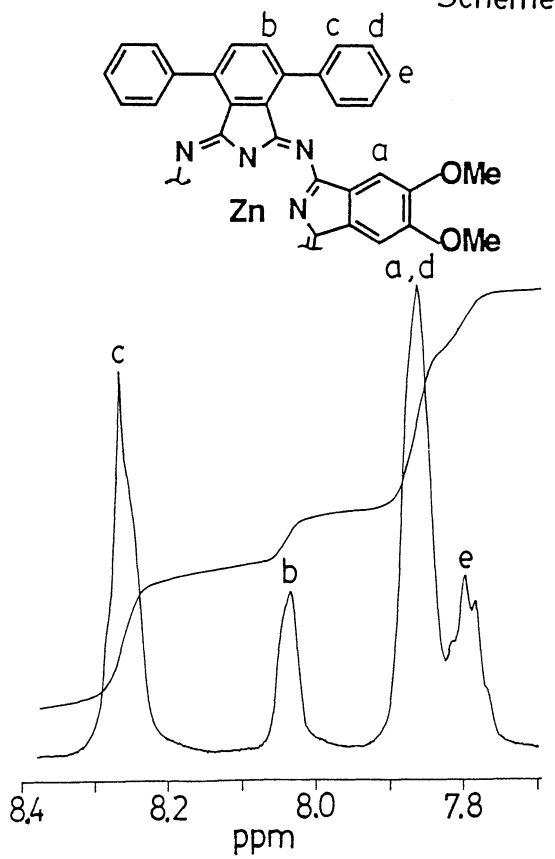


Fig. 1. Partial 500 MHz ^{1}H NMR spectrum of **3a** in CDCl3-DMSO-*d*6 (1:1 v/v) (ref. TMS). [**3a**]/M = *ca.* 3 x 10^{-4}. Assignments are shown.

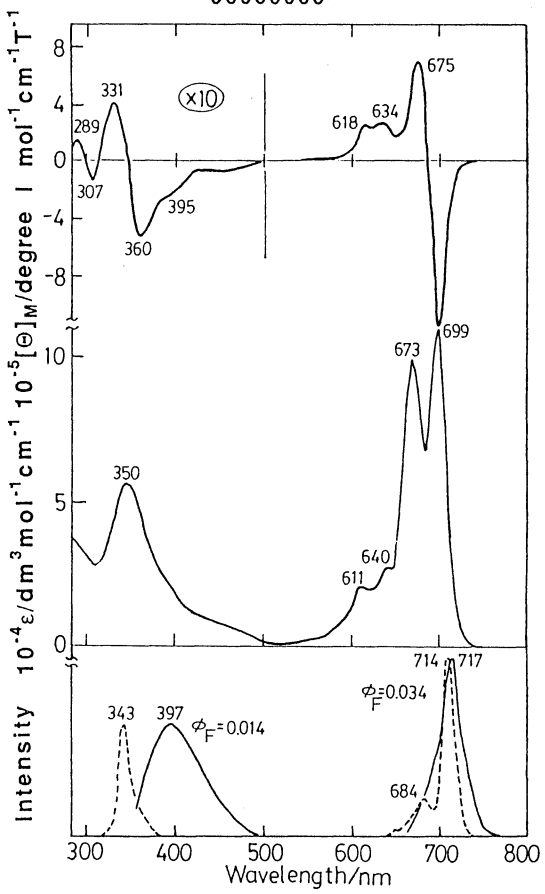


Fig. 2. MCD (top), absorption (middle), and fluorescence emission and excitation spectra (bottom) of **3a** in chloroform.

figure (five different aromatic hydrogens in a ratio of 1:1:2:2:1 in the order of **a** to **e**) indicates that the compound is **3a**.[8] In the case of **3b**, one can predict that the NMR of the aromatic protons of the two types of phenyl groups would become more complex due to crowding or overlap.

The argument of the absorption spectroscopy also supports the structure **3a**. According to the results of molecular orbital calculation within the framework of the LCAO[9] and PPP[10] methods, the Q band of C_{2v} *i.e.* "*adjacent*" type MtPcs does not split or may split negligibly, but that of D_{2h} *i.e.* "*opposite*" type does split, since the excited state degeneracy is removed to a fair extent. The absorption spectrum of the compound obtained

