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A New Synthesis of ε-Form Nickel Phthalocyanine by Using DBU at Low Temperature

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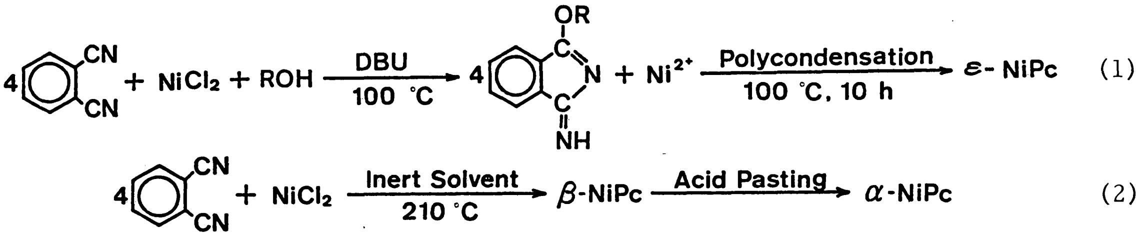
A new crystal named ε-form nickel phthalocyanine(NiPc), has been synthesized from $NiCl_2$ and phthalonitrile by using 1,8-diaza-bicyclo(5,4,0)undecene-7(DBU) in 2-butoxyethanol at 100 °C. The X-ray powder diffraction pattern of ε-NiPc was distinguishable from other polymorphs. The IR and electronic absorption spectra suggest that this ε-NiPc forms a new crystal phase of an intermediate atate.

Phthalocyanines(Pcs) are very attractive organic materials because of their excellent electronic properties.[1,2] The electronic properties of Pcs are influenced by the electron density and morphology of the central metals.[1] A variety of works have been performed on Pcs in many fields. One area of investigation based on Pcs has been developed for the synthesis of charge generation materials(CGMs) for photoreceptors.[3]

Pcs have two typical polymorphic forms, the β-form is thermally stable and the α-form is metastable. In addition, the intermediate state such as the τ-,[4] and X-form[5] metal-free phthalocyanines(H_2Pcs), and the ε-form[6] copper phthalocyanine(CuPc), have been reported. Many intermediate states of Pcs show high photocurrent or photovoltage in spite of low dark conductivities. Therefore, these materials are suitable for the CGM of the layered photoreceptors.[4] Other Pcs have scarcely been investigated on account of the difficulties of crystal conversions. We have already directly synthesized the τ-H_2Pc, which is the intermediate state of H_2Pc, from phthalonitrile by the seeding procedure in the presence of 1,8-diaza-bicyclo(5,4,0)undecene-7(DBU) as a reaction stimulator in alcohol.[7,8] Nickel phthalocyanine(NiPc) has been reported to have the α- and β-forms.[9] In this paper, we applied this DBU method to obtain the new intermediate state of NiPc, and directly synthesized ε-NiPc from phthalonitrile and nickel chloride with DBU. The properties of the ε-NiPc are also discussed based upon the analytical results.

The ε-NiPc was directly synthesized as shown in Eq. 1. Phthalonitrile(0.2 mol) and $NiCl_2$(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 temperature was maintained at 100 °C. After 10 h of heating, the product was collected by filtration, washed with water, and purified by the acetone and methyl alcohol. The β-NiPc was synthesized



Scheme 1.

from phthalonitrile and NiCl$_2$ at 210 °C as shown in Eq. 2. The α-NiPc was obtained from the β-NiPc by acid pasting method, which is a technique of phase conversion. That is, the β-NiPc was dissolved in 98 wt.% sulfuric acid and precipitating the α-NiPc by pouring the solution into a large volume of water.

X-Ray diffraction(XRD) patterns were measured by reflection geometry scanning, using Ni-filtered CuKα radiation. IR spectra were obtained by the KBr disk method. Electronic absorption spectra were measured for NiPcs dispersed in chloroform. Chloroform was selected in order to observe the aggregated state of NiPcs.

Since the DBU supports the formation of the Pc precursor and promotes the polycondensation at lower temperatures from 80 to 130 °C, the ε-NiPc could be synthesized as low as 100 °C. It can be presumed that this synthesis is not only polycondensations of Pc precursors but also the crystal transformation of Pcs at the same time.

The XRD patterns of NiPcs shown in Fig. 1 are different from each other. The β-NiPc single crystal, grown by sublimation, was analyzed to be the monoclinic space group (P21/a) by X-ray diffraction.[9] The probable space group of α-NiPc is P4/m, and the d-values were also calculated.[8] On the other hand, the XRD pattern of ε-NiPc has the main lines, $2\theta = 7.6°$ and $9.2°$, which are rather similar to those of ε-CuPc than those of α- and β-NiPc.[10] The lines show the distances of b-axis of Pcs arrangements. Since the Ni and the Cu have almost the same ionic radii(Ni = 1.25 Å, Cu = 1.28 Å), the crystal arrangements of both Pcs might be packed in same direction.

