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Characterization of Monomeric and Polymeric (Octacyanophthalocyaninato)metals in Thin Films

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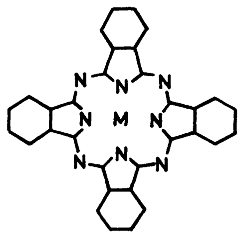
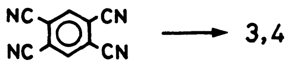
Thin films were prepared by the reaction of 1,2,4,5-tetracyanobenzene with Ni, Co, Fe, Zn films at various temperatures. The films were characterized by infrared, UV/visible and photoelectron spectroscopy and analytical electron microscopy in comparison with films prepared on substrates of a KCl single crystal and a Cu film. The films produced on the metal films below 400 °C were composed of tentacle-like crystals growing from the surface and an amorphous layer condensed over the metal substrate. The tentacle-like crystals were soluble in concentrated sulfuric acid and were identified as intercalation compounds of (octacyanophthalocyaninato)metal with the respective metal atoms. The amorphous layers contained polymerization products with a polynitrile structure, which were insoluble in concentrated sulfuric acid. The films produced on the metal films at 450 °C were composed of a thick layer and had a very limited solubility in concentrated sulfuric acid. They were ascribed to metal complexes of polyphthalocyanines(poly-M(Pc)) and cross-linked polymers with structure elements such as polynitrile and triazine.

(Phthalocyaninato)metals(M(Pc))$^{1-7)}$ (**1**) and their polymeric derivatives$^{8-11)}$ have recently attracted a good deal of attention as new functional materials because of their interesting electronic and optical properties. According to Wöhrle et al.$^{12,13)}$ phthalocyanine polymers were synthesized by a reaction of 1,2,4,5-tetracyanobenzene(TCNB) (**2**) with metal salts or metals, and (octacyanophthalocyaninato)metals (M[Pc(CN)$_8$]) (**3**) were produced as precursors of polymeric (phthalocyaninato)metals (poly-M(Pc)). The structure of polymeric phthalocyanines has been considered that phthalocyanine units link each other by the peripheral benzene ring to form either a ribbon or a sheet of parquet pattern (**4**).

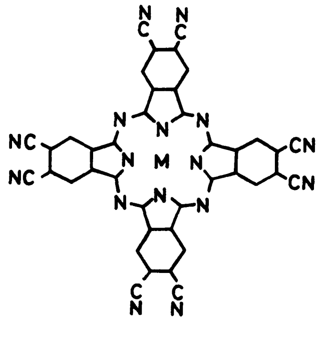
In order to prepare thin films of these phthalocyanine derivertives, the synthesis has been proceeded by a reaction of TCNB vapor with substrates such as a KCl crystal and a Cu plate in an evacuated tube.$^{14)}$ The films produced on these substrates at temperatures between 250 and 400 °C were composed of tentacle-like crystals which were characterized as M[Pc(CN)$_8$] (M=K$_2$,Cu). The films included extra metals, more than would be required for coordination in phthalocyanine rings; the metals were distributed uniformly in the film. High-resolution electron microscopic observation of the thin crystal produced on KCl$^{15)}$ has elucidated that the film is composed of an intercalation compound of K$_2$[Pc(CN)$_8$] with potassium atoms coordinated to the peripheral cyano groups of the Pc molecules. The reaction of TCNB with KCl or a Cu plate above 450 °C produced amorphous and continuous films of poly-M(Pc) (M=K$_2$, Cu). The ratio of polymeric phthalocyanine to monomeric one increased with elevating reaction temperature. However, their structure and molecular weights have not been examined in detail, owing to the poor solubility of the polymers. Wöhrle et al.$^{13)}$ has pointed out that the structure of polymer is affected by the condition of the reaction and polymeric phthalocyanines with uniform structure are obtained only in a reaction with specific metals.



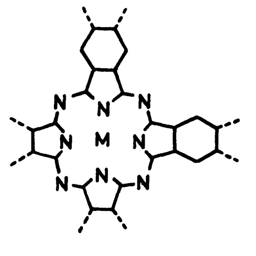
1 : M(Pc)



2 : TCNB



3 : M[Pc(CN)$_8$]



4 : poly-M(Pc)

In the present work, thin films were prepared by the reaction of TCNB vapor with various metal substrates of Ni, Co, Fe, and Zn films as well as KCl and a Cu film. The products were characterized by infrared(IR) and UV/visible(UV/VIS) spectroscopy and morphologies of the films were observed by scanning electron microscopy(SEM). The compositions of the films produced on the substrates were examined by photoelectron spectroscopy and X-ray microanalysis. The structures of the products are discussed in comparison with those of films produced on KCl and Cu.

