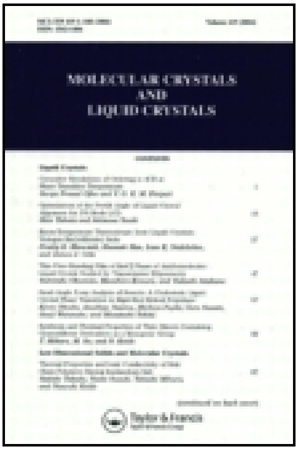

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A New Crystal of Copper Phthalocyanine Synthesized with 1,8-Diaza-Bicyclo- (5,4,0)Undecene-7

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A New Crystal of Copper Phthalocyanine Synthesized with 1,8-Diaza-Bicyclo-(5,4,0)Undecene-7

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A new crystal of copper phthalocyanine (CuPc) named the σ-form was directly synthesized from phthalonitrile and $CuCl_2$ with 1,8-diaza-bicyclo(5,4,0)undecene-7 by a seeding procedure. The σ-CuPc was investigated by X-ray powder diffractometry, spectroscopic and photoelectric measurements. These results were attributable to the formation of newly developed σ-CuPc. The hexagonal columnar crystal of σ-CuPc was observed by a scanning electron microscope.

Keywords: Copper phthalocyanine; synthesis; σ-form, polymorph.

INTRODUCTION

Phthalocyanines have been widely used in the preparation of coloring materials for printing ink, paint and plastic. In recent years, new use of phthalocyanines have been found as photoconductors,[1] photoreceptors[2,3] and optical recording media[4] by many researchers. Thus the investigation of the polymorphism with the phthalocyanines became more important in those fields, because morphology changes gave rise to new or enhanced absorptions and enhanced photosensitivity in near-infrared region.

It is widely known that a typical example of a phthalocyanine is copper phthalocyanine (CuPc) because of its high stability. CuPc has many kinds of polymorphic forms and has been reported in the literature.[5] The β-form is thermodynamically stable, the α- and γ-forms meta-stable. The δ-, ε-, R- and X-forms are quite differently arranged in the middle-energy stages between that of the α- and β-forms. The π-form, however, has a unique polymorphic form.[6] Brach *et al.* have synthesized the π-CuPc from anhydrous cuprous cyanide and phthalonitrile or 1,3-

diiminoisoindoline in a preheated alkylalkanolamine solvent at a temperature of 135 ~ 150°C.[6] This has been the only method of preparing π-CuPc, and further study has not been done up to this time.

In the case of metal-free phthalocyanine (H_2Pc), we have already studied a direct synthetic method for the τ-form, which is the middle-energy stage of H_2Pc, using a strong organic base such as 1,8-diaza-bicyclo(5,4,0)undecene-7 (DBU) by a seeding procedure.[7]

In this paper, we report the new direct synthetic method of newly developed CuPc with DBU by a seeding procedure and the results of various analytical measurements. This new crystal form of CuPc is named the σ-form in this article. We found the characteristic X-ray diffraction lines, infrared spectrum, absorption spectrum, XPS and many electric results of this σ-CuPc, which were distinguished from well-known α-, β-, ε- and π-CuPc.[8]

RESULTS AND DISCUSSION

The FD-mass spectrometry measured for σ-CuPc is shown in Figure 1. In the FD-mass spectral pattern, a monoline corresponding to M^+ (m/z of 575) corresponding to a pure CuPc molecule can be seen. We, therefore, found that this synthesized σ-CuPc had no derivatives. At first, in order to obtain the structural information, the X-ray powder diffraction patterns of the α-, β-, ε- and π-CuPc are given in Figure 2. Furthermore, the peak angles of X-ray powder diffraction patterns of α-, β-, γ-, δ-, ε-, π-, σ-, R- and X-CuPcs are shown in Table I. The patterns of the π-form are quoted from Brach's data.[6] From the peak angles in Table I, the crystal forms of CuPc are distinguished to the four polymorphic stages like as metastable, middle-energy, complex and stable types, respectively. The two strong peaks in the 5° ~ 10° (2θ) region of α, β and ε-CuPc suggest the distance of the *b*-axis of phthalocyanine molecules packed at various angles. The π-form shows a characteristic pattern less than 10° (2θ) region, i.e., it has five peaks of 5.1°, 7.0°, 8.8°, 9.1° and 10.0° in this region. From the five peaks below 10.0°, it could be presumed that this π-form synthesized by Brach's method would be composed of either several different crystal forms or a complex with CuPc. Thus these peaks below 10.0° are devoted to suggestion on the complicating arrangements of each CuPc molecules with π-CuPc.

