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Electrochromism of Octacyanophthalocyanine Thin Film. Investigation by Means of in situ Visible and Raman Spectroscopies

Kimiya Takeshita, Yuko Aoyama, and Michio Ashida*
Department of Industrial Chemistry, Faculty of Engineering, Kobe University, Nada, Kobe 657
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The electrochromism of an octacyanophthalocyanine ($H_2Pc(CN)_8$) thin film was investigated by in situ visible and Raman spectroscopies in acid and alkaline electrolytes. A new absorption band was observed in the range 700—900 nm of the visible spectra during a reduction of the film. The absorbance reached a constant value at 2 F mol^{-1} of the cathodic electricity in an alkaline electrolyte. The Raman spectra showed a spectral change in the vibration range which is attributed to the macrocycle and the isoindole moiety; hence, the reduction seems to occur in the azaporphyrin ring. From both the visible and Raman spectra, it was revealed that $H_2Pc(CN)_8$ was protonated at the nitrogens in positions 6,13,20,27 by electrochemical reduction. The protonated $H_2Pc(CN)_8$ shows absorption in the near-infrared region in both acid and alkaline electrolytes. The mechanism for the formation of protonated $H_2Pc(CN)_8$ is considered to be analogous to that of hydrogen evolution in alkaline electrolytes. Both the visible and Raman spectra were reversible during reoxidation.

(Phthalocyaninato)metals (MPcs) are composed of a tetraazaporphyrin ring; their structures are analogous to porphyrins, which are important functional compounds found in nature. On account of both chemical and thermal stability, CuPc has been used for a long time as a blue pigment. Recently, MPcs have attracted a good deal of attention as new functional materials, such as catalysts,[1)] semiconductors,[2—4)] and photoconductors.[5—8)] A redox state of MPcs plays an important role in their properties. The electrochromism of MPcs caused by the redox reaction has attracted attention regarding applications in display devices. Since Nicholson and co-workers investigated the electrochromism of lutetium diphthalocyanine films,[9)] several other groups have reported results for rare-earth diphthalocyanine.[10—12)] Single-ring MPcs (M=Fe, Co, Ni, Cu, Zn, and Mg) films also show electrochromism in the oxidized state.[13,14)] In these electrochromic processes, a charge-compensating anion for MPc cation formed by electrolysis usually penetrates into the film from an electrolyte. The charge-compensating anion can be considered to be a dopant to MPcs. According to Marks and co-workers as well as Orr and Dahlberg,[15,16)] carefully designed, doped phthalocyanines can show metallic conductivity. Furthermore, modified electrodes with MPcs show catalytic activity induced by the electrochemical redox reaction of MPcs.[17,18)] It therefore seems to be useful to investigate the electrochromism of MPc films precisely.

We have recently reported that (Octacyanophthalocyaninato)metal ($MPc(CN)_8$) is synthesized from tetracyanobenzene (TCNB) vapor on metal or alkaline halide substrates.[19)] Wöhrle and co-workers have reported that thin films of $MPc(CN)_8$ (M=2H, Cu, Zn) show stable electrochromic redox behavior at the reduced state in an aqueous electrolyte.[20)] The eight cyano groups of the molecule play an important role in the redox behavior of $MPc(CN)_8$. According to Louati and co-workers,[21)] half-wave potentials of the reduction wave of $MPc(CN)_8$ in *N,N*-dimethylformamide (DMF) shifted to the anodic direction by 0.5—1.0 V, as compared with those of MPcs. This finding indicates that $MPc(CN)_8$ is reduced more easily than MPcs. They mentioned that the property of $MPc(CN)_8$ is very close to an organic electron acceptor, such as tetracyanoquinodimethane (TCNQ).

The redox state of MPcs has generally been investigated using an electrochemical method in company with a spectroscopic type. In most studies, in situ electronic transition spectra have also been reported with electrochemical results. In the case of MPc films, however, the electronic transition spectra may not be used to investigate the electrochromism, since the electronic spectra of MPcs depend on their crystal structures. The change in the spectra is caused not only by electrochemical reactions, but also by a structure change due to the solvent.[22)] The possibility of an alternation in the molecular packing or crystalline structure has also been recognized for the electrochromism of MPcs by Kahl and co-workers.[14)] This suggests that an investigation of the vibrational spectra should be carried out at the same time. The vibrational spectra during electrochromism of an MgPc film were only reported by Kahl and co-workers.[14)] Unfortunately, Wöhrle and co-workers have not reported any in situ electronic and vibrational spectra of $H_2Pc(CN)_8$ film during electrochromism.[20)]

In this work, we found a new absorption band in the near-infrared (NIR) region during the electrochromism of $H_2Pc(CN)_8$ films in aqueous electrolytes, and investigated the electrochromism with electronic transition and vibrational spectroscopies.