Experimental

Synthesis. TCNB was synthesized from pyromellitic dianhydride by the method of Bailey et al.[16] The crude TCNB was purified by recrystallization from acetic acid. The substrate materials used were a cleavage surface of a KCl single crystal and metallic films. As metallic films, Cu, Ni, Co, Fe, and Zn were evaporated on a cleavage surface of KCl which had been preheated at 150 °C and then kept at room temperature in a vacuum of 1×10^{-4} Pa. Thickness of the metallic films was estimated to be about 100 nm by a quarts crystal microbalance. The refined TCNB and the substrate material were sealed in an evacuated Pyrex glass tube at 10 Pa after flushing with argon gas. The tube was heated at temperatures between 250 and 450 °C for 10 h in a hot air oven. After the reaction the tube was opened in air at room temperature.

IR and UV/VIS Spectra. IR spectra were recorded on a Shimazu 20 DXB spectrometer. The produced films were milled and pressed together with the substrates and examined by the KCl tablet method. The films were dissolved in concentrated sulfuric acid and UV/VIS spectra of the solutions were recorded by a Shimadzu UV-240 spectrometer.

Photoelectron Spectroscopy. X-Ray photoelectron spectra (XPS) were taken on a KRATOS EXAM800, using Mg $K\alpha$ radiation ($h\nu=1254$ eV). A produced film on a substrate was directly attached to a sample holder. All measurements were performed at a pressure of 1×10^{-7} Pa in the analyzing chamber. Surface cleanliness was checked by scanning through the region of binding energy from 0 to 1150 eV. The binding energy was calibrated by a thin gold film vacuum-deposited on the sample, taking the $Au(4f_{7/2})$ peak as a reference at 83.8 eV. The C(1s) spectra were deconvoluted with Gaussian curves after subtraction of the background. The spectra of the films were compared with those of metal-free octacyanophthalocyanine ($H_2[Pc(CN)_8]$) synthesized by Wöhrle et al.[12] and copper phthalocyanine (Cu(Pc)) evaporated on a cleavage surface of KCl. The sample of powdered $H_2[Pc(CN)_8]$ was examined on an indium plate.

Scanning Electron Microscopy and X-Ray Microanalysis. The morphology of the films produced on substrates was observed by the SEM mode of a JEM-200CX electron microscope. The metal distribution in the films was analyzed by a Kevex-7000 energy dispersive X-ray spectrometer(EDS).

Results and Discussion

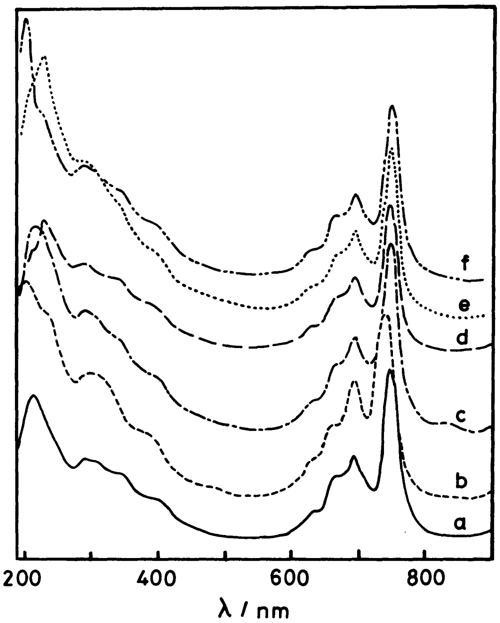


Fig. 1. UV/VIS spectra (in concd sulfuric acid) of films produced on KCl(a), Cu(b), Ni(c), Co(d), Fe(e), and Zn(f) at 300 °C.

UV/VIS Spectra. Films with green or dark blue color were formed on the substrates of Ni, Co, Fe, and Zn films by reaction of TCNB at temperatures between 250 and 400 °C. The films produced below 300 °C were completely soluble in concentrated sulfuric acid. Figure 1 shows the UV/VIS absorption spectra of solutions of the films produced at 300 °C. The films produced on Ni, Co, Fe, and Zn films showed identical absorption bands as those of $M[Pc(CN)_8]$ reported by Wöhrle and Hündorf.[12] The intense bands in the 600—750 and 200—400 nm regions are assigned, respectively, as the Q-band and the Soret band caused by π-π^* transitions in phthalocyanine macrocycles. The maximum peaks in the Q-band of those products appear at a shorter wavelength than those of M(Pc).[17] This shift of the Q-band peaks is caused by an electron-withdrawing effect of the peripheral cyano groups in $M[Pc(CN)_8]$ molecules. Because the electronegative cyano groups attract a certain amount of electrons from the conjugated π electron system of the Pc macrocycle, the ground state of the π electrons becomes a lower energy level, giving rise to an increase in the π-π^* transition energy. Therefore, the Q-band peaks of $M[Pc(CN)_8]$ shift to shorter wavelengths. The films became less soluble in concentrated sulfuric acid upon elevating the reaction temperature. The films produced at 350 °C contained a small amount of insoluble portion in concentrated sulfuric acid, and those at 400 °C contained a considerable amount of the insoluble one. The soluble portions of the films produced on the substrates at 350 and 400 °C, except the film produced on Zn at 400 °C, showed the same spectra as those produced at 300 °C. The films produced on the substrates at 450 °C were gray and black color with a metallic gloss and had a very limited solubility in concentrated sulfuric acid. Figure 2 shows the UV/VIS absorption spectra of the soluble portions of the films produced at 450 °C. The film produced on Zn at 400 °C showed the same spectrum as that at 450 °C. The absorption bands became broader and the maximum peaks in the Q-band shifted to shorter wavelengths by 15 to 21 nm than those of the films produced at 300 °C. The blue shifts of the Q-bands have been observed for associated

