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Aggregation Effects on Electrochemical and Spectroelectrochemical Properties of [2,3,9,10,16,17,23,24-Octa(3,3-dimethyl-1-butynyl)phthalocyaninato]cobalt(II) Complex

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The title complex, [Co(odmbpc)], which is a single isomer and is highly soluble in common organic solvents, has been prepared and investigated electrochemically and spectroelectrochemically in dichloromethane solutions. The cyclic voltammograms of this complex at a concentration of ca. 6×10^{-5} mol dm^{-3} exhibited two reversible reduction waves at $E_{1/2} = -0.67$ V (vs. ferrocenium$^+$/ ferrocene) and -1.74 V, which were attributed to cobalt-centered and triple-bond-centered (in a peripheral substituent) reductions, respectively, and three quasi-reversible oxidation waves at 0.26, 0.46, and 0.74 V, the former two and the latter one of which were attributed to phthalocyanine-chromophore-centered and cobalt-centered oxidations, respectively. Some of these assignments were supported by the electronic absorption spectra of the electro-generated species. The first reduction wave was not observed at 6×10^{-4} mol dm^{-3} until the applied potential was swept to the second reduction wave. Nevertheless, under the same conditions, the controlled-potential electrolyses in an optically transparent thin-layer electrode at potentials around the first reduction wave gave rise to drastic spectral changes without any preliminary electrolysis at potentials around the second reduction wave. Such strange phenomena are discussed in terms of molecular aggregation of the complexes in solutions. The peripheral alkynyl group has been found to be slightly electron-donating.

The electrochemistry of metallophthalocyanines (MPcs) has attracted much attention in relation to photosensitization,[1] electrocatalytic properties,[2] electrochromic properties,[3] semiconductivity,[4] and so on. The redox potentials of numbers of MPcs, where the central metals may be redox active or not, have been reported.[5,6] Although spectroelectrochemistry using optically transparent thin-layer electrode (OTTLE) techniques have played an important role in assigning them,[7—10] limited solubility of unsubstituted MPcs in electrochemically useful solvents has made it difficult to carry out such spectral measurements because of short optical path lengths of OTTLE cells.[11,12] In order to improve the solubility of phthalocyanines, some research groups have tried to introduce bulky groups, such as the *t*-butyl[13] or the neopentyloxy group,[14] into the peripheral benzene rings of the MPc macrocycle (earlier spectroelectrochemical research has accomplished mostly on tetra-neopentyloxy-substituted MPcs).[7—9] This did improve the solubility of MPcs in common organic solvents but such MPcs are mixtures of four geometric isomers because each of the four benzene rings has only one substituent. These isomers will all have similar spectra and redox potentials and hence the presence of isomers will not give rise to any serious problem in conventional electronic spectral measurements under conditions where molecular aggregation is not significant. However, this is not true under conditions where conventional electrochemical or spectroelectrochemical measurements are carried out; this is because such measurements are usually done at much higher concentrations (in the order of 10^{-3}—10^{-4} M (1 M = 1 mol dm^{-3}) than spectral measurements (in the order of 10^{-5}—10^{-6} M), and hence aggregation, which is common in the field of phthalocyanine chemistry,[15—19] will occur under the former conditions. Possible conformations of a specific aggregate should be influenced by which of the possible four isomers is concerned because the cofacial aggregate is apparently not formed with equal ease by all geometric isomers.[19] Each of such aggregates may have different optical or redox properties because the difference in conformation may give rise to a different degree of coupling between the two macrocycles and higher aggregation will make the problem more complicated. Therefore, it is important in measurements at high concentrations to employ MPcs which are single isomers. Quite recently, octaalkynylphthalocyanines and their zinc complexes have been synthesized in our laboratory.[20] They are single isomers and highly soluble in common organic solvents and hence these types of compounds should be useful in electrochemical and spectroelectrochemical investigations for the reasons described above. In this paper, we wish to report the electrochemistry and spectroelectrochemistry on the title complex (Fig. 1).

During the course of this study on the title complex, we have found that the electrochemical behavior of the title com-

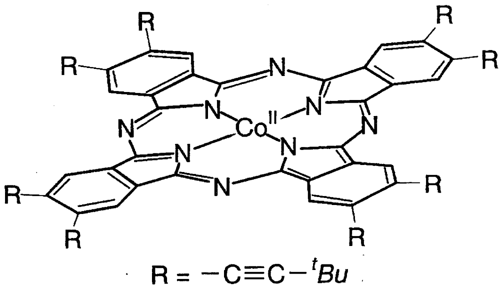

Fig. 1. The molecular structure of [Co(odmbpc)].

plex in more concentrated solutions was different from that in less concentrated solutions, as will be described below. Since the complex is a single isomer, any possibility of the presence of aggregates composed of different isomers can be safely ruled out. Therefore, we have only to take aggregates, to which only one isomer will contribute, into consideration. In this paper, we will also report the concentration-dependent electrochemical behavior of the title complex and will discuss the observation in terms of aggregation of complex molecules.

Experimental

Materials. Metal free 2,3,9,10,16,17,23,24-octa(3,3-dimethyl-1-butynyl)phthalocyanine, H_2(odmbpc), its zinc complex, [Zn(odmbpc)], and their precursors were prepared in the same manner as described in the literature.[20] Dichloromethane (DCM), used for electrochemical and spectroelectrochemical measurements, was dried and distilled over diphosphorus pentaoxide under an argon atmosphere just prior to use. The other solvents used were reagent grade and were used as received unless otherwise noted. Commercially available tetrabutylammonium hexafluorophosphate (TBAH), which was used as supporting electrolytes for electrochemical and spectroelectrochemical measurements, was twice recrystallized from ethyl acetate/hexane. Commercially available ferrocene, used for the calibration of potentials, was purified by sublimation three times.