The X-ray powder diffraction patterns of the formation process of σ-CuPc syn-

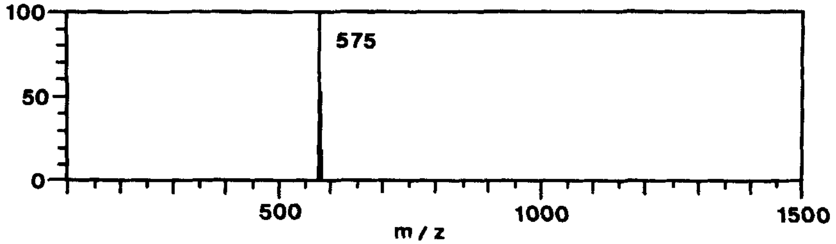


FIGURE 1 FD-Mass spectrometry of σ-CuPc.

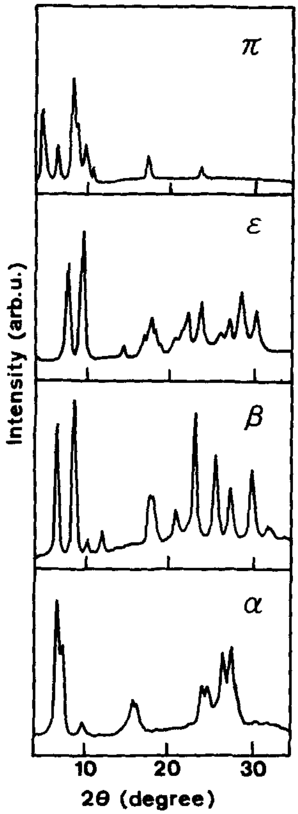


FIGURE 2 X-ray powder diffraction patterns of CuPc.

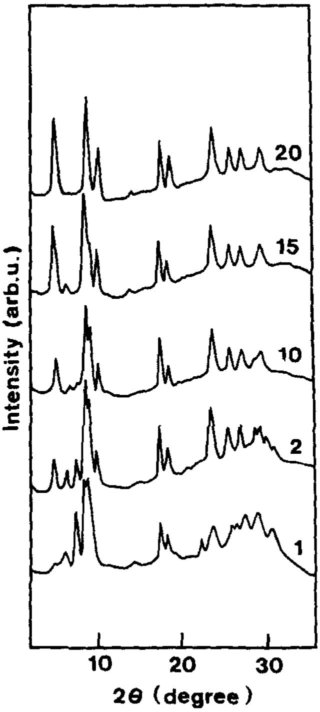


FIGURE 3 X-ray powder diffraction patterns of σ-CuPc. This figure suggests the conversion process of crystal, and the numerals in figure suggest the reaction time of synthesis.

thesized from phthalonitrile, copper dichloride and a seeding nucleus (ε-CuPc) with 1,8-diaza-bicyclo(5,4,0)undecene-7 are shown in Figure 3. The numerals in Figure 3 suggest the reaction hours, after the temperature rises above 100°C. The characteristic peaks of σ-CuPc can be seen. This synthesized crystal was identified as the π-form by comparing the position and intensity of X-ray powder diffraction peaks. Furthermore, the intensity of the six peaks of σ-CuPc over 17° were very intense, therefore, we could presume these peaks appeared to be made up of more closely packed molecules than the π-form.

The infrared spectra of the CuPcs are shown in Figure 4, and the absorption frequencies in the 700 ~ 800 cm^{-1} region are also summarized in Table II. The frequencies in this region are assigned as the out-of-plane C—H bending modes of the peripheral benzene rings of the CuPc molecules.[9] The small difference between the π-form and σ-CuPc suggests very similar overlapping states of π-orbitals; however, the band of 771 cm^{-1} in σ-CuPc clearly differentiates between them. Furthermore, the differences in X-ray powder diffraction patterns between them offers a more pronounced distinction between the two forms. For the π-form