Table 1. IR Spectra of $K_2[Pc(CN)_8]$, $Cu[Pc(CN)_8]$, and Synthesized Films[a)]

Assignment	Compound					
	$K_2[Pc(CN)_8]$[14)]	$Cu[Pc(CN)_8]$[14)]	Film on Ni	Film on Co	Film on Fe	Film on Zn
	716w	720m	710w	712w	715w	715w
def.(C–H)	787s	800m	765m	765m	765m	766m
					795w	
	924m	870w	915w	910m	910m	915m
			995m	996m	995w	995m
	1022m	1020m	1025w	1025w	1020w	1020w
	1082s		1075m	1080m		1080s
	1105s	1095s	1100s	1100s	1100s	1100s
str.(C–C)	1165w	1165w	1165w	1164w	1168m	1160w
str.(C–N)	1231m	1230s	1220w	1225w	1220m	1225w
str.(C=N)	1318s	1310s	1310s	1310s	1310s	1305s
	1449w	1460m	1410w		1400w	1440w
	1498m	1500w	1500m	1510m	1510s	1500m
	1555w	1550w	1540m		1560m	1550m
	1610w	1615w	1620m	1610s	1620m	1620m
str.(C≡N)	2231s	2230s	2225s	2230s	2220s	2240s
$\frac{I_{2220-2240}}{I_{1095-1105}}$	0.51	0.78	1.01	1.32	1.33	1.04

a) Frequencies in cm^{-1}; intensity: s=strong, m=medium, w=weak.

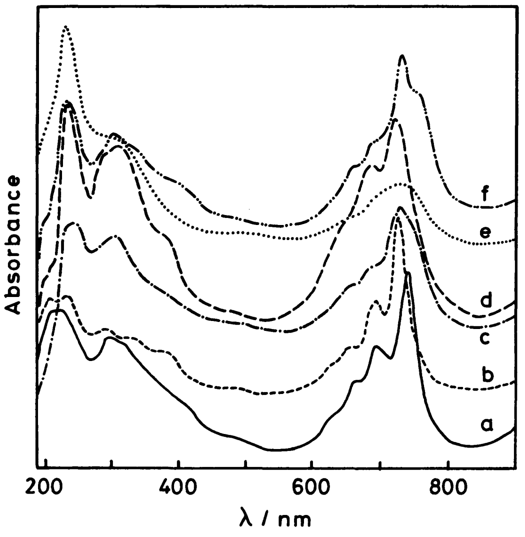


Fig. 2. UV/VIS spectra (in concd sulfuric acid) of films produced on KCl(a), Cu(b), Ni(c), Co(d), Fe(e), and Zn(f) at 450 °C.

porphyrins[18)] and Pc's,[19,20)] dimeric Pc's,[21,22)] and cofacially polymerized Pc's.[9)] These shifts have been discussed in terms of exciton coupling,[23)] which is based on the interaction between the excited states of Pc molecules. On the other hand, Wörhle et al.[13)] have found a red shift of the maximum peak in Q-band for polymerized M(Pc), and concluded that the red shift was caused by an intramolecular π electron delocalization in the Pc polymer. In the present case, it is considered that the soluble portion of the films produced at 450 °C is associated or oligomeric $M[Pc(CN)_8]$ and that the insoluble portion of the films produced above 350 °C is polymerization products of TCNB.