Synthesis of [2,3,9,10,16,17,23,24-Octa(3,3-dimethyl-1-butynyl)phthalocyaninato]cobalt(II). To 10 ml of absolute ethanol was added a lithium-wire (100 mg) and the solution was refluxed under an argon atmosphere for 30 min. After all of the lithium reacted, the solution was allowed to cool to room temperature and then was added dropwise to a suspension of H_2(odmbpc) (30 mg) in dry THF (5 ml), which had been distilled over a mixture of sodium and benzophenone under an argon atmosphere. A solution of Li_2(odmbpc) was prepared in this way. To this solution was added 150 mg of anhydrous $CoCl_2$ and the solution was refluxed at 80 °C for 2 h under an argon atmosphere. The reaction was monitored by TLC with hexane/toluene (1 : 3) as eluent and by the electronic absorption spectra of the reaction mixture. After unreacted H_2(odmbpc) had disappeared on a TLC, the reaction mixture was allowed to cool to room temperature, and then the crude product was precipitated by the addition of 20 ml of 50% methanol/water containing 1 ml of concentrated hydrochloric acid. The precipitate was collected by centrifugation. The solids were dissolved into a small amount of chloroform and were precipitated by the addition of acetonitrile. This procedure was repeated until the supernatant was colorless. The crude products were pre-adsorbed on classical silica gel and then flash-chromatographed over a silica-gel column. A small amount of unreacted green H_2(odmbpc) (ca. 10% vs. the starting phthalocyanine) and then a large amount of blue [Co(odmbpc)] were eluted out with hexane/toluene (1 : 1) and (1 : 3), respectively, in this order. Some yellowish-brown material remained on the top of the silica-gel column, which did not move even with chloroform as eluent.[21] The chromatographic procedure was repeated twice until no H_2(odmbpc) was detected in the eluate. The blue chromatographic band containing the cobalt complex was collected and the solvent was evaporated under reduced pressure. The solid was dissolved into a small amount of toluene and was again flash-chromatographed over a silica-gel column using hexane/toluene (1 : 3) as eluent. After the blue band passed, no colored species remained on the silica-gel column. The solvent was evaporated under reduced pressure; the solids were recrystallized from toluene/hexane to give blue crystals of the desired [Co(odmbpc)]: Yield, 16 mg (51% on the basis of the starting H_2(odmbpc)). Found: C, 79.28; H, 6.80; N, 9.20%. Calcd for $C_{80}H_{80}N_8Co$: C, 79.25; H, 6.65; N, 9.24%. FAB MS (M, 1213).

Measurements. Electronic absorption spectra were recorded on a Hitachi U-3500 spectrophotometer for conventional spectral measurements. Magnetic circular dichroism (MCD) spectra were measured by a JASCO J-720 spectropolarimeter equipped with a 0.45-T permanent magnet. The voltammetric measurements were performed with either a Hokuto Denko HA-501 potentiostat/galvanostat or a PAR Model 174 potentiostat. Differential pulse voltammetry (DPV) experiments were performed with a PAR Model 174 potentiostat. Conventional three-electrode-cells were used, where platinum disk, platinum wire, and AgCl-coated Ag-wire were used as working, auxiliary, and pseudo reference electrodes, respectively. The controlled-potential electrolyses were carried out within a gas tight optically transparent thin-layer electrode cell (optical path length = 0.2 mm, Pt minigrid (32 wires/cm) working and auxiliary electrodes, AgCl/Ag pseudo-reference electrode)[12] equipped with quartz windows for measurements of electronic absorption spectra of electrochemically-generated species. All the spectroelectrochemical measurements were performed with a Hokuto Denko HA-301 potentiostat/galvanostat and a Perkin–Elmer lambda-5 spectrophotometer equipped with a 3600 data station and attached to an MS-DOS personal computer under the following conditions: 6×10^{-4} M [M(odmbpc)] (where M = cobalt(II) and zinc(II)) and 0.1 M TBAH in DCM saturated with dry argon gas. The potentials were calibrated by ferrocenium$^+$/ferrocene (Fc^+/Fc) redox couple as an internal standard. Hereafter, all of the potentials are referred to Fc^+/Fc. All of the measurements were done at room temperature (24±1 °C).

Results

The [Co(odmbpc)] complex was prepared from the corresponding metal free phthalocyanine via its lithium salt. The complex was highly soluble in common organic solvents, such as toluene, benzene, chloroform, DCM, ether, THF, and acetone, and slightly soluble even in hexane, but was insoluble in acetonitrile and ethanol. The complex was stable in those solvents except for aged THF, in which the complex was rapidly bleached, and also was stable against water or acid; no demetallation was observed by the contact (up to 1 h) with concentrated hydrochloric acid or water.

Although the electronic absorption and MCD spectra of [Co(odmbpc)] (Fig. 2) in DCM solutions are normal for known MPcs,[22] its electronic absorption spectra were concentration-dependent, as is shown in Fig. 3. Absorbance

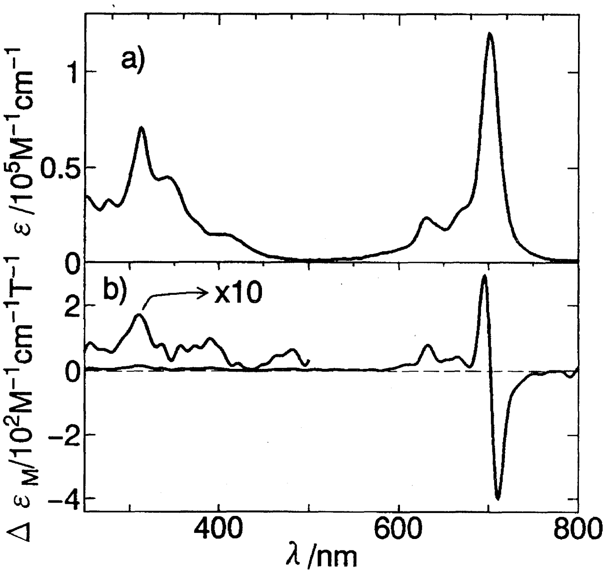

Fig. 2. The a) electronic absorption and b) MCD spectra of [Co(odmbpc)] in a DCM solution ([complex] = 2.77×10^{-6} M).

