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Chemical Oxidation of Tetra-*t*-butylphthalocyanine and Its Complexes with Cobalt(II), Nickel(II), Copper(II), and Zinc(II)

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Synopsis. While the title compounds were oxidized by $NOBF_4$, DDQ only oxidized the cobalt(II) and zinc(II) complexes in dichloromethane. To confirm their chemical oxidation, a cyclic voltammetry was measured.

It is well-known that the electrical conductivity of metallophthalocyanine complexes drastically increases in partial oxidation;[1] the single crystals grown by a slow diffusion of the complexes and oxidants or an electrochemical method exhibit a metallic conductivity, and their detailed properties have been investigated.[2,3] The conductivity also increases in partial reduction of the complexes or their analogues.[4,5] The metallophthalocyanine complexes are partially oxidized by iodine which might have difficulty oxidizing the complexes judging from their redox potentials. That is, the partial oxidation of the complexes is cooperatively promoted by a stacking effect of the oxidized complexes.

The partial oxidation of unsubstituted metallophthalocyanine complexes has been extensively investigated, but few studies have been reported on the oxidation of the complexes with peripherical substituents.[6] This paper describes the oxidation of the soluble metallophthalocyanine complexes peripherically substituted by *t*-butyl groups to investigate the effects of central metal ions and oxidants on the chemical oxidation.

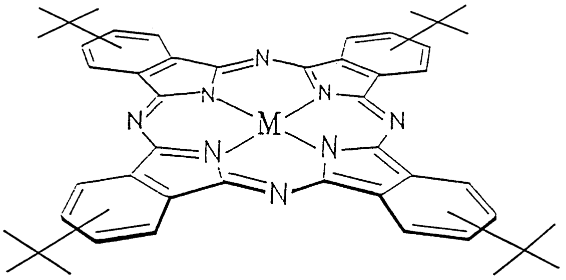

Fig. 1. Schematic representation of the MPc(t-Bu)$_4$ complex.

Experimental

Materials. Metal-free phthalocyanine and its cobalt(II), nickel(II), copper(II), and zinc(II) complexes were prepared by a method similar to that described in the literature.[6–8] 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was recrystallized from benzene under an argon atmosphere. Nitrosyl tetrafluoroborate ($NOBF_4$) was used without further purification.

Measurements. The electronic spectra in solution were measured on a Hitachi 200-20 spectrophotometer. The ESR spectra were measured with a JEOL-1X spectrometer. The cyclic voltammetric measurements were performed in a dichloromethane solution containing tetrabutylammonium perchlorate (0.1 mol dm^{-3}) on a Hokuto Denko HA-501 potentiostat with a Hokuto Denko HF-201 function generator. A glassy carbon disk, a platinum coil, and a saturated calomel electrode (SCE) were used as a working electrode, a counter electrode, and a reference electrode, respectively.

Results and Discussion

The metallophthalocyanine complexes are generally insoluble in common organic solvents, but the complexes which are peripherically substituted by *t*-butyl groups readily dissolve in organic solvents such as dichloromethane, chloroform, benzene, and pyridine; e.g., the solubility of ZnPc(t-Bu)$_4$ in dichloromethane is ca. 2×10^{-2} mol dm^{-3}.

Chemical Oxidation. The blue dichloromethane solution of these compounds turned reddish purple upon the addition of a strong oxidant such as $NOBF_4$. In the case of ZnPc(t-Bu)$_4$, the Q band (679 nm) extensively decreased in intensity, and new bands appeared at 528 and 721 nm. Similar spectral changes were observed in the addition of $NOBF_4$ to the dichloromethane solution of H_2Pc(t-Bu)$_4$ and its cobalt(II), nickel(II) or copper(II) complexes. It was reported that oxidation at a central metal ion slightly shifts the Q band, while ring oxidation decreases the intensity of the Q band.[9,10] The intensity of the Q bands of the compounds used in the present study decreased when the compounds were oxidized by $NOBF_4$ in dichloromethane. On the other hand, with an organic oxidant