Experimental

$H_2Pc(CN)_8$ was synthesized following the method of

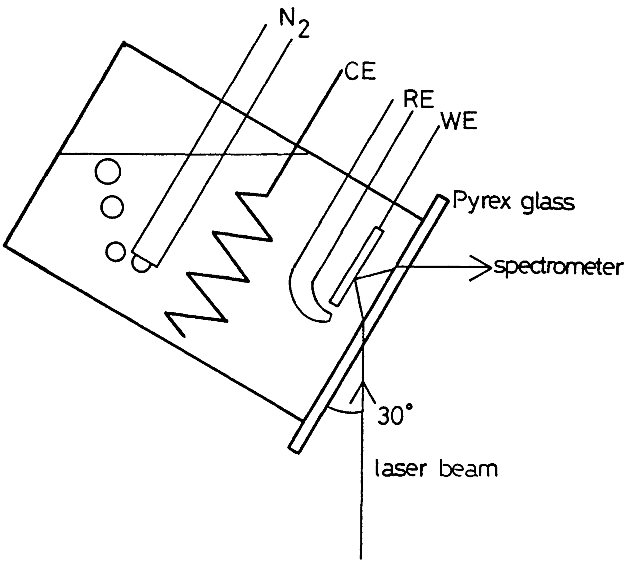

Fig. 1. Experimental setup for in situ Raman spectroscopy of thin film $H_2Pc(CN)_8$ electrodes.

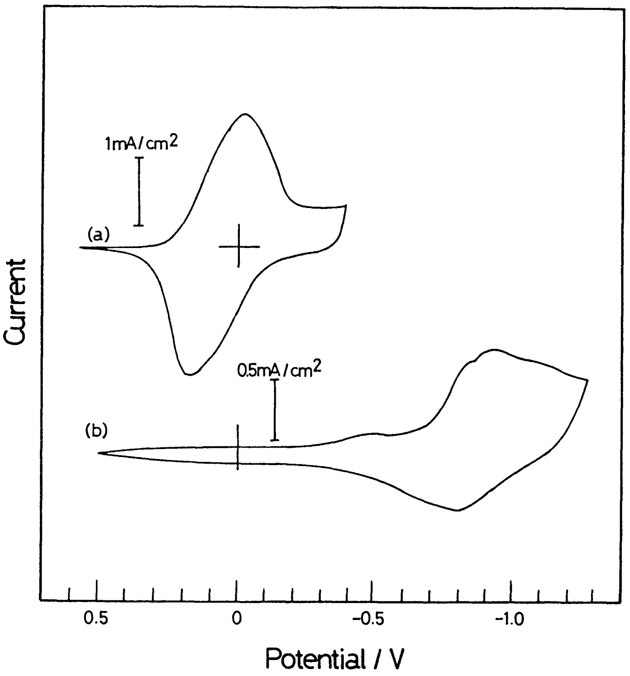

Fig. 2. Stable cyclic voltammograms of $H_2Pc(CN)_8$ films in 1 M HCl (a) and 0.1 M KOH/1 M KCl (b). Thichness of the film are 670 nm (a) and 580 nm (b), respectively. Scan rate 40 mV s^{-1}.

Wöhrle and co-workers,[23] and was purified by column chromatography with silica gel and DMF. $H_2Pc(CN)_8$ was dissolved into DMF and was cast onto an ITO (tin doped indium oxide coated glass) for an optical transparent electrode. The film on ITO was dried in vacuum at 373 K. The amount of $H_2Pc(CN)_8$ on ITO was estimated to be about 10^{-7} mol from the specific gravity of the bulk material (1.49 g cm^{-3}) and the cross section of the film by a direct observation with a scanning electron microscope.