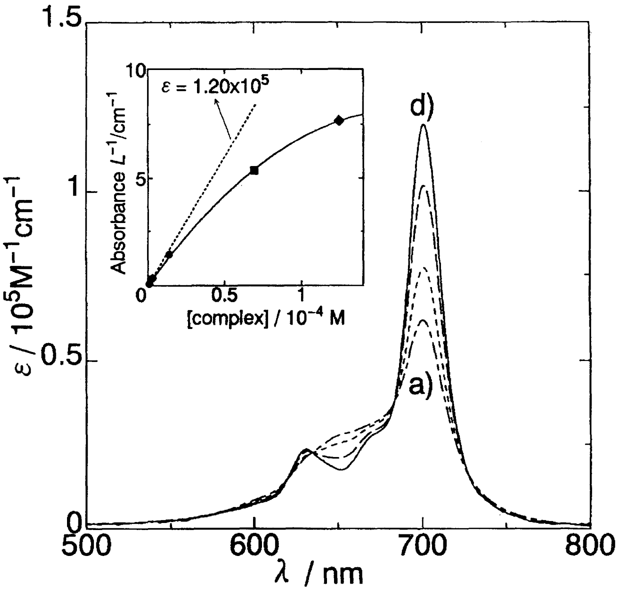

Fig. 3. Concentration dependence of electronic absorption spectra of [Co(odmbpc)] in DCM solutions (Q-band region): a) 1.24×10^{-4} M; b) 6.93×10^{-5} M; c) 1.39×10^{-5} M; d) 2.77×10^{-6} M. No observable spectral change was detected in the Soret region. The inset shows Beer's law plots (absorbance at the 701-nm Q-band of [Co(odmbpc)] monomer); the broken straight line has a slope of $\varepsilon = 1.20\times10^{5}$ M^{-1} cm^{-1} (Beer's law behavior for [Co(odmbpc)] monomer); (●) optical path length (L) = 1 cm; (■) 0.2 cm; (◆) 0.1 cm.

at the most intense band at 701 nm (so-called Q-band) did not obey Beer's law above 1×10^{-5} M and its apparent molar extinction coefficient at the Q band became smaller with an increase in the concentration of the complex (the inset in Fig. 3). In turn, new absorption bands arose at the blue edge of the Q-band above 2.77×10^{-6} M and grew in intensity with an increase in concentration. No concentration-dependence was observed in the Soret region (250—450 nm). These concentration-dependent spectral changes are typical of molecular aggregation of known MPcs.[15,16] No concentration-dependent spectral change was detected below 2.77×10^{-6} M (the electronic and MCD spectra shown in Fig. 2 were measured at 2.77×10^{-6} M).

Figure 4 shows typical cyclic voltammograms of [Co(odmbpc)] in a DCM solution containing 0.1 M TBAH as supporting electrolyte ([complex] = ca. 6×10^{-5} M). Two reduction waves (**a** and **b**) and three oxidation waves (**c**, **c′**, and **d**) were observed. The reduction waves, **a** ($E_{1/2} = -1.74$ V) and **b** ($E_{1/2} = -0.67$ V), were fully reversible; peak current ratios (i_p^a/i_p^c) were essentially unity irrespective of scan rates (ν) in the 20—200 mV s^{-1} range; $i_p\nu^{-1/2}$ values were almost constant; and potential separations (ΔE_p) between cathodic and anodic peaks were $60 < \Delta E_p/\mathrm{mV} < 84$ in the ν range studied. In the positive scan, the following three quasi-reversible oxidation waves were observed; **c** ($E_{1/2} = 0.26$ V; $\Delta E_p = 60$ mV), **c′** ($E_{1/2} = 0.46$ V; $\Delta E_p = 70$ mV), and **d** ($E_{1/2} = 0.74$ V; $\Delta E_p = 90$ mV; $i_p^a/i_p^c = 1$). Rotating-disk-electrode voltammograms ($\nu = 20$ mV s^{-1}) showed that the couples **b** and **c**+**c′** were equal in magnitude of limiting current (i_L) and that the i_L values of the (**c**+**c′**) were proportional to the square root of the rotation rates. The DPV experiments showed that the relative currents of **c** and **c′** were scan-rate-dependent; the current at **c** was much greater than at **c′** at a scan rate of 5 mV s^{-1} while the wave **c′** almost disappeared at 2 mV s^{-1}, and re-reduction peak of **c′** was not observed

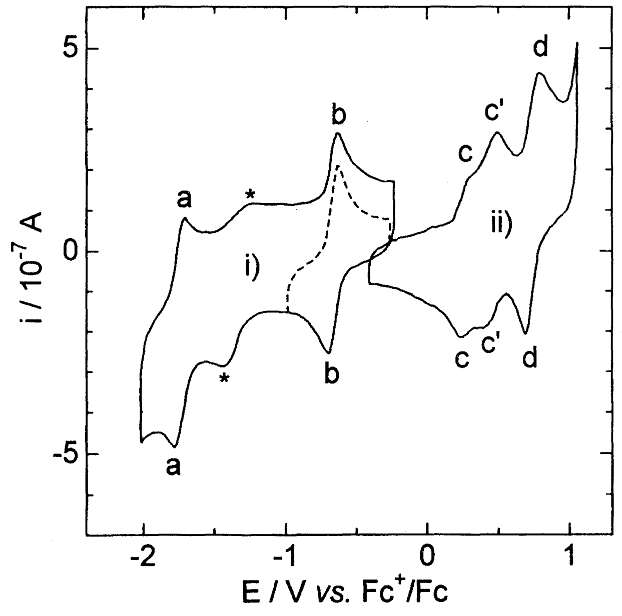

Fig. 4. Typical cyclic voltammograms of [Co(odmbpc)] in a DCM solution containing 0.1 M TBAH as supporting electrolytes ([complex] = 6×10^{-5} M): i) negative and ii) positive scans ($\nu = 100$ mV s^{-1}). **a**; alkynyl-centered reduction, **b**; cobalt-centered reduction, **c** and **c′**; pc-ring-oxidation, and **d**; cobalt-centered oxidation; see text for more details. The asterisked waves are background. The broken line around the **b** is the first scan.

at reverse scans. The ratio in current heights given in Fig. 4 indicates that the numbers of electrons involved in the **a**, **b**, **c**+**c**′, and **d** steps are identical.

