Cobalt Phthalocyanine Crystal Synthesized at Low Temperature

Toshio Enokida* and Ryo Hirohashi†

Graduate School of Science and Technology, Chiba University, 1-33 Yayoi-cho, Chiba-shi, Chiba 260, Japan, and Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Chiba-shi, Chiba 260, Japan

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A new crystal of CoPc, ϵ-CoPc, was synthesized from $CoCl_2$ and phthalonitrile by using 1,8-diazabicyclo[5,4,0]undecene-7 (DBU) as a catalyst in 2-butoxyethanol at 100 °C. The characteristics of ϵ-CoPc can be summarized as follows: The X-ray diffraction pattern is distinguishable from other polymorphs. The wavelength of the C–H out-of-plane vibration is located between that of α-CoPc and β-CoPc. The electric absorption spectrum shows weak absorbance resulting from the π–π* transition. However, a new absorption peak appears at 808 nm. These results suggest that this ϵ-CoPc is a new crystalline form intermediate in energy between the α and β forms. The results of X-ray photoelectron spectroscopy also support these phenomena.

Introduction

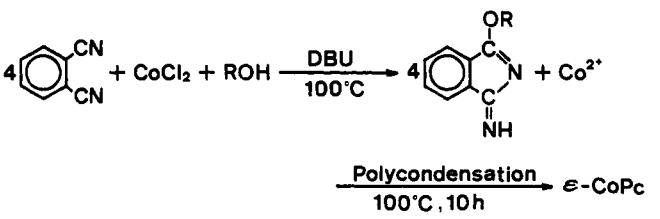
Phthalocyanines (Pc's) are a very interesting class of organic materials because of their excellent properties in fields such as solar cells,[1] organic semiconductors,[2,3] liquid crystals,[4] and optical data recording media.[5] A variety of work has been performed in the above fields. One area of investigation of organic photoconductors based on Pc's has been developed for the purpose of making charge generation materials (CGM) for photoreceptors used in laser beam printers.[6-8] Electronic properties of organic materials such as phthalocyanines are influenced by the electron density of the central metals and morphology.[2,3]

Metal-free phthalocyanine (H_2Pc) and divalent metallophthalocyanines (MPc's) have two typical polymorphic forms, the β form, which is thermally stable, and the α form, which is metastable. In addition, the middle-energy stages such as the τ-[9] and X-H_2Pcs[10] and the δ-,[11] ϵ-,[12] R-,[13] and X-form[14] copper phthalocyanines (CuPc's) have been reported up to this time. Pc's of the middle-energy stages have usually shown a high photocurrent or photovoltage in spite of low dark conductivities; therefore, these materials are suitable for photoconductors such as the CGM of the dual-layered organic photoreceptors.[7] Other Pc's, which have the middle-energy stages, have scarcely been investigated on account of the difficulties of crystal preparations. We have already directly synthesized the τ-H_2Pc, which is the middle-energy stage of H_2Pc, from phthalonitrile by the seeding procedure in the presence of 1,8-diazabicyclo[5,4,0]undecene-7 (DBU) as a reaction stimulator in alcohol.[15-17]

Cobalt phthalocyanine (CoPc) has been investigated with its properties[18] and applications for catalysis,[19] magnetic field,[20] and photoconductors.[21,22] CoPc has the α and β forms.[18] The middle-energy stage of CoPc was scarcely studied so far. The X form is the only case exhibiting the middle-energy stage of CoPc,[21] which is prepared as a thin film by sublimation. Therefore, the CoPc powder that has the middle-energy stage has not been obtained thus far.

We applied the DBU methods to obtain the CoPc of middle-energy state. In this study, we report a new direct synthetic method of newly developed CoPc with DBU and the results of various analytical measurements. This new crystal was named the ϵ form. In addition, the α- and β-CoPcs were also synthesized by this DBU method by controlling the temperature.