Infrared Spectra. The IR absorption spectra of the films produced on metal substrates at 350 °C are listed in Table 1. The spectra of the films produced on Ni, Co, Fe, and Zn showed similar absorption bands to those of $K_2[Pc(CN)_8]$ and $Cu[Pc(CN)_8]$,[14)] though slight changes in the wave number occurred. The absorption bands in a range from 1000 to 1600 cm^{-1} are characteristic ones of Pc's, which are assigned to C–C and C–N stretching in a Pc skeleton. The absorption bands with high intensity at 2220—2240 cm^{-1} are ascribed to a C≡N stretching of peripheral cyano groups of $M[Pc(CN)_8]$ molecules. In the case of $M[Pc(CN)_8]$ the band appears at 2220 cm^{-1} being independent of metals.[13)] In the present case, however, the bands are of higher wave number than 2220 cm^{-1}, depending on the kinds of metal. In a previous study,[15)] we found that the product formed on KCl could be identified as an intercalation compound of $K_2[Pc(CN)_8]$ with potassium atoms coordinated to the peripheral cyano groups of the Pc molecules. It is assumed that a certain amount of charge is transferred from the potassium atom to the cyano groups by this coordination. The band of C≡N may be affected by this charge transfer, which depends on the electronic configuration of metal atoms. Therefore, the shift suggests that the films produced on the metal substrates form similar complexes between the cyano groups and the respective metals. The formations of these complexes have been confirmed by direct imaging of the thin films with high-resolution electron microscopy.[24)] The ratio of the absorption intensity of the cyano group at 2220—2240 cm^{-1} to the characteristic band of M(Pc) at 1095—1105 cm^{-1}, listed in Table 1, reveals the quantitative value of the cyano groups per Pc unit.[25)] Those ratios of the films produced on Ni, Co, Fe, and Zn are larger than those of $K_2[Pc(CN)_8]$ and $Cu[Pc(CN)_8]$.[14] This suggests that Pc skeletons are less produced and other products having cyano groups, such as polynitrile, are yielded in reactions with Ni, Co, Fe, and Zn, in comparison with the reaction with KCl and Cu. It is also noted that the films on Ni, Co, Fe, and Zn show absorption bands at 1610—1620cm^{-1} which are stronger than those of the films on KCl and Cu. Lin et al.[26] have observed this band for polymeric Cu(Pc) and Wöhrle et al.[13] have reported that this absorption band is attributed to a -C=N-C=N- linkage in the polynitrile structure **5** produced by the polymerization of the cyano groups. Therefore, it is considered that the films produced on Ni, Co, Fe, Zn contain a certain amount of polynitrile, and the products on these substrates are not so structurally uniform in comparison with those on KCl and Cu. Figure 3 shows the IR spectra of the films produced on Ni at various reaction temperatures. The films produced at 300 and 350 °C showed almost same absorption bands. The spectrum of the film produced at 400 °C showed some signs of structural change. The absorption of C≡N stretching at 2225 cm^{-1} decreased significantly and other absorption bands became broader than those of the fimls produced below 350 °C. The spectrum of the film produced at 450 °C showed a very weak absorption at 2225 cm^{-1} and a broad band without fine structure between 1600 and 1000 cm^{-1}. The ratio, I_{2225}/I_{1100}, decreases with elevating reaction temperature. The films produced on Co, Fe, and Zn showed a similar spectral change upon elevating the reaction temperature. It seems that Pc units polymelize by their residual peripheral cyano groups to form poly-M(Pc) and polynitriles, and that extensive reaction causes a cross linkage such as triazine structure[13] **6** at high temperature. These polymeric products are considered to correspond to the insoluble portions of the films in concentrated sulfuric acid, as mentiond in the previous section.

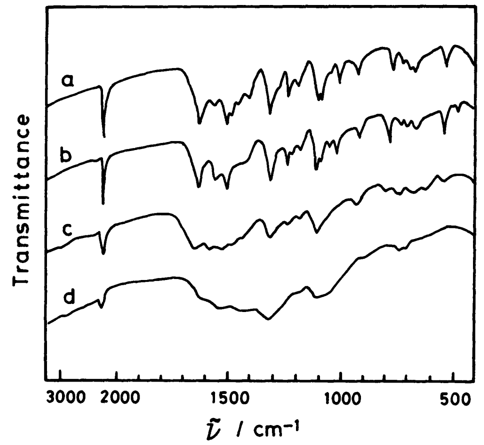
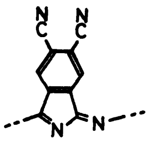


Fig. 3. Infrared spectra of films produced on Ni at 300 °C (a), 350 °C(b), 400 °C(c), and 450 °C(d).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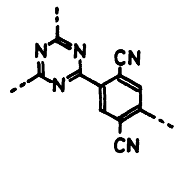
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Photoelectron Spectroscopy. Figure 4 shows the C(1s) XPS spectra of Cu(Pc), $H_2[Pc(CN)_8]$, and the films produced on KCl and Cu at 350 °C. The spectra were deconvoluted to the bands shown with dashed

Table 2. Cls Spectra of Cu(Pc), $H_2[Pc(Cn)_8]$, and Synthesized Films

Compound	BE/eV	FWHM/eV[a]	Integrated area/%[b]
Cu(Pc)	284.8	1.2	72.5
	286.1	1.2	25.9
$H_2[Pc(CN)_8]$	284.7	2.0	66.5
	286.4	1.8	20.7
	288.6	2.5	11.6
Film on KCl	284.6	1.7	59.7
	286.3	1.8	42.3
Film on Cu	284.5	2.2	51.2
	286.5	2.5	46.2

a) Full width at half maximum. b) The areas evaluated from deconvoluted bands are considered accurate to ±5%.