On the other hand, the first wave **b** was not observed until the potential applied was swept to the second wave **a** under the same conditions but at a higher concentration (6×10^{-4} M). Figure 5 shows the negative scans of the cyclic voltammogram of the same compound. The current heights at **a** on the third, fourth, and fifth scans were 86, 79, and 74% of that on the second scan (the potential applied on the first scan was not swept to **a**), respectively, and thereafter current heights reached almost constant values. In turn, the wave **b** gradually grew in its peak current, with its potential separation (ΔE_p) values being smaller (closer to 60 mV), as scans were repeated.

The electronic absorption spectral changes of [Co(odmbpc)] in a DCM solution during the controlled-potential electrolyses at potentials around the waves **b** and **c** (and **c**′) were reversible and are shown in Figs. 6 and 7, respectively ([complex] = 6×10^{-4} M). Although bulk-electrolyses around the wave **a** did not give rise to any detectable spectral change, reoxidation at the positive of the wave **b** did not reproduce the initial spectrum but a spectrum similar to that of an unaggregated phthalocyanine. Controlled-potential electrolyses around the wave **d** gave rise to irreversible spectral changes (not shown).

Figure 8 shows the electronic absorption spectra of [Zn(odmbpc)] in DCM solutions at various concentrations. Absorbance at the 711-nm Q-band did not obey Beer's law; the plots deviated from linearity above 5×10^{-6} M. As is the case for [Co(odmbpc)], the concentration-dependence is typical of molecular aggregation of known MPcs.[15,16)]

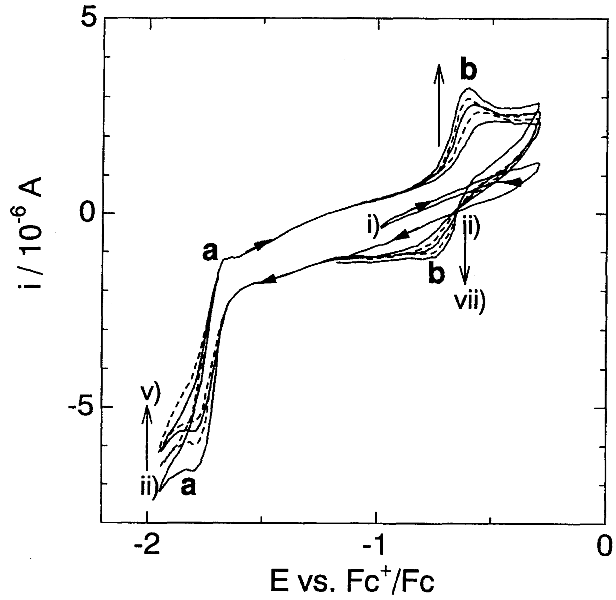

Fig. 5. Negative scans of the cyclic voltammogram ($v = 200$ mV s^{-1}) of [Co(odmbpc)] in a DCM solution containing 0.1 M TBAH as supporting electrolytes ([complex] = 6×10^{-4} M); i—vi) the first–sixth scans, and vii) the twelfth scan, respectively. The arrows indicate the direction of the changes. The waves **a** and **b** involve alkynyl-group-reduction and cobalt (II/I) process, respectively; see text for more details.

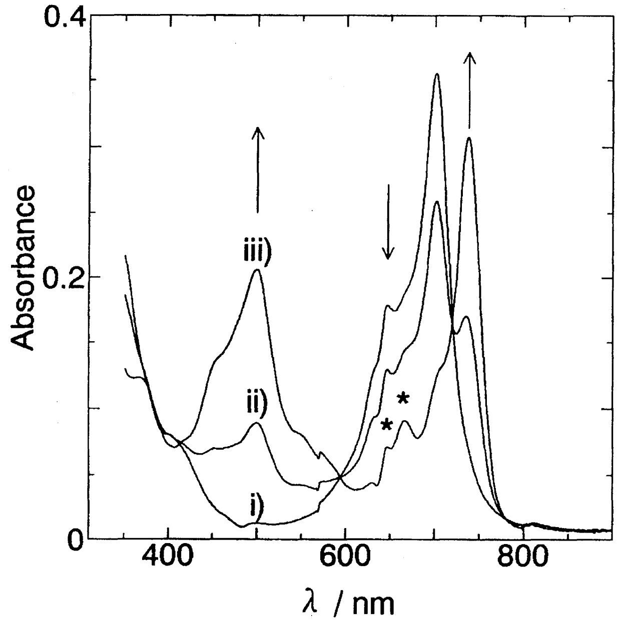

Fig. 6. Spectral changes of [Co(odmbpc)] in a DCM solution containing 0.1 M TBAH as supporting electrolytes ([complex] = 6×10^{-4} M) during the electrolyses at potentials around the first reduction wave **b**; i) no potential applied; ii) electrolyzed at −0.69 V; and iii) −0.79 V). The asterisked signals are artifacts generated by the spectrometer used.

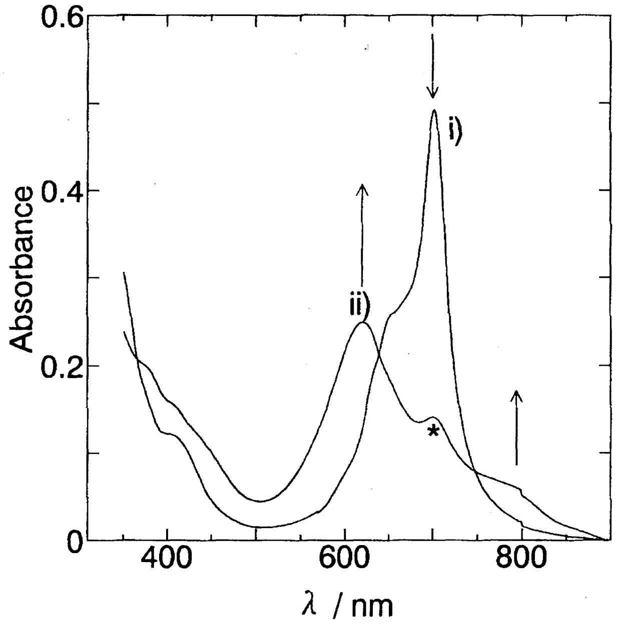

Fig. 7. Spectral changes of [Co(odmbpc)] in a DCM solution containing 0.1 M TBAH as supporting electrolyte ([complex] = 6×10^{-4} M) i) no potential applied and ii) at a potential positive of the second oxidation waves **c**′. The asterisked peak is due to residual initial species.