Scheme I. Synthetic Process of ϵ-CoPc from Phthalonitrile and $CoCl_2$ Using DBU in 2-Butoxyethanol



Experimental Section

Materials. The ϵ-CoPc was directly synthesized as follows. Phthalonitrile (0.2 mol) and $CoCl_2$ (0.8 mol) were dissolved in 2-butoxyethanol (200 mL) with stirring at 100 °C. Then, DBU (0.2 mol) was added dropwise to the solution, and the temperature was maintained at 100 °C. After 10 h of heating, the product was

* To whom correspondence should be addressed at the Graduate School of Science and Technology. On leave from Electronic Materials Division, Toyo Ink Mfg. Co., Ltd., 1 Sakae, Kawagoe-shi, Saitama 350, Japan.

† Faculty of Engineering.

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Table I. X-ray Powder Diffraction Lines

α-CoPc			β-CoPc			ε-CoPc		
2θ, deg	d, Å	I/I_0	2θ, deg	d, Å	I/I_0	2θ, deg	d, Å	I/I_0
6.8	13.0	100	7.0	12.6	100			
7.3	12.2	72				7.6	11.6	100
			9.2	9.6	93	9.2	9.6	77
10.0	8.9	17	10.5	8.4	9			
			12.5	7.1	22			
			14.0	6.1	12	14.4	6.3	18
15.6	5.7	26	18.1	4.9	44	17.0	5.2	14
16.2	5.5	24	18.7	4.8	33	17.7	5.0	23
			21.5	4.2	5	20.7	4.3	14
24.1	3.69	29	23.8	3.74	8	21.1	4.2	25
24.8	3.59	14	26.2	3.40	5	22.8	3.90	8
25.3	3.52	20	28.4	3.14	8	25.9	3.45	16
26.8	3.33	46	30.5	2.93	7	27.4	3.25	32
27.8	3.21	58	31.4	2.85	8	29.3	3.05	23

collected by filtration, washed with water, and purified by the solvent extraction technique with acetone and methyl alcohol. The α- and β-CoPc's were synthesized by the same technique at temperatures of 80 and 130 °C, respectively.

Measurements. All samples were checked by mass spectroscopy and confirmed fragmentation patterns with common peaks. X-ray diffraction (XRD) patterns were measured by reflection geometry scanning, using Ni-filtered Cu Kα radiation on a RU-200 (Rigaku Co.) diffractometer. IR spectra were obtained on powder mixed with KBr using a diffusion reflection method by an Infrared spectrometer IR-700 (Japan Spectroscopic Co., Ltd.). Electronic absorption spectra were measured on a UV-visible recording spectrophotometer UV-2100S (Japan Spectroscopic Co., Ltd.) for CoPc's dispersed in chloroform. X-ray photoelectron spectra (XPS) of powdered CoPc's were measured by using a Perkin-Elmer PHI-5400 ESCA system with a Mg Kα X-ray target.

Results and Discussion

Synthesis. The ε-CoPc was synthesized by the procedure described in Scheme I. In general, the crude Pc's are synthesized from phthalonitrile or Pc precursors above 200 °C.[23] However, this ε-CoPc was done at 100 °C with DBU, which supports the making of the Pc precursor and promotes the polycondensation at lower temperatures (from 80 to 130 °C). In the case of this synthetic method, pure α- and β-CoPc's were obtained directly below 80 and above 130 °C, respectively. These results suggest that the synthesized CoPc's in this work are dependent on the temperature of synthesis. Therefore, it can be presumed that this synthesis comprises not only polycondensations of Pc precursors but also concomitant crystal transformations of Pc's.