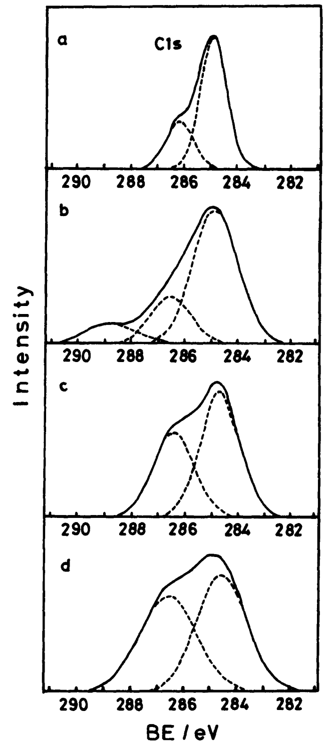

Fig. 4. Carbon 1s photoelectron spectra of Cu(Pc)(a), $H_2[Pc(CN)_8]$(b), and films produced on KCl(c) and Cu(d) at 350 °C.

lines; the data are summarized in Table 2. The spectrum of Cu(Pc) consists of two C(1s) bands with an intensity ratio of 1:3. The band with high energy is attributed to eight carbon atoms bonding with two meso-position nitrogens, and the band with low energy is attributed to 24 carbon atoms in benzene rings of a Cu(Pc) molecule.[27,28] The spectrum of $H_2[Pc(CN)_8]$ shows three C(1s) bands in relative intensity of about 1:2:6. The lowest-energy band is attributed to the carbons of the benzene rings and the intermediate band to the carbons bonding with the two meso-position nitrogen atoms. The third band with a FWHM of 2.5 eV is observed at 288.6 eV. It is well known that a satellite band accompanied with the C(1s) band is observed at about 288 eV for $H_2(Pc)$ and M(Pc).[28,29] However, the third band indicates a considerably strong intensity and a large FWHM for $H_2[Pc(CN)_8]$, as compared with that of the satellite band. Chemical shifts in the photoelectron spectrum of the core electrons are caused by a variation of the valence electron state. Cyano groups polarize to draw the valence electrons from the carbon atom to the nitrogen atom, and the core electrons in the carbon atom are attracted to the nucleus more tightly than those in an isolated carbon atom. Therefore, the binding energy of the C(1s) electron in the cyano groups is higher than that of the normal carbon atoms. Thus, the third band of $H_2[Pc(CN)_8]$ may be assigned to the carbon of the peripheral cyano groups. However, the intensity ratio of the cyano group is smaller than that estimated from the molecular structure of $H_2[Pc(CN)_8]$, which would give an intensity ratio of 1:1:3. This finding suggests that a sample of $H_2[Pc(CN)_8]$ would include a certain amount of polymeric products, such as poly-M(Pc) and triazine structure, since the contents of the cyano groups in these compounds are lower than that of $H_2[Pc(CN)_8]$. The C(1s) spectrum of the film produced on KCl showed two bands with an intensity ratio of 2:3; however, the third band, ascribed to the cyano groups, was not observed in the spectrum and the intensity of high energy band was twice of that of Cu(Pc). The film produced on KCl is composed of an intercalation compound of $K_2[Pc(CN)_8]$ with potassium atoms, in which half of cyano groups coordinate to the intercalated potassium atom and other ones overlap in antiparallel between the adjacent $K_2[Pc(CN)_8]$ molecules, owing to counterbalance of the opposite polarity of $-\overset{\delta+}{C}\equiv\overset{\delta-}{N}$.[30] Because the polarization in $-C\equiv N$ is relaxed by the coordination and antiparallel overlap, the C(1s) spectrum from cyano groups in the complex crystal would shift to an energy lower than that of the cyano groups in $H_2[Pc(CN)_8]$. Consequently, the band of high energy in the film produced on KCl is ascribed to eight carbons in the cyano groups and eight carbons bonding with meso-position nitrogen atoms in a Pc ring, and the band of low energy to 24 carbons in the benzene rings of a $K_2[Pc(CN)_8]$ molecule. The C(1s) spectrum of the film produced on Cu showed two bands similar to that of the film produced on KCl and did not show the third band ascribed to isolated cyano groups. It suggests that the film on Cu is composed of an intercalation compound of $Cu[Pc(CN)_8]$ with copper atoms isomorphous to that of $K_2[Pc(CN)_8]$ with potassium atoms.