A typical cyclic voltammogram (Fig. 9) of [Zn(odmbpc)] in a DCM solution containing 0.1 M TBAH as support-

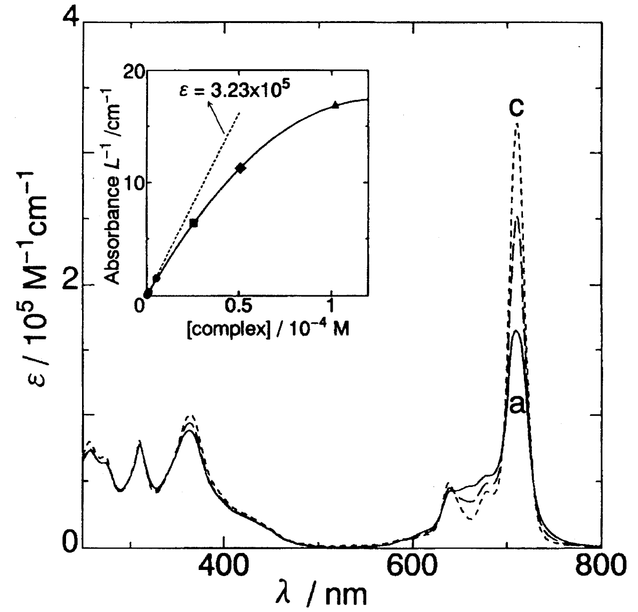

Fig. 8. Electronic absorption spectra of [Zn(odmbpc)] in DCM solutions at various concentrations; a) 1.02×10^{-4} M, b) 2.54×10^{-5} M, c) 1.02×10^{-6} M. The inset shows Beer's law plots (absorbance at 711-nm Q-band of [Zn(odmbpc)] monomer); the broken straight line in the inset has a slope of $\varepsilon = 3.23\times10^{5}\,M^{-1}\,cm^{-1}$ (Beer's law behavior for [Zn(odmbpc)] monomer); (●) optical path length (L) = 1 cm; (■) 0.5 cm; (◆) 0.2 cm; (▲) 0.1 cm.

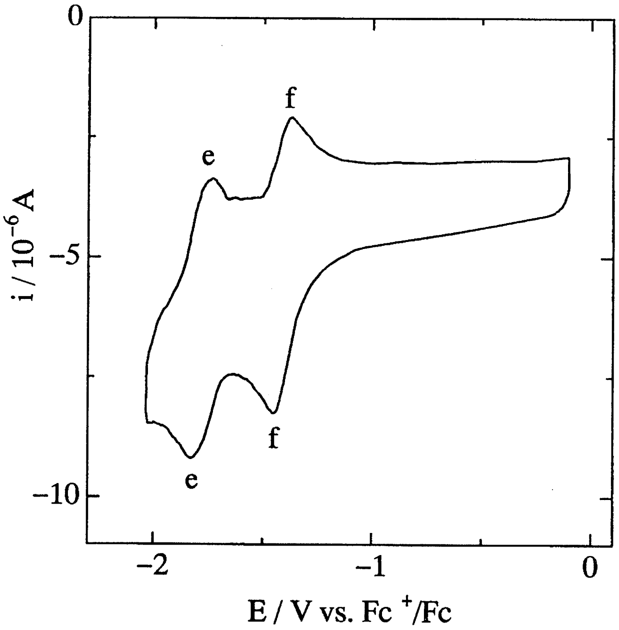

Fig. 9. A typical cyclic voltammogram (negative scan; v = 100 mV s^{-1}) for [Zn(odmbpc)] ([complex] = 2×10^{-4} M) in a DCM solution containing 0.1 M TBAH as supporting electrolyte. **e**; pc-ring-centered reduction and **f**; alkynyl-centered reduction; see text for more details.

ing electrolyte ([complex] = ca. 2×10^{-4} M) showed two reversible reduction waves **e** and **f** at $E_{1/2} = -1.80$ V and $E_{1/2} = -1.41$ V), respectively; peak current ratios (i_p^a/i_p^c) were essentially unity irrespective of scan rates (v) in the 20—200 mV s^{-1} range; $i_p v^{-1/2}$ values were almost constant; and potential separation (ΔE_p) between cathodic and anodic peaks were $65 < \Delta E_p/\text{mV} < 80$ in the v range studied. The ratio in current height at **e** and **f** indicates that identical numbers of electrons are involved.

The electronic absorption spectral changes of [Zn(odmbpc)] in a DCM solution during the controlled-potential electrolyses at potentials around the waves **e** and **f** are shown in Fig. 10a and 10b, respectively, which were observed using the OTTLE cell ([complex] = 6×10^{-4} M).

