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Partial Oxidation of [Octakis(dodecyloxy)phthalocyaninato]zinc(II) with 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone

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Synopsis. While an organic oxidant such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone oxidized [Zn{Pc($OC_{12}H_{25}$)$_8$}] in a chloroform solution, it did not oxidize $H_2Pc(OC_{12}H_{25})_8$ and [Cu{Pc($OC_{12}H_{25}$)$_8$}]. Oxidation was confirmed by the electronic and ESR spectra, as well as cyclic voltammograms. The electrical conductivity of the zinc(II) complex increased 10^5 times in partial oxidation.

The partial oxidation of metallophthalocyanines with iodine, bromine or nitrosyl tetrafluoroborate($NOBF_4$) significantly increased their electrical conductivity.[1] The electrochemical oxidation of the complexes was carried out in solution, resulting in single crystals which exhibit metallic conductivity.[2] The conductivity also increased in a partial reduction of the complexes with metallic potassium or sodium dithionite.[3,4] Furtheremore, phthalocyaninatosilicon(IV) polymers bridged by a halogen or an oxygen atom were prepared, and showed good conductivity under partial oxidation.[5]

It was recently reported that metallophthalocyanine complexes with long-chain alkyl or alkoxy substituents were transformed to discotic mesophase.[6,7] It is of interest to prepare the oxidized metallophthalocyanine derivatives which show conductivity in the mesophase.[8] We previously reported the chemical oxidation of tetra-*t*-butylphthalocyanine, $H_2Pc(t\text{-}Bu)_4$, and its metal(II) complexes with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to confirm their oxidation behavior by chemical oxidants.[9] This paper describes the chemical oxidation of [octakis(dodecyloxy)phthalocyaninato]zinc(II), [Zn{Pc($OC_{12}H_{25}$)$_8$}], with DDQ, and its conductivity both in the solid state and in the mesophase.

Experimental

Materials. $H_2Pc(OC_{12}H_{25})_8$, [Cu{Pc($OC_{12}H_{25}$)$_8$}], and [Zn{Pc($OC_{12}H_{25}$)$_8$}] were prepared in a similar method described in the literature.[7] Bu_4NBF_4 was prepared and purified using the method shown in a text book.[10] DDQ was recrystallized from benzene under an argon atmosphere.

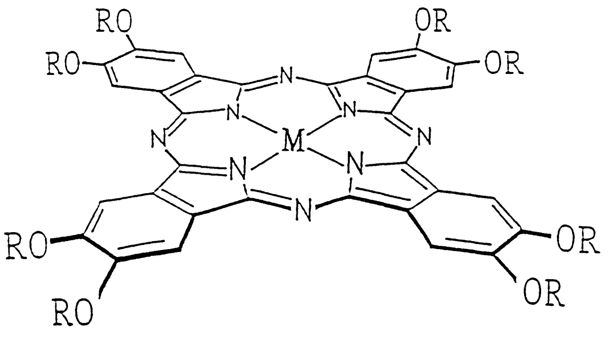

Fig. 1. Schematic representation of the [M{Pc(OR)$_8$}] complex:
OR=$OC_{12}H_{25}$.

Partial Oxidation. The zinc(II) complex was dissolved into a solvent mixture of chloroform and hexane (7 : 3, v/v), to which the chloroform solution of DDQ was added dropwise under a nitrogen atmosphere. The mixture was subsequently stirred at room temperature for several min, and then the dark-black precipitates were obtained upon the concentration of the solution under reduced pressure. The oxidized complex was dried at room temperature under reduced pressure.

Measurements. The electronic spectra in solution were measured on a Hitachi 200-20 spectrophotometer. The ESR spectra were measured with a JEOL-IX spectrometer. Cyclic voltammetric measurements were performed in a chloroform solution containing Bu_4NBF_4 (0.1 mol dm^{-3}) on a Hokuto Denko HA-501 potentiostat with a Hokuto Denko HF-201 function generator.[9] Differential scanning calorimetry experiments were carried out on a Shimadzu DSC-50. Conductivity measurements of pressed pellets were carried out with a two-probe method.

Results and Discussion

By the addition of adequate amounts of DDQ, the green solution of [Zn{Pc($OC_{12}H_{25}$)$_8$}] changed to reddish purple; in the absorption spectrum, the intensity of the Q band at 680 nm decreased, while new bands appeared at 545 and 721 nm. On the other hand, the spectra of the green solution of $H_2Pc(OC_{12}H_{25})_8$ or its copper(II) complex did not change upon the addition of DDQ.