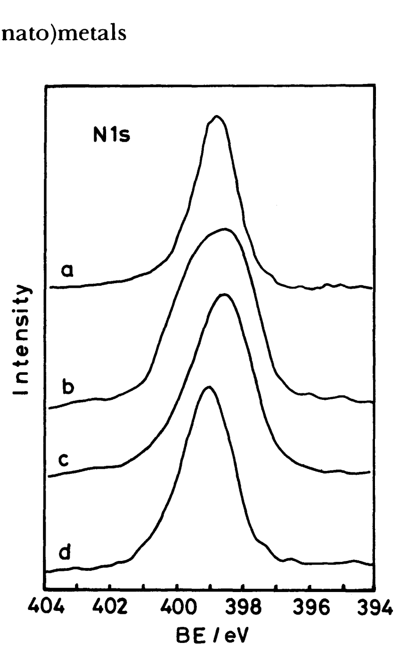

Fig. 5. Nitrogen 1s photoelectron spectra of Cu(Pc)(a), $H_2[Pc(CN)_8]$(b), and films produced on KCl(c) and Cu(d) at 350 °C.

Figure 5 shows the N(1s) spectra of Cu(Pc), $H_2[Pc(CN)_8]$, and the films produced on KCl and Cu at 350 °C. The N(1s) band of $H_2[Pc(CN)_8]$ is broad because a $H_2[Pc(CN)_8]$ molecule has four kinds of nitrogen atoms, that is, four pyrrole nitrogens(two -NH- and two -N=), four meso-position nitrogens, and eight nitrogens of the peripheral cyano groups. On the other hand, the N(1s) spectrum of Cu(Pc) showed a narrow band, since the energy separation between the four equivalent pyrrole-ring nitrogens and the four meso-position nitrogens is estimated to be small.[29] The N(1s) spectra of the films produced on KCl and Cu also showed relatively narrow bands. The nitrogen atoms of the peripheral cyano groups seem to have a binding energy close to those of the other nitrogens in $K_2[Pc(CN)_8]$ and $Cu[Pc(CN)_8]$ molecules, owing to formation of the complex crystals. The films produced on Ni, Co, Fe, and Zn at 350 °C showed similar N(1s) spectra to those of films produced on KCl and Cu.

Figure 6 shows C(1s) and K(2p) spectra of the films produced on KCl at various temperatures. The film produced at 300°C shows one broad C(1s) band, which can not be separated into two bands by deconvolution. This suggests that $M[Pc(CN)_8]$ is not completely formed at 300 °C, and that the films contain a certain amount of products with low molecular weights. In a film produced at 400 °C, the high-energy band of the C(1s) spectrum shows a large intensity and the K(2p) spectrum emerges clearly. The film produced at 450 °C shows a C(1s) shoulder of low energy at about 283 eV. Such a low-energy C(1s) band is well-known for graphite, which consists of a planar conjugated system of π electrons. It seems that the film produced at 450 °C is composed of poly-M(Pc) and cross-linked planar polymers with structure elements such as polynitrile and triazine. The intensity of the K(2p) band increased with elevating the reaction temperature. This indicates that more potassium atoms diffuse from the substrate to the surface of the produced film as temperature increases.

Figure 7 shows the valence band spectra of the films produced on various substrates at 350 °C. The spectrum of a film produced on KCl is in good agreement in binding energy from 8 to 30 eV with that of phthalocyanines reported by Höchst et al.[28] The valence band spectra in this region of M(Pc) could be explained as the spectra of benzene and pyrrole; the spectra were not interfered with by the bond between the central metals and the Pc ligands.[28,29] The spectrum of the film produced on Cu shows similar bands to those of the film produced on KCl, although their relative intensities are different. The spectral features of the films produced on Ni, Co, Fe, and Zn deviate from that of the film produced on KCl and the relative intensities in their spectra are different from that of M(Pc). It seems that the spectral deviation is ascribed to a smaller yield of M[Pc(CN)$_8$] in these films, as compared with the films produced on KCl and Cu.

Scanning Electron Microscopy and X-Ray Microanalysis. Figure 8 shows scanning electron micro-

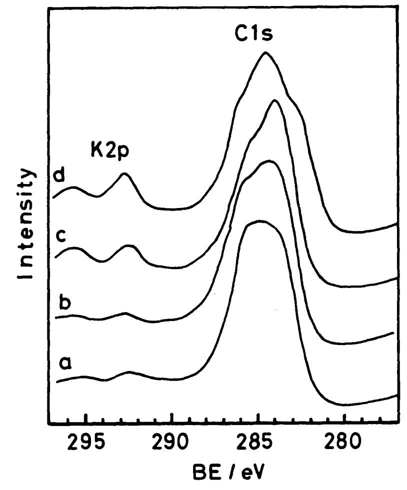

Fig. 6. Carbon 1s and potassium 2p photoelectron spectra of films produced on KCl at 300 °C(a), 350 °C(b), 400 °C(c), and 450 °C(d).