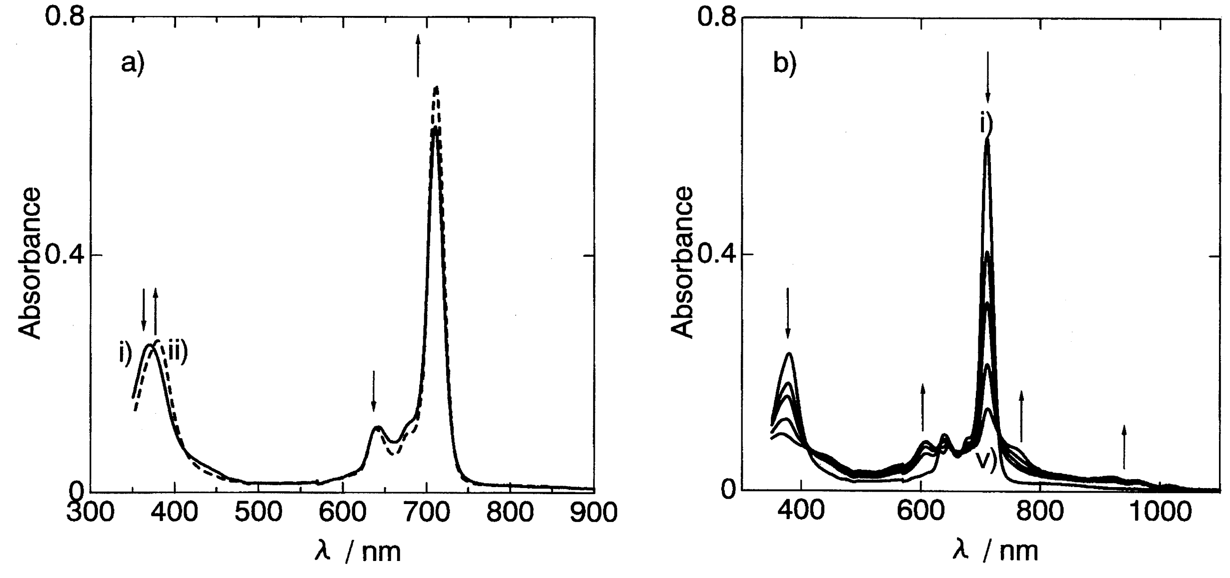

Fig. 10. Spectral changes of [Zn(odmbpc)] in a DCM solution containing 0.1 M TBAH as supporting electrolyte ([complex] = 6×10^{-4} M) during the electrolyses a) at potentials around the first reduction wave **f**; i) no potential applied; ii) electrolyzed at −1.60 V; and b) at potentials around the second reduction wave **e**; i) electrolyzed at −1.60 V; ii) −1.75 V, iii) −1.81 V, iv) −1.86 V, and −1.91 V.

Discussion

Synthesis. The [Co(odmbpc)] complex was successfully synthesized by metal-insertion into its parent H_2(odmbpc) through Li_2(odmbpc) although quantitative metallation was not achieved. Prolonged reaction time up to 12 h resulted in a low yield of the complex (10%) probably due to decomposition of the complex formed. Some portion of the starting H_2(odmbpc) still remained unmetallated also in this case. Although we could not verify that the complex was a single isomer by NMR spectroscopy because of its paramagnetism due to cobalt(II), Terekhov et al. confirmed that the parent H_2(odmbpc) and its zinc complex were single isomers.[20] Decomposition or polymerization of the peripheral substituents, especially of the triple bond, could have occurred in some molecules during the metallation, but both the elemental analytical and mass-spectral data were in good agreement with the theoretical values. Therefore, we may conclude that the finally obtained species is the desired complex and is a single geometric isomer.

Spectroscopy. The electronic absorption spectrum of [Co(odmbpc)] in DCM solution (Fig. 2a) is typical of the known MPcs,[22] but the Q-band ($\lambda_{max} = 701$ nm) is considerably bathochromically shifted from those of unsubstituted,[23] alkyl-,[24], and alkoxy-substituted cobalt(II)-phthalocyanine complex[25] by approximately 900 cm^{-1} as is the case for the corresponding metal free ligands and zinc complexes.[26] In the MCD spectrum (Fig. 2b), a distinctive Faraday *A*-term was observed, which was centered at the Q-band maximum, indicating that this transition is orbitally doubly degenerate in its excited state.[19] This is reasonable because the eight alkynyl groups are symmetrically located and hence the [Co(odmbpc)] molecule has D_{4h} symmetry (in MPcs with D_{4h} symmetry; the Q-band is assigned as a transition from nondegenerate $\mathbf{a_{1u}}$ to doubly degenerate $\mathbf{e_g}$ orbital in character[19]). As is shown in Fig. 3, the electronic absorption spectra of [Co(odmbpc)] in the Q region were concentration-dependent. The apparent molar extinction coefficients at the Q-band maximum decreased with an increase in [Co(odmbpc)] concentration, but those at the blue of the Q-band increased. This can be explained in terms of aggregation of [Co(odmbpc)] molecules in solutions, as is common in the field of phthalocyanine chemistry.[15—19] The blue-shift, broadening, and lowering in intensity of the Q-band clearly indicate molecular aggregation in a face-to-face fashion.[19]

Electrochemistry and Spectroelectrochemistry. The cyclic voltammograms of [Co(odmbpc)] at 6×10^{-5} M exhibited two reversible reduction waves in negative scans, as shown in Fig. 4. The first reduction wave **b** is readily assigned as cobalt-centered (i. e., cobalt(II) to cobalt(I)). Controlled-potential electrolysis at potentials around wave **b** gave rise to drastic spectral changes, as shown in Fig. 6, typical of $Co^I(pc^{2-})$[27] formation.[7,28,29] The spectrum is characterized by the appearance of an intense band at 500 nm, which is attributed to an MLCT from the cobalt(I) ($d_{xz/yz}$) to pc^{2-} ($\mathbf{b_{1u}}(\pi^*)$),[28,29] and by a slight red-shift and lowering in intensity of the Q-band. The appearance of an obvious Q-band reveals that the electrogenerated species disaggregated to monomers, probably due to electrostatic repulsion between the negatively charged molecules.

The second wave **a** is attributable to a triple-bond-centered reduction (in one of the peripheral substituents) because essentially no spectral change was observed during the bulk-electrolysis around the **a**; if the reduction were phthalocyanine-chromophore-centered (that is, pc^{2-}/pc^{3-})[27], drastic spectral changes both in intensity and peak positions would be observed.[6b,9,28,30] Thus, the redox couple **a** is not related to a reduction of either the chromophore or cobalt. This assignment of **a** is supported by electrochemical and spectroelectrochemical studies of the zinc analogue under the same conditions. The negative scans in the cyclic voltammogram showed two reversible reduction waves **e** and **f**, which were assigned as alkynyl- and phthalocyanine-chromophore-centered reductions, respectively, on the basis of the spectroelectrochemical results (Fig. 10). The appearance of the two waves seems normal for the known zinc-phthalocyanines.[8,31] So far as the known zinc complexes are concerned,[5,8] both the two reduction waves are assigned as phthalocyanine-chromophore-centered (i.e., pc^{2-}/pc^{3-} and pc^{3-}/pc^{4-} couples).[27] However, this is not true in this case as is described below: The controlled-potential electrolysis at the first reduction wave **f** gave rise to a small spectral change; its Q-band grew in intensity (without any change in its peak wavelength) and sharpened, and the blue edge of the Q-band lowered in intensity (Fig. 10a). In addition, the absorption band at 363 nm slightly blue shifted. On the basis of the very small changes observed when the zinc and cobalt complexes are reduced at **a** and **f** respectively, we conclude that a peripheral alkyne is being reduced. Akiyama et al. have reported that a quasi-reversible one-electron reduction of an alkynyl group attached to aromatic rings for some compounds. They indicated that the half-wave potentials were -1.305—-1.434 V vs. Ag^+/Ag in DMF,[32] the values of which were close to those of the waves **a** and **f** in this work.[33] Thus, it is not surprising that the alkynyl group in the compounds in this work was reduced before the phthalocyanine-chromophore. In addition, since the eight peripheral alkynyl groups in [M(odmbpc)] interact with each other via an extended π-conjugation system, it is not surprising that the eight alkynyl groups are stepwise reduced. There must be some chemical changes after the reduction at **a** on the bulk-electrolysis time scale because reoxidation positive of **b** did not reproduce the initial spectrum although the wave **a** was fully reversible on the cyclic-voltammetry time scale (Fig. 4).