A copper lead wire was attached with silver paste to the ITO, which was used as a working electrode. They were covered with epoxy resin to adjust the electrode area of 1 cm^2. All electrochemical measurements were carried out under an N_2 atmosphere at 298 K with a Hokuto Denko HA-301 potentio/galvanostat and a Hokuto Denko HB-104 potential sweeper. A working electrode, a Ag/AgCl reference electrode and a Pt wire counter electrode were set in an electrochemical cell with quartz windows for optical measurements. Visible spectra of the film in the cell were measured under electrolysis with a Shimadzu UV-240 spectrometer. In the case of potentiostatic electrolysis, visible spectra were recorded when the current reached a stationary state after about 15 min from an application of the potential. The transient time was controlled to be about 30 s in order to avoid any influence of convection and an electric double layer during the galvanostatic electrolysis.

A cell for in situ Raman spectroscopy was shown in Fig. 1. A Raman measurement was made using a Spex Ramalog 5 Raman spectrometer controlled by an NEC PC-9801VM personal computer. An NEC GLS-3300 Ar^+ laser was used as an excitation source. The light power at the sample point was less than 30 mW. The spectral slit width of the spectrometer was set at 4 cm^{-1}.

Results and Discussion

Stable cyclic voltammograms of $H_2Pc(CN)_8$ films on ITO are shown in Fig. 2. In the cathodic scan from the potential of 0.6 V to −0.4 V vs. Ag/AgCl in 1 M HCl (1 M=1 mol dm^{-3}), the film turned from green to blue at ca. 0 V and from blue to purple at ca. −0.2 V. In the reversal scan, the film turned from purple to blue at ca. 0.2 V and from blue to green at about 0.4 V. In a cathodic scan from 0 V to −1.22 V in 0.1 M KOH/1 M KCl, the film turned from green to blue at ca. −0.7 V and from blue to purple at ca. −0.8 V. In the reversal scan, the film turned from purple to blue at ca. −0.7 V and from blue to green at ca. −0.5 V.

The electrochemistry of an $H_2Pc(CN)_8$ film on the Au electrode was intensively investigated by Wöhrle and co-workers.[20] They mentioned that $H_2Pc(CN)_8$ films showed stable electrochromism during reduction in an acid electrolyte, as follows:

$$H_2Pc(CN)_8 + ne^- + nH^+ \longrightarrow H_2Pc(CN)_8^{n-}\cdot nH^+ \quad (n=1\text{—}3).$$

The cyclic voltammogram of the film showed two reduction peaks; the first and second reduction peaks of the films were 81 and 20 mV vs. Ag/AgCl in 1 M HCl, respectively. On the other hand, the first and second reduction peaks of the films were −756 and −866 mV in 0.1 M KOH/1 M KCl, respectively. They suggested on the basis of those results that the rate-determining step in alkaline electrolytes was the transport of charge-compensating cations in the redox process of $H_2Pc(CN)_8$ film. They did not, however, mention the mechanism of the redox process in an alkaline electrolyte. Although the $H_2Pc(CN)_8$ film on Au electrode showed two distinctive reduction

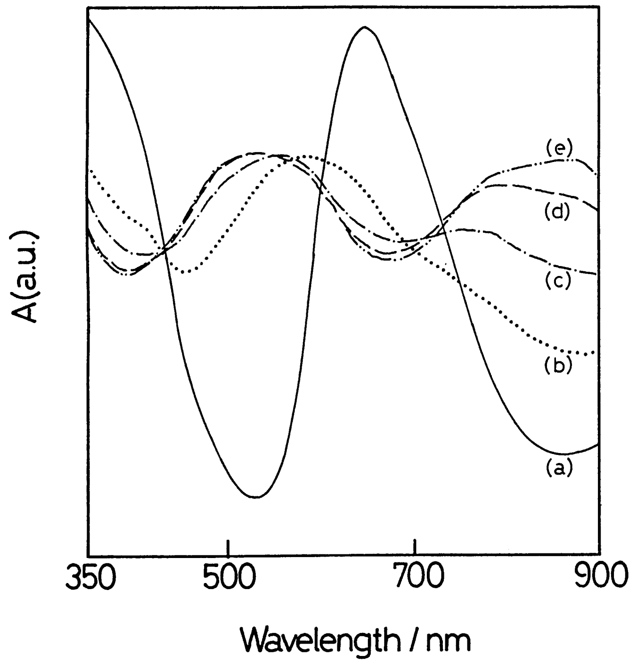

Fig. 3. In situ visible spectra of $H_2Pc(CN)_8$ films in 1 M HCl: original film (a) and films reduced at 0.025 V (b), −0.05 V (c), −0.175 V (d), and −0.4 V (e).