XRD Patterns. Figure 1 and Table I show the XRD patterns and lines of CoPc's. The α- and β-CoPc's are identical with the patterns of other MPc's reported by Ebert et al.[24] A single crystal of β-CoPc was grown by sublimation and analyzed by X-ray diffraction; the monoclinic space group is $P2_{1/a}$.[23] The α-CoPc is obtained by dissolving β-CoPc in 98 wt % sulfuric acid and precipitating the α type by pouring the solution into a large volume of water. The probable space group of α-CoPc is $P4/m$, and the d values were also calculated.[23] The ε-CoPc has a different pattern, and the main lines are similar to those of ε-CuPc.[25] As the Co atom and the Cu atom have almost the same covalent radii (Co, 1.16 Å; Cu, 1.17 Å), the crystal arrangements of both Pc's may pack in the same way. The characteristic diffraction lines are shown in Table I.

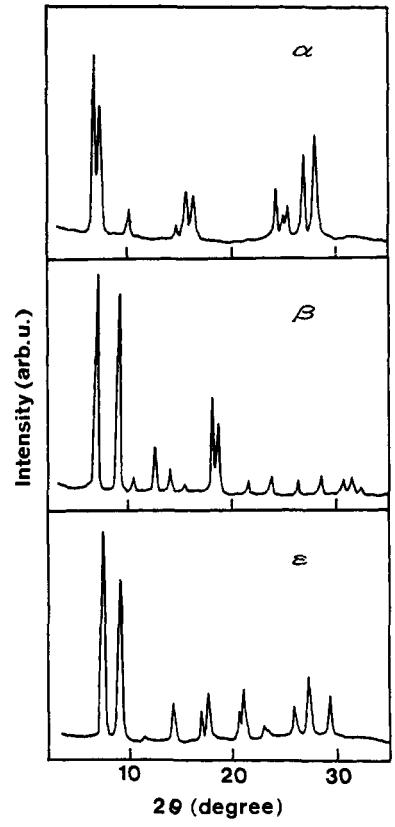

Figure 1. X-ray powder diffraction patterns of CoPc's.

IR Spectra. The IR spectra and frequencies and their assignments are summarized in Table II. The frequencies corresponding to the out-of-plane C–H bending modes of the peripheral benzene rings of the CoPc's, peaks 6, 8, 10, 12, and 18, evidently suggest differences due to polymorphic forms. The wavenumbers of β-CoPc peaks 6, 8, 10, 12, and 18 are larger than those of α-CoPc due to its greater force of molecular packing, involving stronger intermolecular forces and decreased symmetry. Peak positions of ε-CoPc situate in the middle position of α-CoPc and β-CoPc. Such a position of the frequencies suggests and new packing mode having middle-energy stages.

Electronic Absorption Spectra. Electronic absorption spectra of CoPc's are shown in Figure 2. The assignment of spectra of Pcs is well documented,[26] and these peaks can be assigned to the characteristic bands. The N band at 285 nm, the B or Soret band ($\pi-\pi^*$) at 335 nm, the Q band of the $\pi-\pi^*$ transition at approximately 650 nm are assigned, and a band attributed to aggregation of

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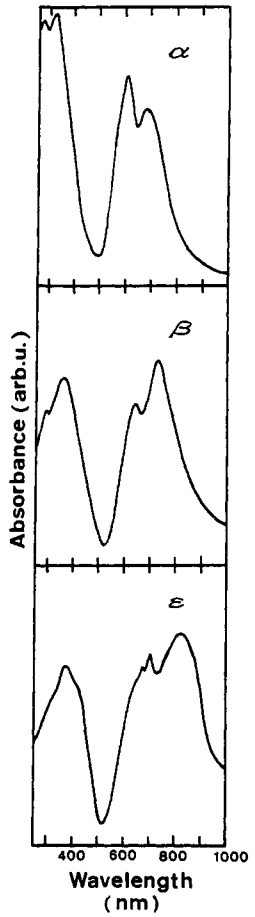

Figure 2. Electronic absorption spectra of CoPc's dispersed in chloroform.

ϵ-CoPc particles above 800 nm was also observed.