TABLE I

Peak angles of X-ray powder diffraction pattern with copper phthalocyanines

meta-stable				middle energy								complex				stable	
α		γ		δ		ε		R		X		π		σ		β	
2θ	d	2θ	d	2θ	d	2θ	d	2θ	d	2θ	d	2θ	d	2θ	d	2θ	d
6.8	13.0	6.5	13.6									5.1	17.3	5.0	17.7		
7.2	12.3	7.4	11.9	7.7	11.5	7.6	11.6	7.6	11.6	7.7	11.5	7.0	12.6			7.0	12.6
												8.8	10.0	8.7	10.2		
9.9	8.9	9.7	9.1			9.2	9.6	9.1	9.7	9.5	9.3	9.1	9.7			9.2	9.6
		10.4	8.5	10.1	8.8	11.4	7.8					10.0	8.8	10.0	8.8	10.5	8.4
15.5	5.7	15.9	5.6	11.8	7.5	14.2	6.2	14.2	6.2	14.2	6.2					12.5	7.1
16.2	5.5					17.1	5.2	16.8	5.3					17.3	5.1		
				17.6	5.1	17.5	5.1	17.5	5.1	17.5	5.1					18.1	4.9
														18.4	4.8	18.5	4.8
																21.3	4.2
						20.6	4.3	20.4	4.4								
		21.3	4.2			21.3	4.2										
						21.8	4.1	21.9	4.1								
		23.8	3.74	23.5	3.79	23.6	3.77	23.6	3.77					23.2	3.83	23.5	3.79
24.0	3.71																
24.9	3.58	24.9	3.58														
		26.3	3.39	25.4	3.51	25.9	3.44							25.4	3.51	26.0	3.43
26.6	3.35													26.8	3.33		
27.5	3.24	27.7	3.22					27.0	3.30							27.8	3.21
						28.7	3.11	28.4	3.14					28.5	3.13		
		30.3	2.95			30.1	2.97	30.2	2.96							30.3	2.95

$\lambda = 2d \sin\theta$; 2θ (°), d (Å)