peaks in the cyclic voltammogram, the $H_2Pc(CN)_8$ film on ITO showed one reduction peak. This may be attributed to a complicated characteristic of a semiconductive ITO electrode.

In Situ Spectra in Acid Electrolyte. In situ visible spectra of $H_2Pc(CN)_8$ films during potentiostatic electrolysis in 1 M HCl are shown in Fig. 3. With the progress of reduction, the absorption peak at 640 nm shifted to a lower wavelength, and a new absorption appeared in the NIR region. When the film was reduced at −0.05 V, the new absorption had a peak at 760 nm; at −0.4 V the absorption had two peaks at 760 nm and 880 nm. During the reduction, the film turned from green to blue at 0.025 V and to violet at −0.4 V. According to Gaspard and co-workers,[24] the Pc protonated at the nitrogen atoms in positions 6,13,20,27 showed absorption in the NIR region; successive protonation of Pc shifted the NIR absorption to a higher wavelength. Therefore, NIR absorption may be attributed to protonated Pcs. The additional absorption appearing at 880 nm suggests further protonation.

In situ Raman spectra of $H_2Pc(CN)_8$ films during potentiostatic electrolysis in 1 M HCl are shown in Fig. 4. Because the film had absorption at the wavelength of the light source (514.5 nm) under electrolysis, the Raman spectra were affected by a resonance Raman effect. The relative intensity of the Raman scattering was compared with that at 531 cm^{-1}, since the intensity at 531 cm^{-1} was changed little by the electrolysis. Fluorescence could be neglected in the Raman spectra as a result of measurements at a different exciting wavelength. The main bands of the Raman spectra were assigned on a basis of those of H_2Pc reported by Aroca and co-workers,[25] since the Raman spectra of $H_2Pc(CN)_8$ have not been reported. The Raman bands are classified into several groups. The Raman band at 1250—1600 cm^{-1} can be mainly attributed to C=C and C=N stretching in the isoindole moieties. In this range, the original film of $H_2Pc(CN)_8$ shown in Fig. 4(a) has peaks at 1391, 1510, 1527, and 1602 cm^{-1}. The second band at 650—800 cm^{-1} is mainly attributed to macrocycle vibration. When the film was reduced at 0.025 V, the peaks at 1391, 1510, and 1527 cm^{-1} disappeared and new peaks appeared at 1423 and 1455 cm^{-1}. The band at 650—800 cm^{-1} changed at the same potential. The result indicated that the isoindole moiety was strongly affected by reduction and that the azaporphyrin ring was distorted by the electrolysis. The same tendency was observed in the oxidation of MgPc film.[14] This finding coincided with the result of Louati and co-workers, in which the redox reaction of $H_2Pc(CN)_8$ took place on the azaporphyrin ring in the DMF solution.[21]