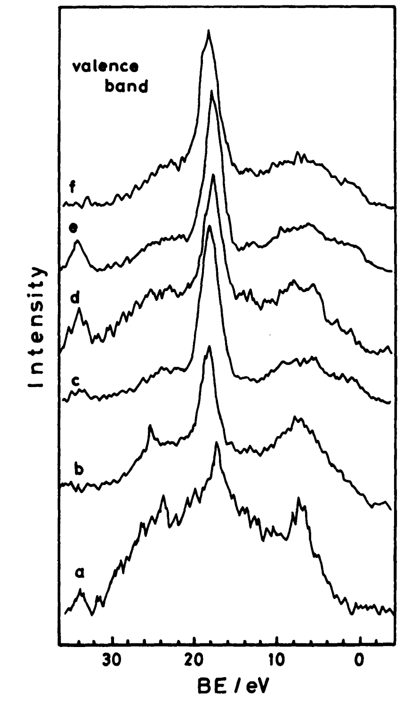

Fig. 7. Valence-band photoelectron spectra of films produced on KCl(a), Cu(b), Ni(c), Co(d), Fe(e), and Zn(f) at 350 °C.

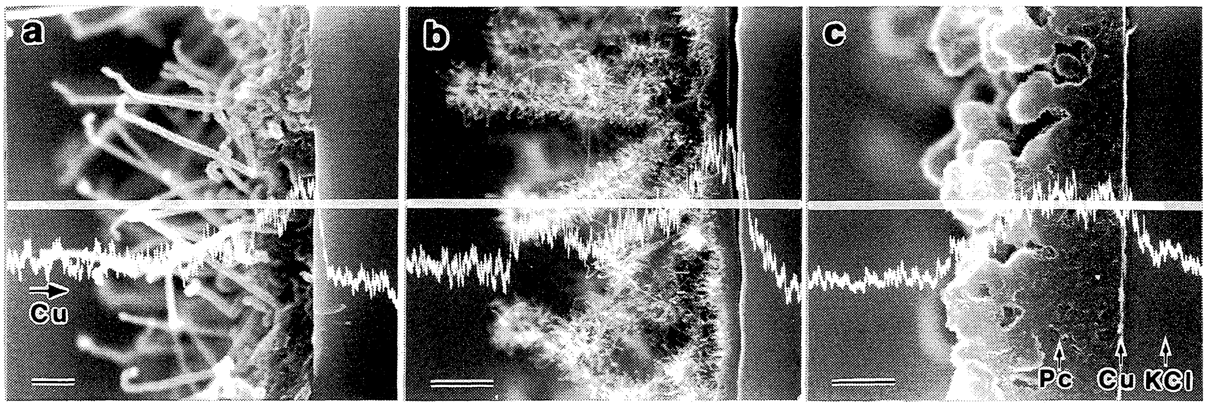

Fig. 8. Scanning electron micrographs and X-ray microanalyses of copper in the films produced on Cu at 250 °C(a), 350 °C(b), and 450 °C(c). Bar=5 μm.

graphs of sections of the films produced on Cu at various temperatures and the distribution of Cu measured by EDS in which the electron beam was scanned from the surface to the bottom of the film along the center line of the figure. The film produced at 250 °C is composed of long and slender crystals of the intercalation compound of $Cu[Pc(CN)_8]$ with Cu atoms. At 350 °C, the crystals grow thin and are a fine tentacle-like type which branch from each thick crystal. The EDS signal shows that Cu atoms are distributed from the bottom to the surface of the film and that the tentacle-like crystals contain Cu atoms. At 450 °C, the film is composed of an amorphous thick layer with bulb-like crystals on the surface. The thick layer is considered to be highly polymerized products of poly-M(Pc) and cross-linked polymers with structure elements, such as polynitrile and triazine, which are insoluble in concentrated sulfuric acid.

Figure 9 shows the morphology of films produced on various substrates at 350 °C and the distribution of the respective metal atoms. The film on KCl is composed of long tentacle-like crystals of the intercalation compound of $K_2[Pc(CN)_8]$ with potassium atoms, as observed previously.[14] These crystals grow directly on the surface of the KCl substrate. On the other hand, the films on Ni, Co, Fe, and Zn consist of three layers: that is, a thin metal layer evaporated on KCl, a thick amorphous layer, and tentacle-like crystals in the top layer. The EDS signals show that the respective metals are distributed from the substrates to the surfaces of the films. The tentacle-like crystals are considered to be intercalation compound of $M[Pc(CN)_8]$ (M=Ni, Co, Fe, and Zn) with the respective metal atoms, because their morphology resembles that of the $K_2[Pc(CN)_8]$ complex. It seems that the amorphous layer contains polynitriles which condense among the tentacle-like crystals. Furthermore, this layer may correspond to the insoluble portion in concentrated sulfuric acid, because the film on Cu (Fig. 8(b)) which has only a thin amorphous layer shows a higher solubility than the others.