In the spectrum of α-CoPc, the N band and Soret band are well split, and almost the same intensities can be seen. The intensity at the 690-nm peak is smaller than that of the Q band. It is known that the Davydov splitting of the Q band results from the dipole–dipole interactions in Pc crystals.[27] These interactions in α-CoPc can therefore be presumed. On the other hand, the intensities of individual peaks attributed to the N, B, and Q, bands of β-CoPc are relatively smaller than those of α-CoPc. As all these bands can be attributed to the allowed π–π*, the β-CoPc does not have the structure to promote the π–π* transitions. In the case of ϵ-CoPc, a new absorption appears at approximately 800 nm and the N band at 285 nm nearly disappears as shown in Figure 3. This result also suggests the formation of the new crystal phase.

XPS Spectra. The measured C_{1s}, O_{1s}, and N_{1s} XPS spectra, the composition of surface atoms, and the binding energies for the CoPc's are shown in Figure 3 and Table III. A few differences can be seen in the composition of surface atoms. As the β-CoPc is stacked closely, the detected oxygens are fewer than those of other polymorphs. We could not observe any visible differences of the C_{1s} spectra with CoPc's because of their extremely stable natures against the active atoms and compounds. The binding energy of the peak for the C–C bond in benzene rings is assumed to be 284.6 eV.[28] The binding energy of 286.0 eV is the C–N bond and/or quaternary carbons. In the case of O_{1s} spectra, the binding energies of peaks are

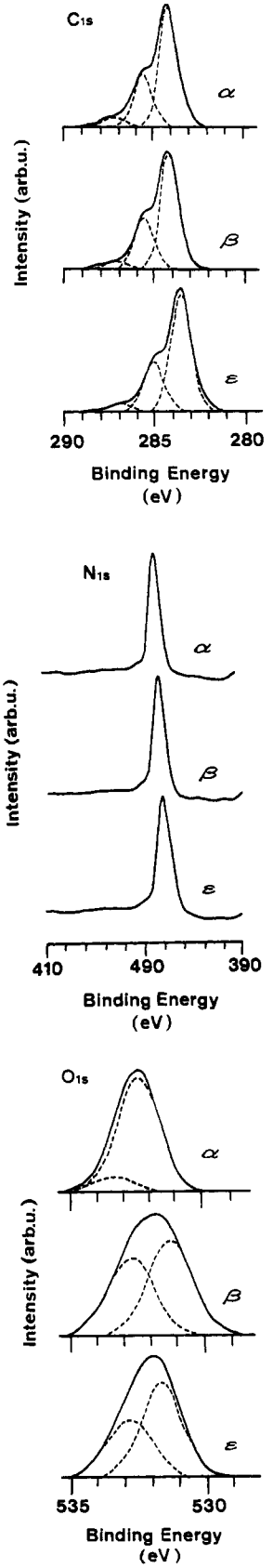

Figure 3. XPS spectra of CoPc's.

different. The binding energy of O_{1s} for both β-CoPc and ϵ-CoPc is separated into two large peaks in the same regions; however, a large peak of the O_{1s} spectrum for α-CoPc in the 532.5–533.4-eV region is observed. Pc's do not have any chemically bonded oxygen, so these differences of the O_{1s} spectra can be assigned to the conditions of absorption

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Table II. IR Spectra of CoPc's (cm^{-1})[a]