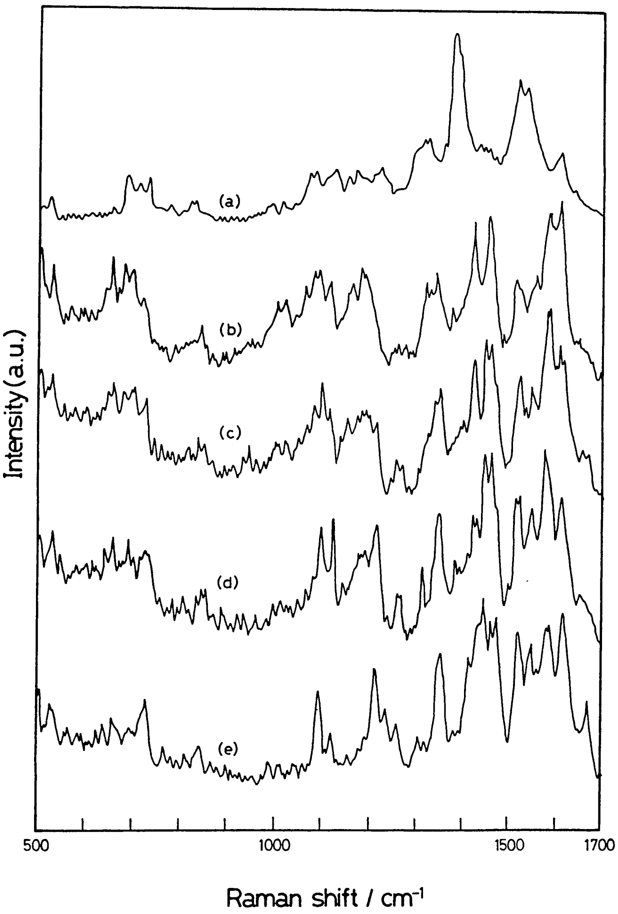

Fig. 4. In situ Raman spectra of $H_2Pc(CN)_8$ films in 1 M HCl: original film (a) and films reduced at 0.025 V (b), −0.05 V (c), −0.175 V (d), and −0.4 V (e). λ_{exc}=514.5 nm.

Many strong bands appeared at 1500—1700 cm^{-1} under the electrochemical reduction. According to Sugimoto,[26] phlorin, which is a protonated porphyrins at the *meso* position, has electronic transitions in the NIR region and vibrational modes at 1500—1700 cm^{-1}. By a comparison with the spectra of phlorin, the absorption in the NIR region and the band at 1500—1700 cm^{-1} in the Raman spectra may be attributed to the protonated $H_2Pc(CN)_8$ in the reduced film.

In Situ Spectra in Alkaline Electrolyte. The in situ visible spectra of $H_2Pc(CN)_8$ films during potentiostatic electrolysis in 0.1 M KOH/1 M KCl are shown in Fig. 5. The film turned from green to blue at −0.85 V, and to purple at −0.97 V. As the films were reduced under a more negative potential, the Q-band shifted to a lower wavelength, as in the case in 1 M HCl, and a new absorption peak appeared only at 880 nm. The dependence of the absorption of $H_2Pc(CN)_8$ films on the potential during potentiostatic electrolysis in 0.1 M KOH/1 M KCl is shown in Fig. 6(a). The absorbancies were normalized by absorbance at 640 nm of the original film. The absorbance at 640 nm decreased and that at 530 nm increased at −0.6 V, while that at 880 nm increased at −0.7 V. The change of absorbancies at 640 and 530 nm before the appearance of absorbance at 880 nm indicates that a two-step electrochemical reaction takes place depending on the potential. The dependence of the absorption of $H_2Pc(CN)_8$ films on charge during galvanostatic electrolysis in 0.1 M KOH/1 M KCl is shown in Fig. 6(b). The absorbance at 640 nm gradually decreased and reached a constant value at about 2 F mol^{-1}. The absorbance at 880 nm increased linealy with charge to 1 F mol^{-1} and increased quickly to a plateau which was saturated at about 2 F mol^{-1}. These findings seem to lead to the conclusion that the NIR absorption of the film in 0.1 M KOH/1 M KCl is attributed to $[H_2Pc(CN)_8]^{2-}$. The new absorption in 0.1 M KOH/1 M KCl, however, could not be attributed to $[H_2Pc(CN)_8]^{2-}$, itself, because $[H_2Pc(CN)_8]^{2-}$ does not show any absorption in the NIR region in the DMF solution.[18] To explain the absorption in the NIR region in more detail, the Raman spectra of $H_2Pc(CN)_8$ film is discussed.