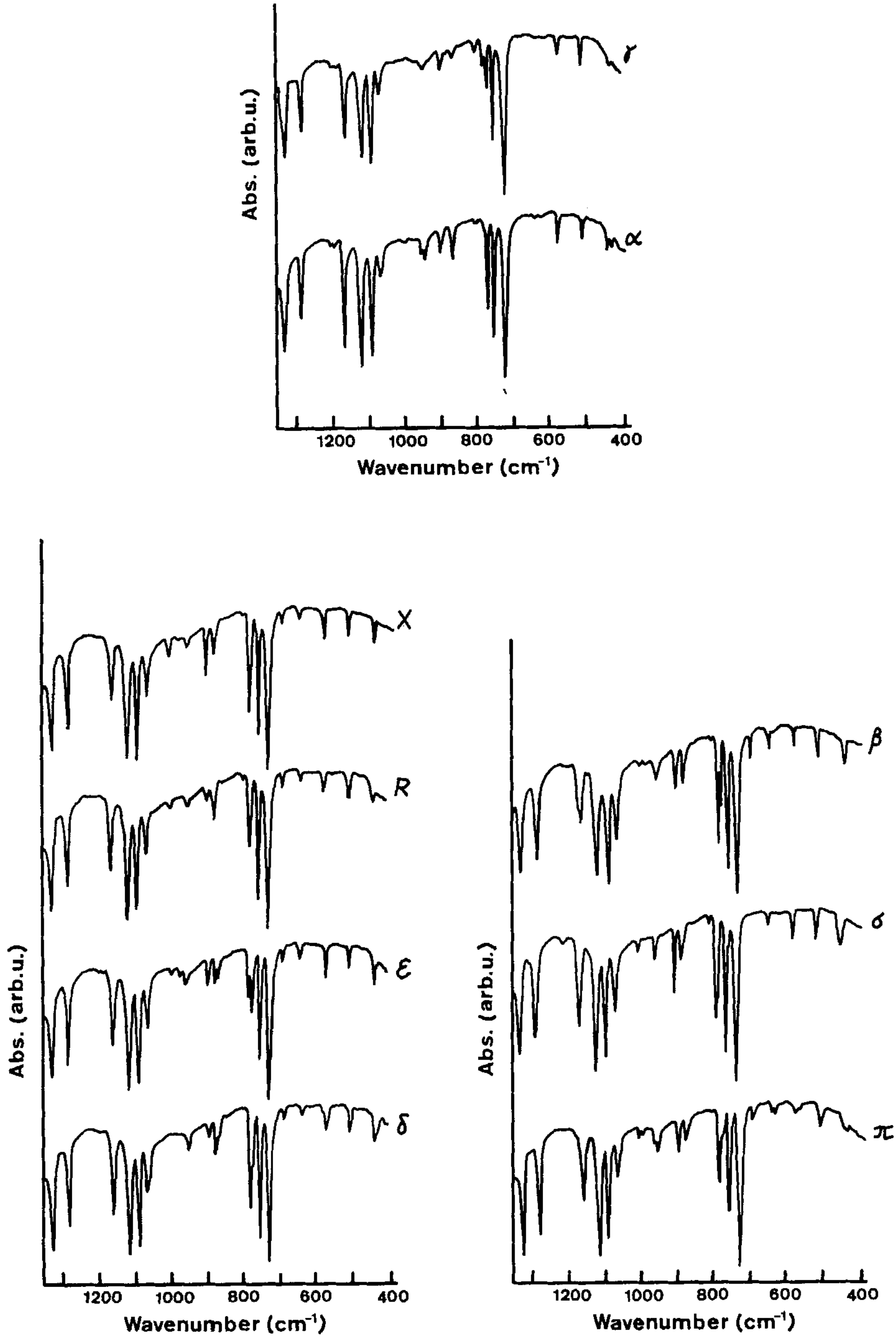


FIGURE 4 Infrared spectra of CuPcs.

TABLE II

Wavenumbers of infrared spectra in the 700 ~ 800 cm^{-1} with copper phthalocyanines[a]

Line	α	γ	δ	ε	R	X	π[b]	σ	β
1	723(vs)	722(vs)							
2			729(vs)	727(vs)	728(vs)	728(vs)	728(vs)	728(vs)	731(vs)
3	755(m)	754(m)	755(m)	754(m)	755(m)	755(m)	755(m)	755(m)	755(m)
4	770(m)	769(m)	772(w)					771(w)	771(m)
5	776(w)	776(w)	779(m)	775(m)	776(m)	774(w)			
6		781(w)		785(w)			781(m)	781(m)	781(m)

a) Positions of absorption bands are shown in wavenumber(cm^{-1}),and relative intensities are labeled as vs = very strong, s = strong, m = medium and w = weak, respectively.

b) These wavenumbers are quoted from Brach's data.

and σ-CuPc, the position of the absorption band (728 cm^{-1}), which was the most intense band in the spectra, was at 723 cm^{-1} for the α-form and 731 cm^{-1} for the β-form. It could therefore be presumed that the energy level of σ-CuPc is between the α- and β-forms, and intermolecular overlapping of π-orbitals is distinct between the α- and β-forms.

The electronic absorption spectra of α-, β-, ε- and σ-CuPc dispersed with 1,4-dioxane, which differ in the positions of the absorption peaks, are shown in Figure 5. Table III shows the wave-length and molecular extinction coefficient of the absorption spectra. The peak at 665 nm has been assigned as the 0–0 transition band to the lowest $\pi-\pi^*$ singlet state in CuPc molecules of D_{4h} symmetry.[10] Since α-, ε- and σ-CuPc are not stable and are less ordered polymorphs than the β-form, their absorption spectra should be closer than those of the monomer, which had a peak at 665 nm. The double maxima peaks either below 650 nm or over 700 nm observed in all CuPc spectra could be attributed to dipole-dipole exciton splitting of the singlet transition, resulting from the interaction of molecules of the dimer. The spectrum of σ-CuPc resembled that of the α-form; therefore, we could presume that the dispersed state of σ-CuPc in 1,4-dioxane resembled that of the α-form. The spectrum of the ε-form also was similar to that of σ-CuPc; however, this new crystal had no absorption peak in the long wavelength region (765 nm) due to the state of aggregation similar to that of the ε-form. The molecular extinction coefficient of σ-CuPc, from 600 to 750 nm, was the smallest among the four polymorphs, due to the largest particle size resulting from direct synthesis without pigmentations.

X-ray photoelectron spectroscopy (XPS) has been applied to the study of the

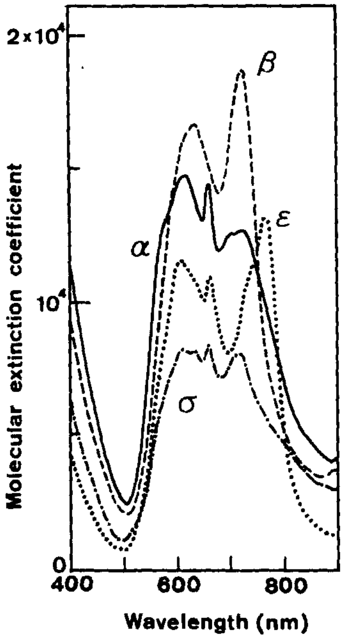


FIGURE 5 Absorption spectra of α, β, ε and σ-CuPc. The particles are dispersed into 1,4-dioxane.