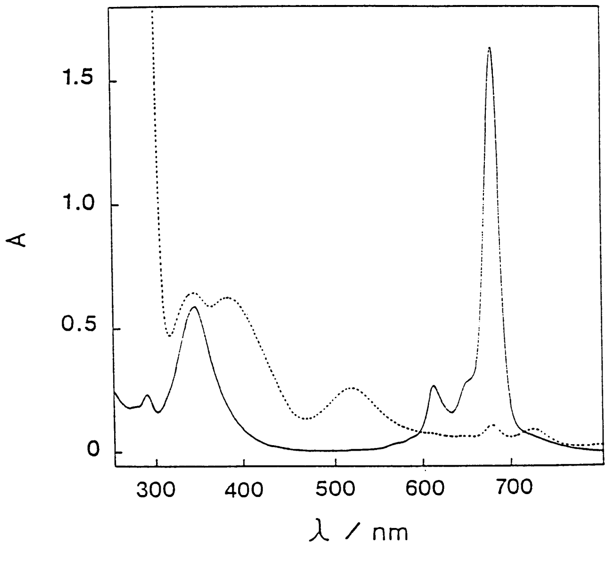

Fig. 2. Electronic spectra of ZnPc(t-Bu)$_4$ in dichloromethane: (——) [complex]=7.4×10^{-6} mol dm^{-3}; (----) [complex]=7.4×10^{-6} mol dm^{-3}, [DDQ]=1.5×10^{-5} mol dm^{-3}.

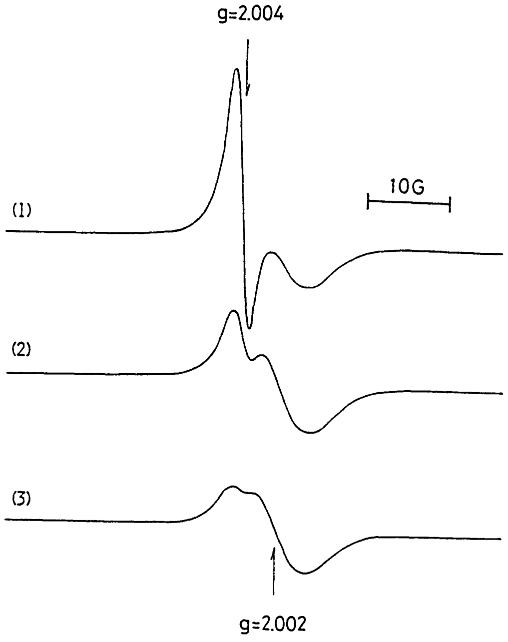

Fig. 3. ESR spectra of $\mathrm{ZnPc}(t\text{-Bu})_4$ oxidized by DDQ in dichloromethane at room temperature: (1) before UV irradiation; (2) irradiated for 2 min; (3) irradiated for 5 min.

such as DDQ, the blue dichloromethane solution of the cobalt(II) or zinc(II) complex turned reddish purple; e. g., the Q band (679 nm) of $\mathrm{ZnPc}(t\text{-Bu})_4$ decreased in intensity, and new bands appeared at 516 and 722 nm (Fig. 2). Within our knowledge, the oxidation of metallophthalocyanine with DDQ only occurs in the case of the polymer complexes of $(\mathrm{SnPcO})_n$ and $(\mathrm{AlPcF})_n$.[11,12] As soluble metallophthalocyanine complexes having simple substituents, these complexes are the first ones which could be oxidized by DDQ.