The in situ Raman spectra of $H_2Pc(CN)_8$ films during potentiostatic electrolysis in 0.1 M KOH/1 M KCl are shown in Fig. 7. When the film was reduced over −0.62 V, the spectrum coincided with that of the original film. At −0.85 V the band at 650—800 cm^{-1} changed and the peak at 1391 cm^{-1} disappeared as well as in the case of 1 M HCl. The band at 1000—1500 cm^{-1} changed to a different type from that in 1 M HCl. These results indicate that the azaporphyrin ring was affected by electrolysis in alkaline electrolyte, as well as in acid electrolyte and that the charge-compensating cation in the film affected the Raman

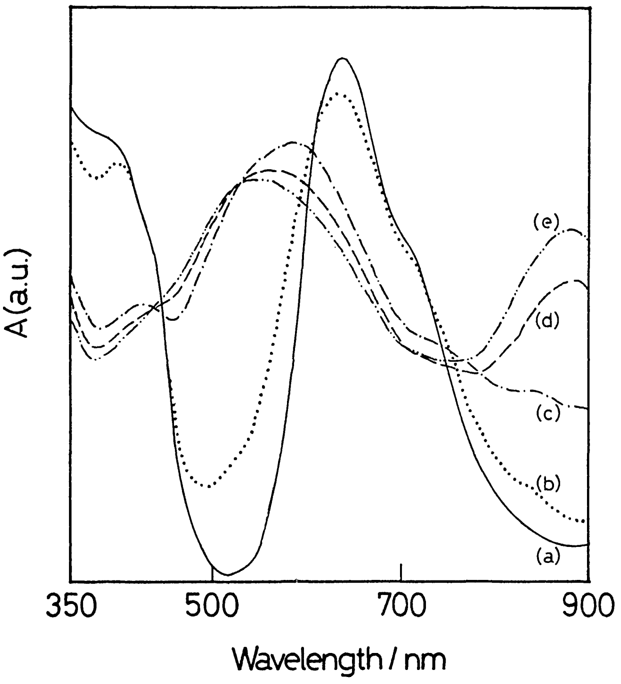

Fig. 5. In situ visible spectra of $H_2Pc(CN)_8$ films in 0.1 M KOH/1 M KCl: original film (a) and films reduced at −0.62 V (b), −0.85 V (c), −0.97 V (d), and −1.22 V (e).

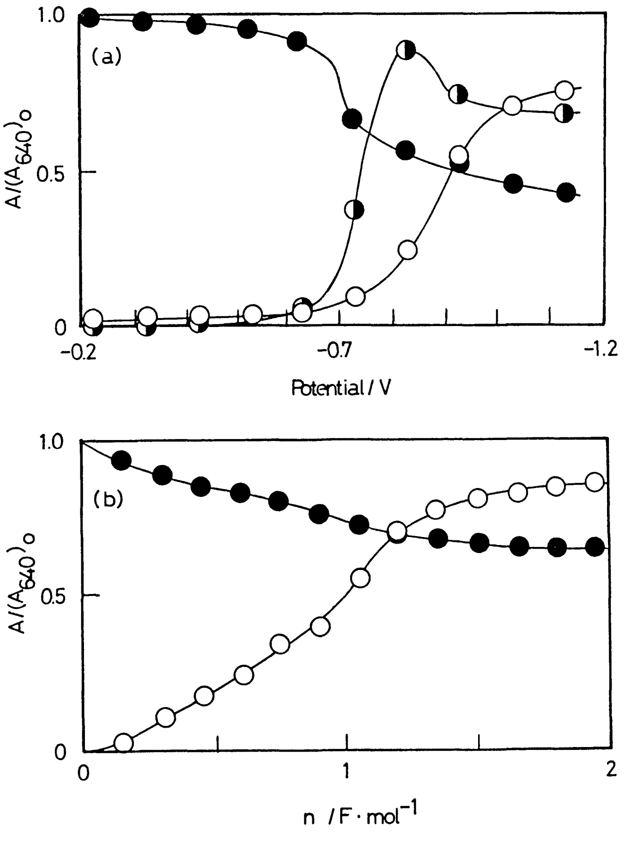

Fig. 6. Dependence of absorbancies of $H_2Pc(CN)_8$ films on potential (a) and charge (b) of the electrolysis in 0.1 M KOH/1 M KCl: ○; at 880 nm, ●; at 640 nm, ◑; at 530 nm.