TABLE III

Wavelength and molecular extinction coefficient of peaks on absorption spectra with copper phthalocyanines[a]

α	β	ε	σ
620(4.17)	638(4.22)	610(4.07)	610(3.92)
			635(3.92)
665(4.16)		665(4.04)	665(3.93)
705(4.10)	720(4.27)		720(3.92)
730(4.10)			
		765(4.12)	

a) Numerals at left-hand represent wavelength (nm), and numerals in parentheses represent molecular extinction coefficient (log ε).

TABLE IV

Chemical shift of XPS spectra for CuPc[a]

Chemical shift (eV)				
CuPc	α	β	ε	σ
C-C	284.6	284.6	284.4	284.3
C-N	286.1	286.1	286.0	285.7
Oxygen (O_{1s})				530.4
	533.2	533.0	533.3	533.1
Nitrogen (N_{1s})	398.8	398.6	398.8	398.8
Copper ($Cu_{2p3/2}$)				933.5
	935.1	934.9	935.5	935.4
($Cu_{2p1/2}$)				953.6
	955.0	954.8	955.5	955.3

a) The sample is irradiated with monoenergetic X-rays of MgKα (1253.6 eV).

electronic structure and surface analysis of phthalocyanines.[11-17] Chemical shifts of XPS spectra for CuPcs are indicated in Table IV, and XPS spectra of σ-CuPc are shown in Figure 6. Wang *et al.*[13] have already reported the results of XPS analysis for α-, γ-, β- and X-CuPc and pointed out the differences in shake-up satelite peaks and valence band spectra, but the chemical shifts of CuPcs are at almost the same positions for every polymorph. We also couldn't find differences in the chemical shifts of the C_{1s} and N_{1s} lines for α-, β-, ε- and σ-CuPc. In each of the four forms, the C_{1s} line was split into two components located at 284.6 and 286.1 eV with a 3:1 intensity ratio for the CuPc. In agreement with the chemical formula, the lower and higher binding energy components were due to the carbon atoms binding the nitrogen atoms and the carbon atoms having an aromatic hydrocarbon character in the phthalocyanine rings, respectively. The profile of the single sharp peak of N_{1s} (approximately 398.8 eV) indicates a small energy separation between the four equivalent central nitrogens. On the contrary, the O_{1s} and Cu_{2p} lines of σ-CuPc are quite different from the other three forms. As a result of

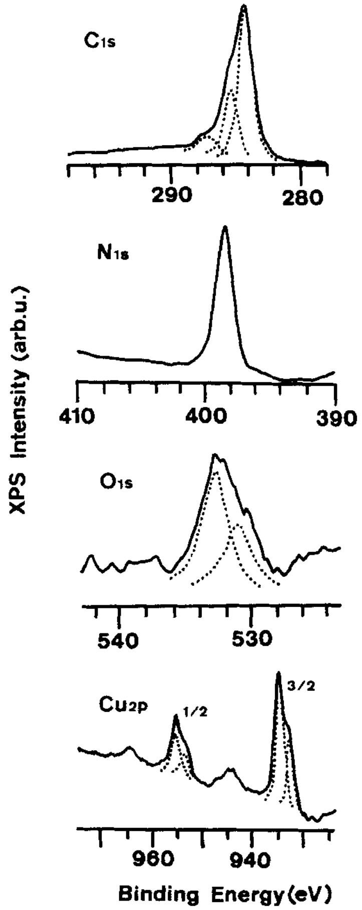


FIGURE 6 XPS spectra of σ-CuPc.

peak separation, the O_{1s} line of σ-CuPc was split into two components located at 533.1 and 530.4 eV, and the ratio of peak intensity for the lower and higher binding energy components was 1:1.4. The other three forms had one O_{1s} line of approximately 533 eV. The lines of Cu_{2p} of σ-CuPc were also split into two components, located at 933.5, 935.4 eV for $Cu_{2p3/2}$ and 953.6, 955.3 eV for $Cu_{2p1/2}$. For both $Cu_{2p3/2}$ and $Cu_{2p1/2}$, the ratio of peak intensity was also 1:1.4. These results will explain that the σ-CuPc consists of at least two kinds of CuPc compounds, which have no derivatives (reference Figure 1). This σ-CuPc may be complexes with two crystal states of CuPcs. Furthermore, it can be seen from Table IV that the lower binding energy component is a characteristic one by comparing the binding energy with those of the other three polymorphs.