On the contrary, at 6×10^{-4} M, the first reduction wave **b** was not observed until the potential applied was swept to the second reduction wave **a**, as is shown in Fig. 5. Nevertheless, the controlled-potential electrolysis of [Co(odmbpc)] under the same conditions at potentials around the wave **b** gave rise to the drastic spectral changes characteristic of Co^Ipc^{2-} formation (Fig. 6). That is, a reduction of the central cobalt did occur at potentials around the wave **b** on the bulk-electrolysis time scale.

The appearance of wave **b** at low concentration and its absence on the first scan at higher concentration must be due to aggregation effects. In the unaggregated species the cobalt(II) is accessible and the cobalt(II/I) process is kinetically fast, while in the aggregated species, the cobalt is less accessible such that some disaggregation must occur prior to reduction. In order to explain the difference in the kinetic rates of the cobalt(II/I) processes, let us consider the presence of columnar aggregates of [Co(odmbpc)] at the higher concentration. Although such a columnar model may be an oversimplification, the presence of cofacially-aggregated species at concentrations used for electrochemical and spectroelectrochemcial measurements is spectrophotometrically evident. A similar model has been proposed elsewhere.[20,34] In such columnar aggregates, the cobalt ions, which are located at the center of the macrocycles, are sterically shielded from the outer environment. Therefore, in such aggregates, the reduction of the central cobalt ions at the electrode surface must be sterically hindered and hence the cobalt(II/I) process must be kinetically too slow to be observed on the cyclic voltammetry time scale. However, since bulk-electrolyses require a much longer time for the cobalt ions in the columnar polymers (or oligomers) to be electrolyzed than cyclic voltammetry does, it is reasonable that the cobalt(II/I) process was observed in spectroelectrochemistry. When the degree of aggregation is small (relatively weak concentration) only dimer is likely to be present, while at higher concentrations, trimer, tetramer, and columnar species occur. The cobalt center will be much more accessible in the dimeric species.

On the other hand, as is shown in Fig. 5, the cyclic voltammogram showed a reversible wave **b** (cobalt(II/I) process) once the potential applied was swept to the negative of the wave **a**. This can be explained as follows; new species, which formed at the wave **a**, has a kinetically faster cobalt(II/I) process than the initial species (it should be noted that the rate of the cobalt(II/I) process of the new species is comparable to that of the initial species at the lower concentration (at 6×10^{-5} M; Fig. 4)). Whereas, in the initial species (columnar aggregates), the cobalt(II/I) process is kinetically so slow that the cobalt ions are not reduced on the cyclic voltammetry time scale as stated above and hence the highly aggregated initial species remain still neutral until the peripheral alkynyl group is electrolyzed at **a**. The wave **a** is attributable to alkynyl-centered-reduction as stated above. Since the triple bonds of the eight alkynyl groups are located at the periphery of the macrocycle and hence are much less sterically hindered than the central cobalt ions, the alkynyl groups must be readily electrolyzed at the electrode surface even in a columnar aggregate. However, once an alkynyl group is reduced, since each complex molecule will be negatively charged, the columnar polymers (or oligomers) will disaggregate due to electrostatic repulsion. Consequently, the central cobalt ions will be exposed to the electrode surface and hence will be reduced even on the cyclic voltammetry time scale. This mechanism is further supported by repeated scans of cyclic voltammogram as shown in Fig. 5. The current at **a** on the second scan was greater than that at the lower concentration; this should be because a reduction of cobalt(II) to cobalt(I) took place at **a** at the same time; as scans were repeated, the current at **a** became smaller and wave **b** grew in intensity with its potential separation (ΔEp) values being smaller (closer to 60 mV). This indicates that the cobalt(II/I) process became faster, suggesting that the steric hindrance around the cobalt ions became smaller.

In order to explain this phenomenon after the reduction at **a**, let us propose two possible mechanisms. One possibility is that reaggregation of the electro-generated species upon reoxidation at **a** was so fast that some of the species reaggregate before all of the cobalt(II) ions are exposed to the electrode surface (and hence all of the cobalt(II) ions are not reduced). Note that the species formed upon reoxidation at **a** is still neutral unless the central cobalt ions are exposed and hence reduced at the electrode. On the other hand, since some cobalts are reduced, the degree of aggregation for the new aggregated species must be lower than those for the initial aggregated species. This mechanism well explains the gradual decrease in peak current at the wave **a** and the gradual increase in that at **b**. This also explains the gradual decrease in the ΔE_p values for the wave **b** because repeated scans lower the degree of aggregation of the cobalt(II) species. Since the reduction center (cobalt(II) ion) of the lower aggregate is less sterically hindered than that of higher aggregate, the cobalt(II/I) process for the former is faster than that for the latter, giving rise to the smaller ΔE_p value: Note that when an electron-transfer at the electrode is slow relative to the diffusion of the electroactive species, the separation between $E_{1/2}$ and E_p value is larger than that for reversible system where the diffusion process is rate-determining. An alternative possible explanation is as follows: Reduction at the wave **a** causes formation of a reduced alkynyl species which disaggregates as shown by the fact that upon reoxidation positive of **b** one sees the electronic absorption spectrum of an unaggregated MPc species. The disaggregated species exhibits the cobalt(II/I) wave in the normal fashion. Repeated cycling around **a** and **b** causes a build up, in the vicinity of the electrode, of the disaggregated species and hence the wave at **b** grows in current intensity. The only problem with this alternative is that this mechanism involves some chemical changes upon the reduction at **a**. As shown in Fig. 4, the second wave **a** is fully reversible in relatively weak solutions and hence the second reduced species must be stable on the cyclic voltammetry time scale. However, the above two ideas are only suggestions since we have not been able to identify this disaggregated reduction product.