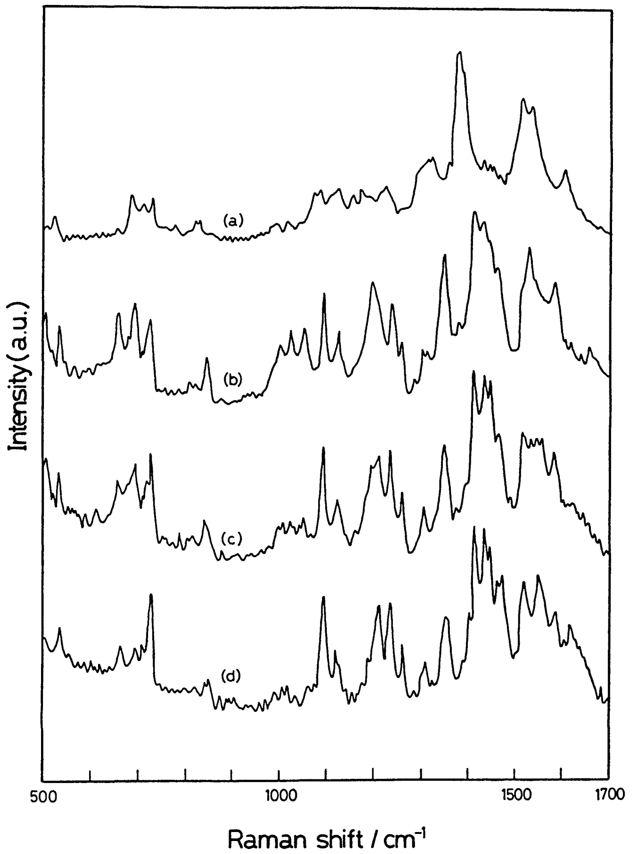

Fig. 7. In situ Raman spectra of $H_2Pc(CN)_8$ films in 0.1 M KOH/1 M KCl: original film and films reduced at −0.62 V (a), −0.85 V (b), 0.97 V (c), and −1.22 V (d). λ_{exc}=514.5 nm.

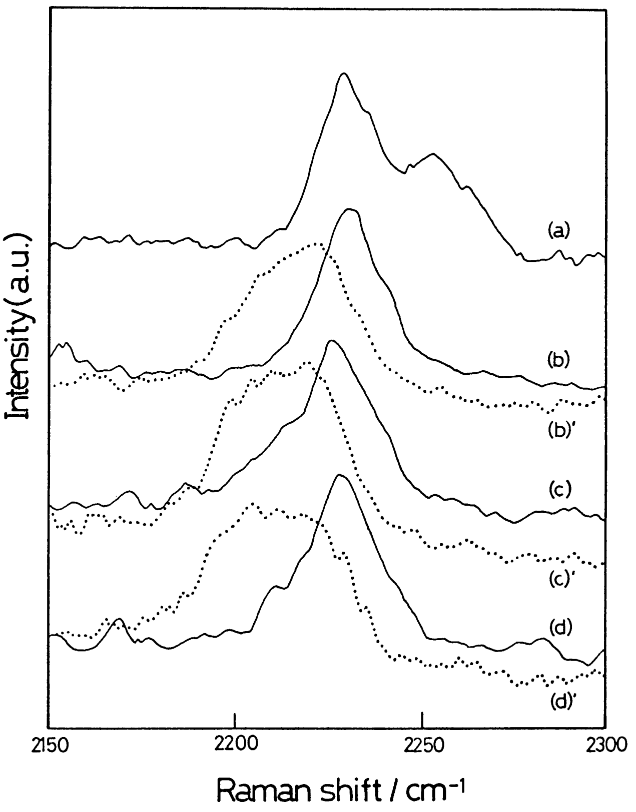

Fig. 8. In situ Raman spectra in $C{\equiv}N$ stretching region of $H_2Pc(CN)_8$ films: original film (a), films reduced in 1 M HCl at 0.025 V (b), −0.05 V (c), and −0.4 V (d), and films reduced in 0.1 M KOH/1 M KCl at −0.85 V (b)′, −0.97 V (c)′, and −1.22 V (d)′. λ_{exc}=514.5 nm.

spectra of the reduced $H_2Pc(CN)_8$. At a potential between −0.97 and −1.22 V, many bands appeared at 1500—1700 cm^{-1}. In consideration of the absorption in the NIR region and for the bands at 1500—1700 cm^{-1}, it seems that $H_2Pc(CN)_8$ is protonated by electrolysis at the potential in 0.1 M KOH/1 M KCl.