In the surface type cells used for photoelectric measurements in this study, dark current and photocurrent were measured at room temperature. The results are shown in Table V, Figures 7 and 8. Phthalocyanine particles contain charge carrier traps, which originate from chemical impurities and structural irregularities. In addition, the crystal structure of α-, β- and ε-CuPc are suggested to be tetragonal, face-centered monoclinic and hexagonal, respectively.[8] Figure 7 shows the dependence of dark current for α-, β-, ε- and σ-CuPc on the electric field. The dark

TABLE V

Darkcurrent (Id) and Photocurrent (Iph) of copper phthalocyanines measured under the pressure of 2 × 10^{-6} Torr at room temperature[a]

CuPc	Id (Å)	Iph(Å)[b]	Iph/Id
α	8.97×10^{-7}	1.69×10^{-5}	19
β	5.17×10^{-10}	7.28×10^{-8}	141
ε	4.20×10^{-8}	6.20×10^{-6}	148
σ	1.23×10^{-10}	8.13×10^{-9}	66

a) Values in Table are represented at the electric field of 10^3 (V/cm).

b) These values are measured by irradiation of no-filtered Xe-lamp. Light intensity is 131 (mW/cm^2) in all measurements of photocurrent.

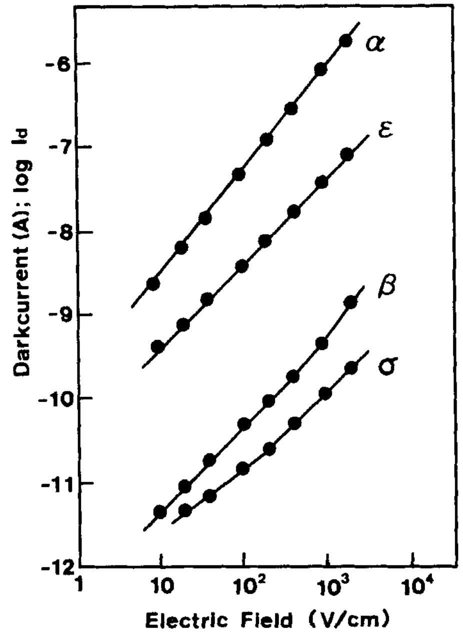


FIGURE 7 Darkcurrent of surface type pellet with CuPc.

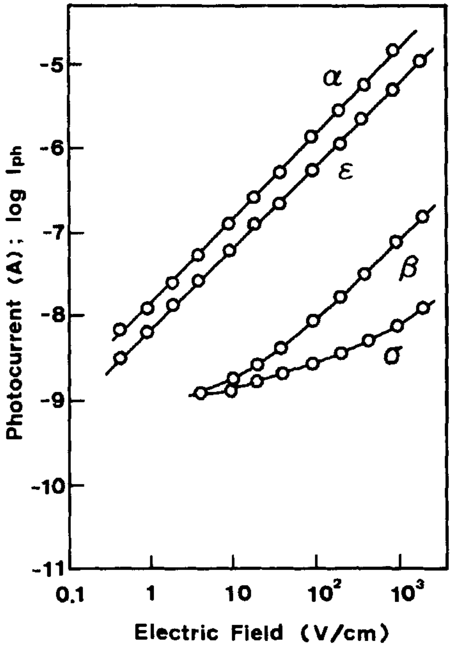


FIGURE 8 Photocurrent of surface type pellet with CuPc. The light is irradiated by Xe-lamp (131 mW/cm^2).

current depended linearly on the electric field corresponding to Ohm's law. On the contrary, β- and σ-CuPc were influenced by high field strength, the straight lines consequently gradually curved due to the lower dark conductivities. For comparison, the dark current of CuPcs differed greatly for the four polymorphs of CuPc. The dark current of α-, ε-, β- and σ-CuPc decreased in that order, and the pellet of α-CuPc was more conductive by three orders of magnitude at 10^3 V/cm than σ-CuPc. Though we could not prove the crystal structure of σ-CuPc in this work, this lowest value of dark current for σ-CuPc could suggest the formation of a more insulated polymorphic structure. Figure 8 shows the dependence of photocurrent for α-, β-, ε- and σ-CuPc on the electric field. For both α- and ε-CuPc, the photocurrent also depended linearly with almost the same slope on the electric field. On the contrary, the slope of photocurrent for β- and σ-CuPc were lower than for the former two polymorphs. The photocurrent of β-CuPc grew linearly with the same slope above 10^2 V/cm. While the photocurrent of σ-CuPc grew nonlinearly, we expect that the photocurrent of σ-CuPc obeys Ohm's law over approximately 10^5 V/cm. This suggests the necessity of a high electric field for Ohmic contact between phthalocyanine and an Au electrode. Table V and Figure 9 show the ratio of photocurrent and dark current. The α-, β- and σ-CuPc decrease with increasing electric field; on the contrary, the ε-CuPc maintains a constant (Iph/Id = 148) from 10^{-1} to 10^3 V/cm. The independence of Iph/Id with electric field suggests the independence of carrier generation for the electric field.