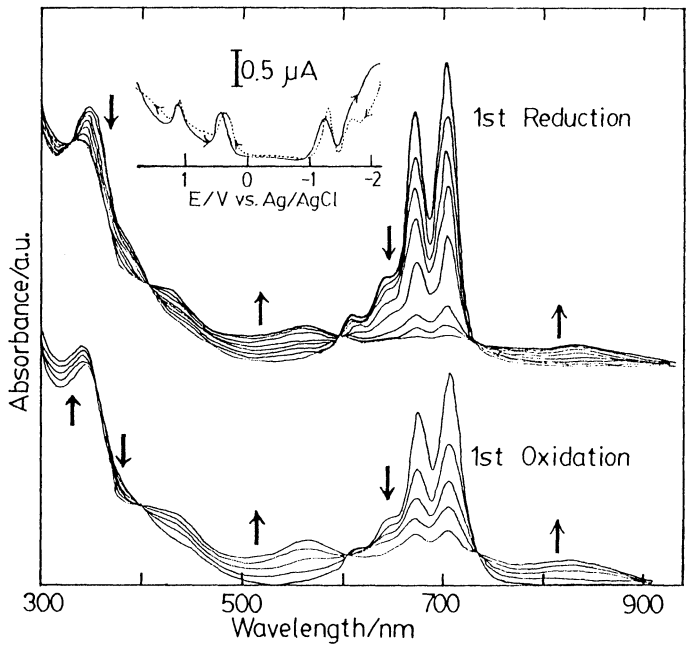


Fig. 3. Development of the electronic spectra of **3a** in DCB, showing the formation of monoanion (top) and monocation (bottom). The inset shows the DP voltammograms of **3a** in DCB. For DP, [**3a**]/M = 6.68 x 10^{-4}, area of electrode/cm^2 = 0.07, and scan rate/(V s^{-1}) = 0.005. All solutions contain 0.03 M TBAP.

above (Fig. 2) showed the four-peak Q band, characteristic of D_{2h} Pcs such as non-metallated Pcs (H_2Pcs).[11] Two peaks at 699 and 673 nm are considered to be the split $Q_{0\text{-}0}$ band, although their energy difference (553 cm^{-1}) is slightly smaller than that of H_2Pc without substituent groups (*ca.* 710 cm^{-1}).[12] Under the symmetry of D_{2h} approximation, these bands are assigned to $a_u \rightarrow b_{2g}, b_{3g}$ transitions.[13] Hence, it is concluded that the compound is the desired "*opposite*" type D_{2h} ZnPc, i.e. **3a**. The shape of the magnetic circular dichroism (MCD) spectrum is also appropriate to that of D_{2h} Pcs.[11] Namely, since there is no degenerated state, the Q band MCD is a superimposition of Faraday *B*-terms, and an exemplary Faraday *A*-term type dispersion curve does not appear.

Figure 2 shows also the emission and excitation spectra for this compound. So-called S_1 and S_2 emissions were detected. Although H_2Pc with four crown ether voids (H_2CRPc) is known to exhibit S_2 emission,[14] this represents the second example of a Pc upper excited state emission. The quantum yields of the S_1 and S_2 emissions, obtained using H_2Pc and ZnPc,[15a] and zinc tetraphenylporphyrin as standards,[15b] are 0.034 and 0.014 in chloroform, respectively. The value for the S_1 emission is one order of magnitude smaller than that of ZnPc without substituent groups in 1-chloronaphthalene (0.30).[15a] Such a remarkable decrease of the quantum yield of S_1 emission accompanying the lowering of the molecular symmetry has been reported recently for tetraazaporphyrin derivatives with C_{2v} symmetry (but mono-substituted type).[16]

Differential-pulse (DP) voltammograms of **3a** in *o*-dichlorobenzene (DCB) are shown in the inset of Fig. 3. Four redox couples at 1.08, 0.39, -1.30, and -1.73 V are attributed to 2nd- and 1st-oxidation, and 1st- and 2nd-reduction of the ligand, respectively. For comparison, those of tetraneopentoxyPc zinc complex (ZnTNPc) having approximate D_{4h} symmetry occur at 1.23, 0.57, -1.07, and -1.45 V vs. Ag/AgCl in the same solvent.[17] Although the potentials of redox couples depend on many factors such as the kind, number, and positions of substituent groups, it is interesting to note that all potential differences in **3a** are larger by 30-50 mV than the corresponding potential differences in ZnTNPc. For example, the potential difference between the 1st-oxidation and -reduction in **3a** (1.69 V) is 50 mV larger than that in ZnTNPc (1.64 V).