From these results, the mechanism of elctrochemical reduction of $H_2Pc(CN)_8$ film in 0.1 M KOH/1 M KCl may be written as follows:

$$H_2Pc(CN)_8 + K^+ + e^- \longrightarrow [H_2Pc(CN)_8]^- \cdot K^+ \qquad (1)$$

and

$$[H_2Pc(CN)_8]^- \cdot K^+ + H_2O + e^- \longrightarrow [H_2Pc(CN)_8\text{-}H]^- \cdot K^+ + OH^- \qquad (2)$$

Reaction (1) takes place at −0.6 V. At −0.7 V, Reaction (2) produces a protonated $H_2Pc(CN)_8$ anion ($[H_2Pc(CN)_8\text{-}H]^-$) which has absorption in the NIR region. Reaction (1) may be the rate-determining step, since the diffusion of K^+ into the film has been found to be the rate determining step.[20] Reaction (2) is analogous to that of hydrogen evolution in alkaline electrolytes ($2H_2O+2e^- \rightarrow H_2+2OH^-$). The same reaction process occurred in the electrochemical reduction of zinc tetraphenylporphyrin (ZnTPP).[27] In that case, ZnTPP in a DMF solution which contained protic solvent was reduced to $[ZnTPP]^{2-}$, followed by rapid protonation to form a phlorin anion ($[ZnTPP\text{-}H]^-$) which showed absorption in the NIR region. Generally, porphyrin and phthalocyanine have quiet similar electrochemical reactivity and overall redox mechanisms. It therefore seems that such a proposed mechanism of electrochemical reduction is reasonable for the $H_2Pc(CN)_8$ film in an alkaline electrolyte.

$C{\equiv}N$ Stretching Vibration. Figure 8 shows the $C{\equiv}N$ stretching of $H_2Pc(CN)_8$ films on ITO during potentiostaic electrolysis in 1 M HCl and 0.1 M KOH/1 M KCl. The phthalocyanine films showed two $C{\equiv}N$ stretching peaks at 2228 and 2253 cm^{-1}, and a doublet band turned to a singlet in this type of electrolysis. The peak of the singlet band shifted slightly in 1 M HCl during the electrolysis. On the other hand, the band in 0.1 M KOH/1 M KCl shifted to the shorter wavenumber direction by about 50 cm^{-1}, indicating that the charge compensating cation affected the electrochemical reaction of $H_2Pc(CN)_8$ film. In the case of TCNQ films reduced by alkaline metals, $C{\equiv}N$ stretchings of TCNQ shifted by about 100 cm^{-1} to a shorter wavenumber.[28] The $C{\equiv}N$ stretchings of TCNQ shifted to a shorter wavenumber by electrolysis to the TCNQ anion in an acetonitrile solution.[29] These findings indicated that the C≡N stretchings of TCNQ were strongly affected by the reduction of TCNQ and the formation of the anion. It is interesting that the C≡N stretchings of the $H_2Pc(CN)_8$ films show a smaller shift than that of TCNQ. For $H_2Pc(CN)_8$, Louati and co-workers mentioned from their electrochemical results that the eight electron-withdrawn cyano groups of $H_2Pc(CN)_8$ interacted indirectly with the conjugated π electron system of the azaporphyrin ring.[21] The reduction of the conjugated π system of $H_2Pc(CN)_8$ probably affects to the cyano group in a weaker way than does that of TCNQ. It therefore seems that the C≡N stretchings of $H_2Pc(CN)_8$ shift less than those of TCNQ by electrochemical reduction.

Spectral Reversibility of $H_2Pc(CN)_8$ Film. The visible and Raman spectra of the film were reversible in the reoxidation process in those electrolytes. When the circuit was opened after the film was completely reduced in the violet state, the film gradually turned to blue during about 10 min, and returned to green after about 30 min. When the film was completely reduced at the violet state and placed into water, it returned to green immediately. The visible and Raman spectra of the film coincided with those of the original film. We have reported that $MPc(CN)_8$ can be synthesized on metal and alkaline halide surfaces, forming a film of an $MPc(CN)_8$-M complex crystal on the substrate. It is expected that $MPc(CN)_8$ in the $MPc(CN)_8$-M film is reduced by an electrochemical reaction and that the electrochromic property of the film is different from that of the $H_2Pc(CN)_8$ film. We are now investigating the electrochromic properties of $MPc(CN)_8$-M films.

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