In order to observe the shape of σ-CuPc, we used a scanning electron microscope (SEM). SEM photographs are shown in Figure 10. The shape of σ-CuPc looked like a chrysanthemum, and the crystals of σ-CuPc grew hexagonal columns. In general, the synthetic temperature of phthalocyanines are above 200°C,[5] however, we can synthesize them under 100°C with a strong base (DBU). Owing to the use of DBU as a strong base, the condition of this reaction consequently became milder, and the polycondensation of phthalocyanine precursors would be accelerated to form phthalocyanine molecules. Under these synthetic conditions, the crystals will

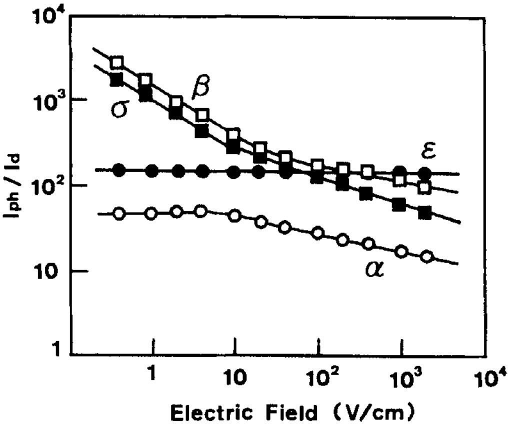


FIGURE 9 Plot of (I_{ph}/I_d) vs. electric field for CuPc.

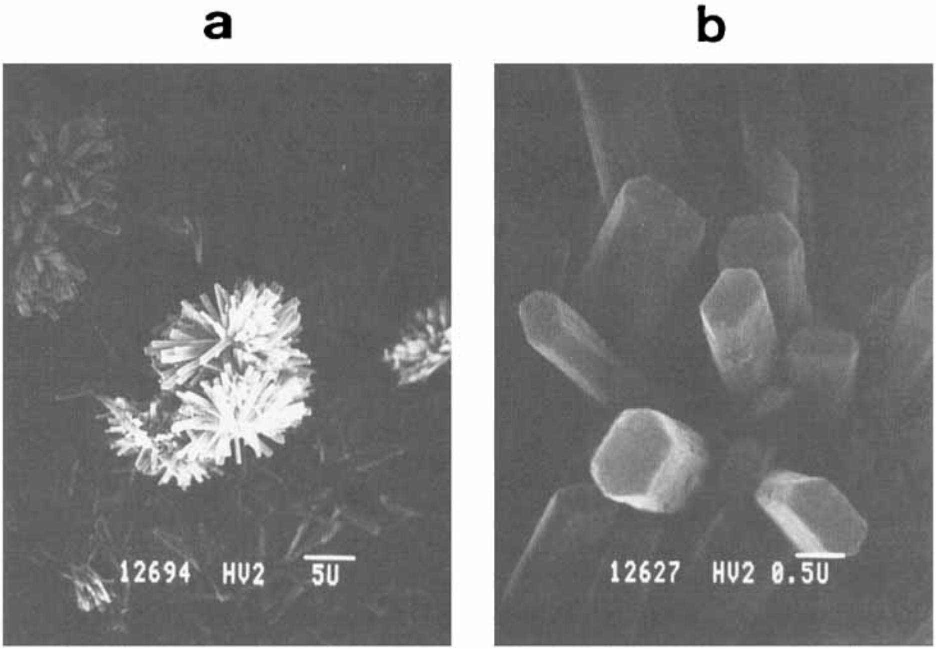


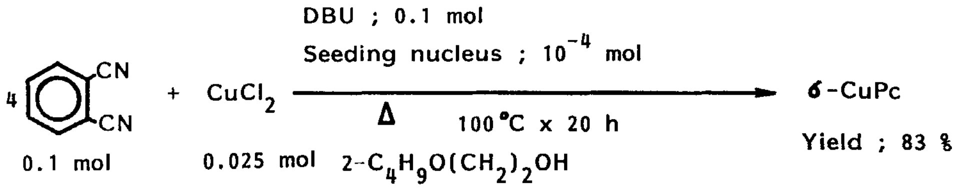
FIGURE 10 Scanning electron microscope photographs of σ-CuPc. The bars in the photographs represent (a) 5 μm, (b) 0.5 μm, respectively.