The dichloromethane solution of $\mathrm{ZnPc}(t\text{-Bu})_4$ oxidized by DDQ showed two ESR signals characteristic of organic radicals (Fig. 3). UV irradiation was employed to clarify the analysis of the signals. The sharp signal (g=2.004) in the lower magnetic field disappeared upon irradiation, and the g value for the signal that remained was estimated to be 2.002. On the other hand, the oxidation of the complex by $\mathrm{NOBF_4}$ showed an ESR signal only at g=2.002. That is, the ESR signals at g=2.002 and 2.004 were assigned to those of the cationic phthalocyanine radical and the anionic DDQ radical, respectively. Furthermore, the ESR signal of the anionic DDQ radical (g=2.004) disappeared at liquid nitrogen temperature and recovered its intensity when rising to room temperature. It was reported that the anionic DDQ radicals form a dimer in the solid state, being ESR silent.[13] The concentration of the dimer in the dichloromethane solution might increase at liquid nitrogen temperature, resulting in the disappearance of the ESR signal.

Electrochemistry. The cyclic voltammograms (CV) of these compounds showed four redox couples.[14] Redox steps on the reduction side are reversible, whereas those on the oxidation side are quasi-reversible or irreversible. To confirm the behavior of the chemical oxidation, the half-wave potentials of the first step on the oxidation side are listed in Table 1. The $\mathrm{CoPc}(t\text{-Bu})_4$ and $\mathrm{ZnPc}(t\text{-Bu})_4$ complexes were easily oxidized compared with $\mathrm{H_2Pc}(t\text{-Bu})_4$, $\mathrm{NiPc}(t\text{-Bu})_4$, and $\mathrm{CuPc}(t\text{-Bu})_4$ in dichloromethane. By considering the potential of the first reduction step of DDQ (0.59 V vs. SCE in dichloromethane), it was obvious that only the cobalt(II) and zinc(II) complexes were oxidized by DDQ. The CV data show that the complexes are oxidized in the order of Co(II)>Ni(II) ≈Cu(II)<Zn(II). It was reported that the less the polarizing power (Ze/r) of the ion, the easier it was to oxidize the phthalocyanine ring.[15] As the ionic radii of the metal(II) ions decreased in the order of Co(II)>Ni(II)>Cu(II)<Zn(II), the order of the potentials might be explained by the polarizing power of the central ion.

Table 1. The Half-Weve Potentials of the First Oxidation Steps[a)]

Compound	$E_{1/2}$[b)]	$E_{1/2}$[c)]
$\mathrm{H_2Pc}(t\text{-Bu})_4$	0.95 (irr)	0.66 (irr)
$\mathrm{CoPc}(t\text{-Bu})_4$	0.57 (60)	0.18 (120)
$\mathrm{NiPc}(t\text{-Bu})_4$	0.97 (irr)	0.89 (130)
$\mathrm{CuPc}(t\text{-Bu})_4$	0.82 (90)	0.81 (irr)
$\mathrm{ZnPc}(t\text{-Bu})_4$	0.52 (90)	0.72 (130)

a) $E_{1/2}=(E_{\mathrm{pa}}+E_{\mathrm{pc}})/2$ (V vs. SCE). b) In dichloromethane. c) In pyridine. Scan rate=100 mV/s^{-1}. The values in parentheses denote ΔE_{p} (mV). The half-wave potentials were estimated from $E_{\mathrm{pa}}/2$ in the case of the irreversible oxidation steps.

The potential of $\mathrm{H_2Pc}(t\text{-Bu})_4$ in pyridine was shifted to the negative side compared with that in dichloromethane (Table 1). It was reported that the acidic protons of the phthalocyanine ring were dissociated in pyridine.[16] Then, the dissociation of the acidic protons resulted in an increase of the electron density on the phthalocyanine ring, leading to the facile oxidation of the ring. The potential of the cobalt complex was also extremely shifted to the negative side in pyridine. With the addition of $\mathrm{NOBF_4}$ into the solution, the Q band (660 nm) of the cobalt complex shifted to 679 nm without a decrease in its intensity. That is, the central cobalt(II) ion might have been oxidized to a trivalent state.[14] The low-spin cobalt(III) ion was stabilized by the coordination of pyridine, resulting in the promotion of the oxidation of the cobalt(II) ion. Moreover, it was notable that the zinc(II) complex showed a fairly large positive shift in the potential of pyridine, but the shifts of the nickel(II) and copper(II) complexes were not so remarkable.

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