Such a phenomenon has not been reported for cobalt complexes of tetra-*t*-butyl-[35] or tetra-neopentyloxy-substituted phthalocyanine,[7] which are likewise highly soluble in common organic solvents but are mixtures of four regioisomers. We believe this is because not only the presence of the bulky substituents but also that of very similar isomers in those systems prevents higher aggregation.[36]

In the positive scans, three quasi-reversible oxidation waves were observed. The potential-controlled electrolyses around the waves **c** and **c′** gave rise to a drastic spectral change, as is shown in Fig. 7. The spectral change is characteristic of phthalocyanine-chromophore-centered oxidation, pc^-/pc^{2-}; the prominent Q-band disappeared and a marker band of phthalocyanine cation radical[7,29,37,38] was observed at 621 nm. The absence of an obvious band in the 800–900 nm region, which is attributed to the Q-band of the cation-radical monomer,[37] suggesting that the electro-oxidized species is strongly aggregated. Since the total number of electrons per molecule transferred during the electrolyses around **c** and **c′** was unity (the rotating-disk-electrode voltammetry revealed that the redox couple **b** and (**c**+**c′**) were equal in magnitude of limiting current), we believe that both the **c** and **c′** are phthalocyanine-chromophore-centered oxidation waves. The appearance of the double wave **c** and **c′** should be due to the difference between oxidations of bulk [Co(odmbpc)] aggregates and monomers; an aggregate is ring-oxidized at **c** to generate a $[Co^{II}(odmbpc^-)]_2{}^{2+}$ while the **c′** involves oxidation of a monomer leading to $[Co(odmbpc)]^+$ which immediately aggregates to $[Co^{II}(odmbpc^-)]_2{}^{2+}$. It is known that ring-oxidized MPcs tend to aggregate more strongly than unoxidized MPcs.[38] If this is true, the relative currents must depend on scan rates, with the first wave **c** being favored at lower scan rates, and rereduction of aggregate alone would be observed at reverse scans. This was confirmed by the DPV experiments. Thus, **c** and **c′** are assigned as oxidation of [Co(odmbpc)] aggregate and monomer, respectively. This mechanism is also consistent with the spectroelectrochemical data mentioned above. The half-wave potential of the pc^-/pc^{2-} redox couple (the wave **c′** is anodically shifted by 0.4 V from that of tetra-neopentyloxy-substituted cobalt(II) complex (+0.03 V in dichlorobenzene).[7] This is not surprising because the neopentyloxy group is a strong electron-donor. Lever has reported that half-wave potentials of the pc^-/pc^{2-} redox couple of cobalt(II)-phthalocyanines linearly depended on the total Hammet substituent constant.[39] Using his empirical equation and the half-wave potential of the pc^-/pc^{2-} redox couple in this work, the total Hammet constant in the [Co(odmbpc)] has been estimated to be -0.07 ± 0.09 (the half-wave potential of the **c′** was employed in this calculation); i.e., -0.01 ± 0.01 per one alkynyl group, indicating that the 3,3-dimethyl-1-butynyl group is slightly electron-donating. Hansch et al., have reported Hammet constants for some alkynyl groups, R–C≡C–: (0.51 for R = CF_3–; 0.23 for R = H–; 0.16 for R = C_6H_5–; and 0.03 for CH_3–)[40] and these values tend to decrease with a decrease in the Hammet values for the “R” groups themselves (0.54 for R = CF_3–; 0.00 for R = H–; −0.01 for R = C_6H_5–; and −0.17 for CH_3–).[40] Since the $C(CH_3)_3$– group (−0.20) is more electron-donating than the methyl group, this value is reasonable for the $C(CH_3)_3$–C≡C– group in this work.

There are three possibilities in assigning the second oxidation wave **d**. That is, the **d** can involve a cobalt-centered oxidation, (i.e. cobalt(III/II)), the phthalocyanine-chromophore (i.e., pc^0/pc^-) or one of the peripheral alkynyl groups. Since the bulk-electrolyses around the **d** gave rise to irreversible spectral changes, none of them can be completely excluded at this point. However, the occurrence of spectral changes upon the oxidation suggests that the oxidation of the peripheral group is the most unlikely; this is because minor changes in one of the peripheral groups would not give rise to significant spectral changes. Of the two remaining possibilities, the **d** seems more likely to involve cobalt(III/II) process because it seems common for the known mononuclear cobalt(II)-phthalocyanines that oxidation of the central cobalt occurs before a pc^0/pc^- process in non-donor solvents.[5]

Conclusion

The title cobalt-phthalocyanine complex, which is highly soluble in common organic solvents and is a single isomer, has been prepared and characterized. Redox potentials of this complex have been determined by cyclic voltammetry and some of the redox couples observed have been assigned on the basis of the electronic absorption spectra of the electrochemically-generated species. This complex showed strange electrochemical behavior. The cyclic voltammograms in the concentrated solution did not show the first reduction wave until the potential applied was swept to the second reduction wave whereas the controlled-potential electrolyses around the first reduction wave under the same conditions gave rise to drastic spectral changes without any preliminary electrolysis around the second reduction wave. These phenomena can be explained in terms of aggregation of the complex molecules, which is common in the field of phthalocyanine chemistry. We believe that the high solubility of the title complex and the absence of geometric isomers allowed the complex molecules to form higher aggregates than dimer or trimer in concentrated solutions and hence enabled us to find such strange behavior of this compound. The 3,3-dimethyl-1-butynyl group has been found to be electron-donating, based on the known linear dependence of half-wave potentials of pc^-/pc^{2-} redox couples of cobalt(II)-phthalocyanines on the Hammet substituent constant of the peripheral substituents.

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