Figure 3 shows also the spectroscopic changes observed on formation of monoanion or monocation of **3a**. In both cases, the initial green solution gave pale yellow solution after electrolysis, and the final spectra are very similar in shape to each other. Of particular interest is the shape of the spectrum of monoanionic species. It differs significantly from that of Mg-, Ni-, or CuPc[18] with D_{4h} symmetry which shows a weak peak at *ca.*

900-1000 nm and two intense peaks at 550-650 nm, suggesting that the shape of the LUMO of **3a** differs markedly from that of e_g orbitals.

Considering that the yield of the ZnPc synthesized from three **1** and one **2** is negligible, we can not but feel that the use of a phthalonitrile with two bulky substituent groups protruding from its 3 and 6 positions is effective in obtaining D_{2h} type MtPcs. We obtained the cobalt complex corresponding to **3a** in almost 20% yield.

References

1) A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, **7**, 27 (1965); F. H. Moser and A. H. Thomas, "The Phthalocyanines," C. R. C. Press, Boca Raton, FL, (1983), Vols. I and II.
2) C. Piechocki and J. Simon, *J. Chem. Soc., Chem. Commun.*, **1985**, 259.
3) C. C. Leznoff, "Phthalocyanines-Properties and Applications," ed by C. C. Leznoff and A. B. P. Lever, VCH publ., New York, (1989), Chap. 1.
4) N. Kobayashi, R. Kondo, S. Nakajima, and T. Osa, *J. Am. Chem. Soc.*, **112**, 9640 (1990).
5) This type of Pcs has been reported as a mixture of *adjacent* and *opposite* isomers. H. Shirai, S. Yagi, A. Suzuki, and N. Hojo, *Makromol. Chem.*, **178**, 1889 (1977). However, dibenzoPc zinc complexes were reported recently. Y. Ikeda, H. Konami, M. Hatano, and K. Mochizuki, *Chem. Lett.*, **1992**, 763.
6) J. Mets, O. Schneider, and M. Hanack, *Inorg. Chem.*, **23**, 1065 (1984). Compound **2** was used by the following three reasons. i) Identification by NMR seemed easy since **3a** should give a singlet for methoxy protons (see Ref.8)). If other types of ZnPcs were obtained, their methoxy proton signals would become more complex. ii) The reactivity of **1** and **2** on Pc formation seemed relatively similar. The use of, for example, 2,3-dicyanopyradine in place of **2** led to unsuccessful results, since its reactivity is much higher than **1** (we obtained zinc tetrapyradinoporphyrazine in *ca.* 50% yield). iii) Since the sizes of **1** and **2** are so different that the separation of various ZnPcs, if produced at all, by gel permeation chromatography seemed possible. In fact, a ZnPc consisting of one **1** and three **2** was separated as a by-product.
7) S. A. Mikhalenko, S. A. Gladyr, and E. A. Luk'yanets, *J. Org. Chem. USSR (Engl. Transl.)*, **8**, 341 (1972).
8) Methoxy protons appeared as a singlet at 4.205 ppm. Elemental analysis of **3a**. Found: C, 71.45; H, 4.36; N, 10.94%. Calcd for $C_{60}H_{40}N_8O_4Zn$: C, 71.89; H, 4.02; N, 11.18%.
9) K. N. Solovyov, V. A. Mashenkov, and T. F. Kachura, *Opt. Spectrosc. (Engl. Trans.)*, **27**, 24 (1969).
10) Y. Ikeda, Thesis, Tohoku University, 1989.
11) M. J. Stillman and T. Nyokong, "Phthalocyanines-Properties and Applications," ed by C. C. Leznoff and A. B. P. Lever, VCH publ., New York, (1989), Chap. 3.
12) M. Whalley, *J. Chem. Soc.*, **1961**, 866.
13) A. M. Shaffer and M. Gouterman, *Theor. Chim. Acta (Berl.)*, **25**, 2 (1972).
14) N. Kobayashi and A. B. P. Lever, *J. Am. Chem. Soc.*, **109**, 7433 (1987).
15) a) P. G. Seybold and M. Gouterman, *J. Mol. Spectrosc.*, **31**, 1 (1969); b) L. Bajema and M. Gouterman, *ibid.*, **39**, 421 (1971).
16) N. Kobayashi, T. Ashida, and T. Osa, *Chem. Lett.*, **1992**, 1567.
17) V. Manivannan, W. A. Nevin, C. C. Leznoff, and A. B. P. Lever, *J. Coord. Chem.*, **19**, 139 (1988).
18) J. W. Dott and N. S. Hush, *J. Chem. Soc.*, **1964**, 4607; A. N. Sidorov, *J. Struc. Chem. USSR (Engl. Transl.)*, **14**, 229 (1973).

(Received July 24, 1992)