peak	α-CoPc	β-CoPc	ε-CoPc	assignment
1	431 (s)	436 (vs)	432 (s)	C–C out-of-plane bending
2	515 (m)	517 (s)	517 (m)	C–C out-of-plane bending
3	572 (m)	572 (s)	573 (m)	C–C out-of-plane bending
4	643 (w)	641 (s)	641 (w)	C–C out-of-plant bending
5	687 (w)	689 (m)	690 (w)	C–C out-of-plane bending
6	726 (vs)	732 (vs)	731 (vs)	C–H out-of-plane bending
7	756 (s)	756 (s)	755 (s)	C–H out-of-plane bending
8	772 (s)	778 (s)	777 (s)	C–H out-of-plane bending
9	806 (w)	804 (w)	804 (w)	metal–N
10	865 (m)	874 (m)	871 (m)	C–H out-of-plane bending
11	913 (m)	913 (s)	913 (m)	metal–N
12	944 (m)	952 (m)	950 (w)	C–H out-of-plane bending
13	999 (w)	1002 (w)	1004 (w)	
14	1074 (m)	1074 (sh)	1074 (m)	C–H in-plane bending
15	1092 (vs)	1089 (vs)	1093 (vs)	C–N stretching
16	1121 (vs)	1123 (vs)	1121 (vs)	C–H in-plane bending
17	1165 (vs)	1167 (vs)	1162 (vs)	C–H in-plane bending
18	1199 (m)	1202 (m)	1201 (w)	C–H out-of-plane bending
19	1289 (vs)	1290 (vs)	1288 (vs)	C–H, C–H stretching
20	1332 (vs)	1333 (vs)	1331 (vs)	C–H, C–N stretching
21		1370 (w)	1389 (w)	C–H, C–N stretching
22	1426 (vs)	1425 (vs)	1424 (vs)	C–H, C–N stretching
23	1469 (m)	1467 (s)	1466 (m)	C–H, C–N stretching
24	1487 (w)	1487 (w)	1487 (sh)	C–H, C–N stretching
25	1523 (vs)	1523 (vs)	1521 (vs)	C–H, C–N stretching
26	1595 (w)	1592 (m)	1589 (w)	C–H, C–N stretching
27	1611 (m)	1609 (s)	1606 (w)	C–H, C–N stretching
28		1652 (w)	1676 (w)	C–H, C–N stretching

[a] vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

Table III. XPS of CoPc's

Composition of Surface Atoms (atom %)

form	C	O	N	Co
α-CoPc	79.8	1.1	17.3	1.8
β-CoPc	79.9	0.8	17.3	2.0
ε-CoPc	81.5	1.3	15.6	1.6

C_{1s} Spectra

	energy, eV			
form	283.7–282.9	284.6	286.0	287.8
α-CoPc	3.01	60.55	29.33	7.11
β-CoPc	5.15	58.88	29.87	6.01
ε-CoPc	2.85	58.96	32.37	5.82

O_{1s} Spectra

	energy, eV			
form	531.4–529.6	532.4–531.5	533.4–532.5	534.2–533.5
α-CoPc	1.10		87.29	11.61
β-CoPc		55.56		44.44
ε-CoPc		60.86		39.14

N_{1s} Spectra

all forms suggested a single peak at 398.1 eV

of oxygen to CoPc molecules.

It is presumed that the intermolecular distances of α-CoPc are large enough to absorb the oxygen easily between their molecules. On the contrary, the intermolecular distances of β-CoPc and ε-CoPc, which are smaller than those of α-CoPc, do not facilitate the absorption of oxygen. Therefore, the oxygen that absorbs to β-CoPc and ε-CoPc is separated into strongly absorbed oxygen and weakly absorbed oxygen. The N_{1s} spectra of all CoPc's suggest a single peak at 398.1 eV. This single peak shows a little energy separation between four equivalent central nitrogens and four equivalent meso-bridging nitrogens.

Conclusions

We have found it possible to synthesize a new crystal of CoPc, which was named ε-CoPc, from $CoCl_2$ and phthalonitrile by using DBU as a reaction stimulator in 2-butoxyethanol at 100 °C. Additionally, the α- and β-CoPc's were also synthesized by the same technique at temperatures of 80 and 130 °C, respectively. The characteristics of ε-CoPc can be summarized as follows: The XRD pattern has unique lines and is distinguished from other polymorphs. The wavelength of the C–H out-of-plane vibrations are located between those of α- and CoPc's The electronic absorption spectrum shows a weak absorbance resulting from the π–π^* transitions; however, a new absorption peak appears at 808 nm. These results suggest that this ε-CoPc is a new crystal phase having a middle-energy stage. The results of XPS also support these phenomena.

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Registry No. DBU, 6674-22-2; CoPc, 147-14-8; phthalonitrile, 91-15-6.