When the zinc(II) complex was oxidized with DDQ in a chloroform solution, two ESR signals arising from cationic phthalocyanine ring and anionic DDQ radicals were observed at g=2.002 (line width=7 G) and 2.005 (3 G) at room temperature, respectively. These results show that although the phthalocyanine ring of the zinc(II) complex was oxidized by DDQ, those of $H_2Pc(OC_{12}H_{25})_8$ and its copper(II) complex were not oxidized, which is consistent with the oxidation results for $H_2Pc(t\text{-}Bu)_4$ and its metal(II) complexes.[9]

Cyclic voltammograms of the phthalocyanine derivatives exhibited four redox couples. The half-wave potentials of the first step on the oxidation side are listed in Table 1 to confirm the chemical oxidation. By considering the potential of the first reduction step of DDQ (0.59 V vs. SCE), the zinc(II) complex was only oxidized by DDQ, which is consistent with the results of the absorption and ESR spectra.

$H_2Pc(OC_{12}H_{25})_8$ and its copper(II) and zinc(II) complexes showed endothermic peaks at 93, 100, and 107 °C, respectively, indicating their transition to the mesophase.[6,7] The zinc(II) complex doped by DDQ (20 mol %) showed endothermic peaks at 100 °C, and its

Table 1. Electrochemical Results in Chloroform ($E_{1/2}$ (V) vs. SCE)

$H_2Pc(OC_{12}H_{25})_8$	$[Cu\{Pc(OC_{12}H_{25})_8\}]$	$[Zn\{Pc(OC_{12}H_{25})_8\}]$	DDQ
0.86[a]	0.87[a]	0.44[a]	0.59[b]
(0.14)	(0.15)	(0.10)	(0.10)

a) Couple for c^+/c. b) Couple for DDQ/DDQ^-. Parentheses denote ΔE_p (V). Scan rate=100 mV s^{-1}.

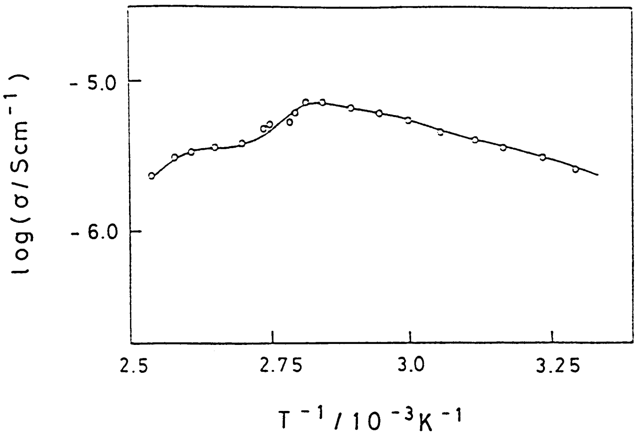

Fig. 2. Specific conductivity (σ/S cm^{-1}) vs. reverse temperature. The concentration of the added DDQ was 20 mol %.

peak reappeared with rising temperature, although the peak shifted to 95 °C with some broadening. Upon the addition of DDQ (more than 20 mol %), the sample did not show the peak.

Although the $[Zn\{Pc(OC_{12}H_{25})_8\}]$ complex was an insulator ($\sigma < 10^{-11}$ S cm^{-1} at room temperature) the complex increased its conductivity (2.5×10^{-6} S cm^{-1} at room temperature) in partial oxidation by DDQ (20 mol %) (Fig. 2). In partial oxidation of the complex with $NOBF_4$ (15 mol %), the conductivity was about 10^{-3} times that of the complex doped by DDQ (20 mol %).[11] This may result from the unsuitable position of the tetrafluoroborate anion in the oxidized sample. It was also reported that the conductivity of [bis{octakis(octadecyloxymethyl)phthalocyaninato}lutetium(III)] partially oxidized by phenoxathin hexachloroantimonate (80 mol %) was 1.6×10^{-7} S cm^{-1} at 60 °C.[8] The long paraffinic chains of these phthalocyanine complexes promote the formation of a hexagonal columnar,[12] which might increase the intracolumnar conduction.

The conductivity of the $[Zn\{Pc(OC_{12}H_{25})_8\}]$ complex doped by DDQ increased with rising temperature, but decreased above 80 °C (Fig. 2). The ESR signal arising from the anionic DDQ radical diminished above 80 °C, while that from the cationic phthalocyanine radical remained. The DDQ radical might form an ESR silent dimer upon heating, as shown in the case of cosublimation of [fluoro(phthalocyaninato)aluminium(III)] and DDQ.[13] Although the conductivity seems to decrease with an increase of the temperature in the mesophase, details are presently unknown, because some deformation of the specimen might occur and cause a decrease in the conductivity.

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