grow hexagonally, centered around a nucleus. We could not synthesize the σ-form without using ε-CuPc as a crystal nucleus. An assumption can therefore be drawn that the arrangements of the ε-form, which have not been analyzed so far, are responsible for making the σ-form as a crystal nucleus. Polycondensation of phthalocyanine precursors near the crystal nucleus will proceed rapidly and successively under the mild conditions for growth of hexagonal columns. Enlargement of the X-ray diffraction line at 17.6 Å in Figure 3 indicates an increase in the amount of crystals having long distances of the *b*-axis, and the transport of carriers in the crystal will be inhibited due to the decrease of overlapping of the orbitals. The lowest dark current of σ-CuPc will be maintained as a result of this inhibition of carrier transport.

EXPERIMENTAL

Materials

The synthetic process for σ-CuPc is shown in Scheme I. Phthalonitrile (12.8 g; 0.1 mol), $CuCl_2$ (3.13 g; 2.5×10^{-2} mol) and a small amount of seeding nucleus, e.g., ε-CuPc (0.06 g; 10^{-4} mol) were dissolved in 2-butoxyethanol with stirring at 60°C. The specific surface area measured by the BET method with ε-CuPc was over 70 m^2/g. Then, 1,8-diaza-bicyclo(5,4,0)undecene-7 (DBU: 15.2 g; 0.1 mol) was added dropwise to the solution. The temperature was maintained at 60°C during the first



Scheme I

1 hour and finally was raised to 100°C. After that, the stirring was continued for the alloted time at 100°C. The product was collected by filtration, washed with methyl alcohol, purified by extraction with acetone, and dried for 2 days. The total yield of the product was 83 wt.% (13.4 g), therefore, the amount of seeding nucleus in the product was within 0.45 wt.%. The α-, β-, and ε-CuPc were obtained from Toyo Ink Mfg. Co., Ltd. and were used without further purification.

Measurements

The differences in crystal forms of CuPcs were measured by X-ray powder diffraction patterns, infrared spectra, electronic spectra, X-ray photoelectron spectra (XPS) and dark and photocurrent at room temperature. The used CuPcs except for the σ-CuPc were obtained from Toyo Ink Mfg. Co., Ltd. Mass spectrometry was done by an FD-mass spectrometer M-300 (Hitachi Ltd.). X-ray powder diffraction patterns were measured in the reflection geometry scanning using Ni-filtered CuKα radiation by RU-200 (Rigaku-Denki, Corp.). Infrared spectra were measured on pellet samples mixed with KBr by Infrared Spectrometer IR-700 (Japan Spectroscopic Co., Ltd.). Electronic spectra were measured on a UV-Visible recording spectrophotometer UV-2100S (Japan Spectroscopic Co., Ltd.) with dispersed samples in 1,4-dioxane. X-ray photoelectronspectra (XPS) were measured using an ESCA system with a MgKα X-ray target (Perkin-Elmer PHI-5400). Dark and photocurrent of a pellet of CuPc pressed at 400 kg/cm^2 were measured by a

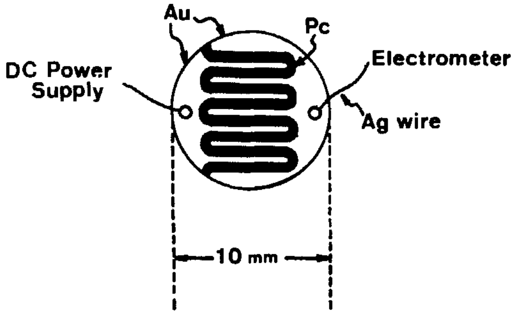


FIGURE 11 Surface cell used in this article. It consists of two interpenetrating combs spaced about 0.5 mm apart. Electrodes are made by depositing Au source through a mask onto the phthalocyanine pellet. The total area of phthalocyanine surface is 24.0 mm^2.

Keithley 617 electrometer. The pellets were placed into the cryostat at a pressure of 2 × 10^{-6} Torr. The Au electrode of the pellet was deposited through a mask onto the surface, and the arrangement of electrodes of this surface type cell is shown in Figure 11. The diameter of the pellet was 10 mm, the distance of the Au electrode was 0.5 mm, and the total measured length of every pellet surface of the phthalocyanines was 48.06 mm, respectively. The shape of σ-CuPc was observed by a scanning electron microscope (SEM).

Acknowledgment

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