In conclusion, the products in the films are summarized in Table 3. The films produced on Cu, Ni, Co, Fe, and Zn below 400 °C contained $M[Pc(CN)_8]$ (M=Cu, Ni, Co, Fe, and Zn) and polymerized products such as polynitrile. The $M[Pc(CN)_8]$ molecules formed tentacle-like crystals of the intercalation compound with the respective metals and were soluble in concentrated sulfuric acid. The intercalation compounds were produced less in these films compared with that in a film produced on KCl. The polymerized products formed amorphous layers, which were insoluble in concentrated sulfuric acid. These polymerized products increased in the films

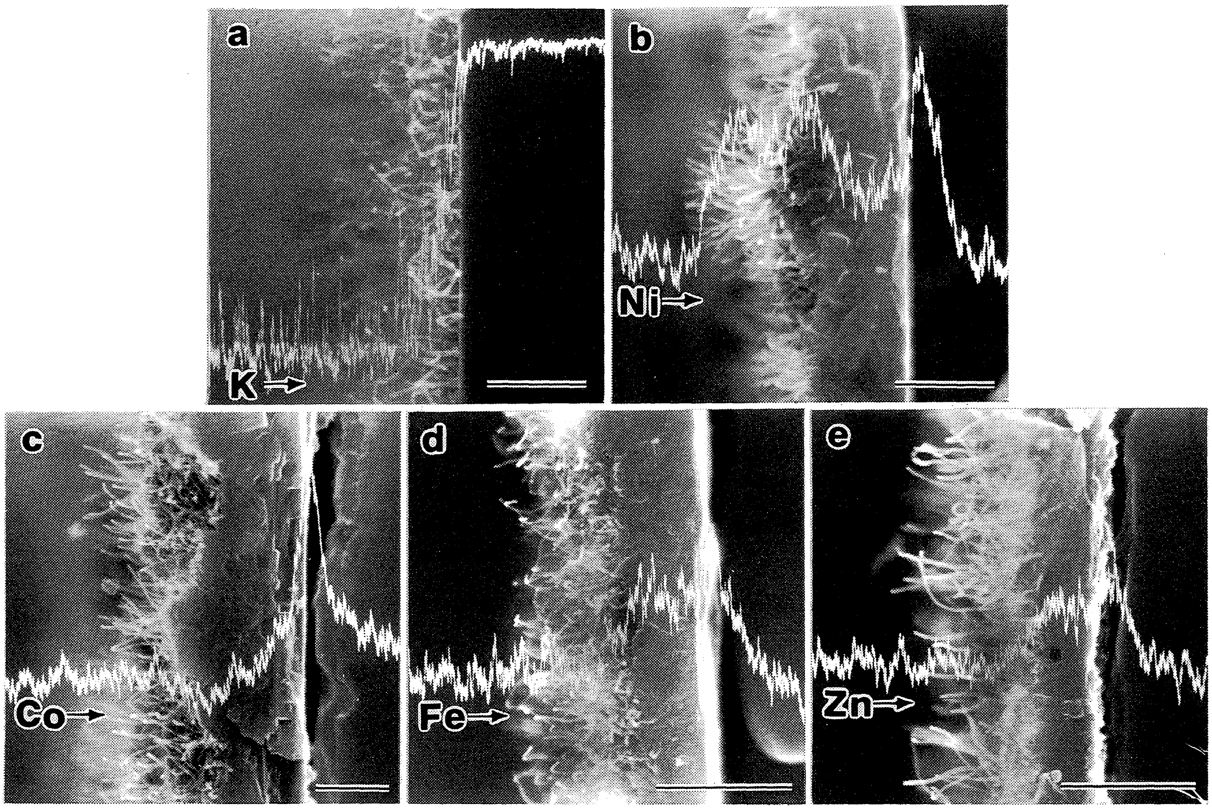

Fig. 9. Scanning electron micrographs and X-ray microanalyses of films produced on KCl(a), Ni(b), Co(c), Fe(d), and Zn(e) at 350 °C. Bar=5 μm.

Table 3. Products[a)] of the Reactions of TCNB with Different Substrates

T/°C	Substrate					
	KCl	Cu	Ni	Co	Fe	Zn
300	3′[b)]	3′	3,3′	3,3′	3,3′	3,3′
350	3′	3′,5	3′,5	3′,5	3′,5	3′,5
400	3′,4	3′,4	3′,4,5	3′,4,5	3′,4,5	3″,4
450	3″,4	3″,4	3″,4	3″,4	3″,4	3″,4

a) Products; 3: $M[Pc(CN)_8]$ ($M=K_2$, Cu, Ni, Co, Fe, Zn), 3′: intercalation compounds of $M[Pc(CN)_8]$, 3″: associated or oligomeric $M[Pc(CN)_8]$, 4: poly-M(Pc) containing structure elements of 5 and 6, 5: polynitrile, 6: triazine. b) $K_2[Pc(CN)_8]$ is not completely formed and a certain amount of products with low molecular weight is contained.

with elevating reaction temperature. The film produced at 450 °C contained highly polymerized products of poly-M(Pc) and cross-linked polymers with such structural elements as polynitrile and triazine. A small amount of the soluble portion in concentrated sulfuric acid was identified as associated or oligomeric $M[Pc(CN)_8]$.

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