The IR spectra and their assignments are summarized in Fig. 2 and Table 1, respectively. The frequencies corresponding to the out-of-plane C-H bending modes of the peripheral benzene rings in the NiPcs (the peaks Nos., 6, 8, and 10) evidently suggest the differences of polymorphic forms. The wavenumbers of the peaks of β-NiPc 6, 8, and 10 are larger than those of α-NiPc due to its greater force of molecular packing, involving stronger intermolecular forces and

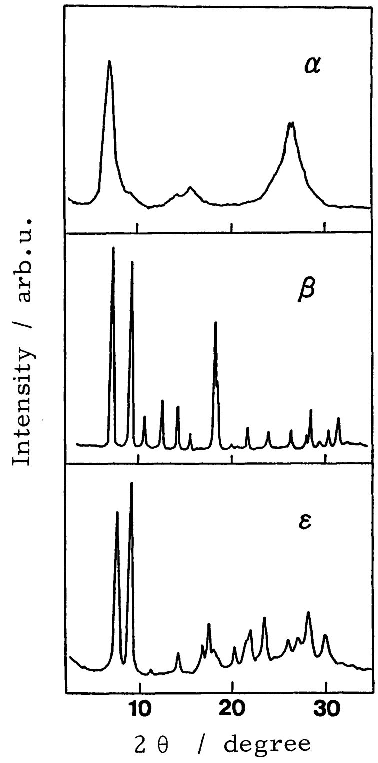


Fig. 1. XRD patterns of NiPcs.

Table 1. Assignments of IR spectra (cm^{-1})

No.	α- NiPc	β- NiPc	ε- NiPc	Assignment
1	431(s)	435(s)		C-C out-of plane bending
2	518(s)	519(m)	518(w)	
3	573(s)	572(m)	572(w)	
4	642(w)	642(m)	641(w)	
5	684(w)	682(w)	687(w)	
6	726(vs)	730(vs)	729(vs)	C-H out-of-plane bending
7	756(s)	756(s)	755(s)	"
8	774(s)	777(s)	776(s)	"
9	805(w)	806(w)		Metal-N
10	866(s)	874(s)	873(m)	
11			899(m)	
12	915(s)	914(s)	915(m)	Metal-N
13	945(m)	952(m)	951(w)	
14	1003(m)	1002(m)		
15			1068(sh)	hydrogen bending
16	1091(vs)	1091(vs)	1092(vs)	1090-1180 cm^{-1} C-H bond
17	1121(vs)	1123(vs)	1120(vs)	in benzene ring
18	1164(vs)	1167(vs)	1163(s)	
19	1200(m)	1203(w)	1201(w)	
20	1290(vs)	1290(vs)	1289(vs)	
21	1332(vs)	1334(vs)	1332(vs)	
22	1397(w)			
23	1428(vs)	1428(vs)	1426(vs)	
24	1471(m)	1469(m)	1465(m)	
25	1490(w)	1492(w)	1506(m)	C-C ring stretching
26	1531(vs)	1532(vs)	1530(s)	
27	1611(s)	1609(m)	1608(m)	1600-1700 cm^{-1} C=N stretching
28		1699(w)		bond in aromatic compound

vs = very strong, s = strong, m = medium, w = weak, sh = shoulder

decreased symmetry. The bands of ε -NiPc situate between the positions of α- and β-NiPc. Such frequencies would suggest a new packing mode of intermediate structure.

Electronic absorption spectra of NiPcs are shown in Fig. 3. These peaks can be assigned to the characteristic bands on the basis of the spectra of Pcs.11) The bands of ε -NiPc are assigned as follows: the N-band at 269 nm, the B- or Soret-band(π-π^*) at 334 nm, the Q-band of π-π^* transition at approximately 621 nm. The band at 747 nm could be attributed to the aggregation of NiPc molecules in chloroform as reported for X-H_2Pc.5) In the spectrum of α -NiPc, the intensity at the 691 nm peak is smaller than that of the Q-band. This is derived from the Davydov splitting of the Q-band, which is known to result from the dipole-dipole interactions in Pc crystal.12) These interaction in α -NiPc can therefore be presumed. The intensities of individual peaks due to the N-, B- and Q-bands of β -NiPc are relatively smaller than those of α - and β -NiPc. Since these bands can reflect the allowed π-π^* transitions, the β -NiPc does not have the structure to promote the π-π^* transitions.

In conclusion, we have synthesized a new crystal of NiPc, which was named ε -NiPc, from $NiCl_2$ and phthalonitrile by using DBU as a reaction stimulator in 2-butoxyethanol at 100 °C. The XRD pattern of ε -NiPc is distinguished from those of other poly-

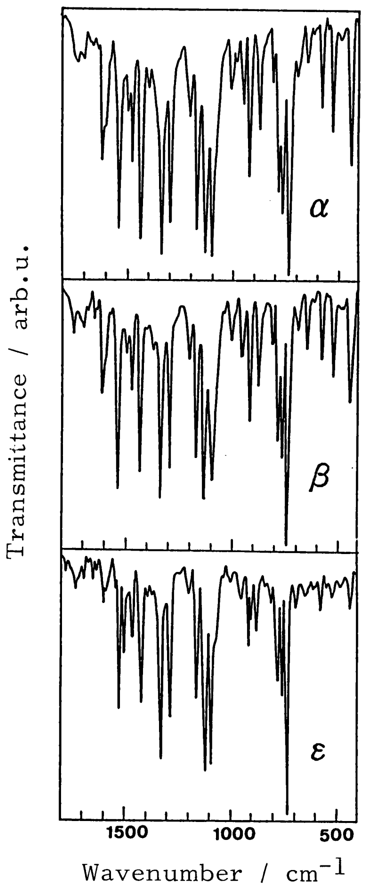


Fig. 2. IR spectra of NiPcs.

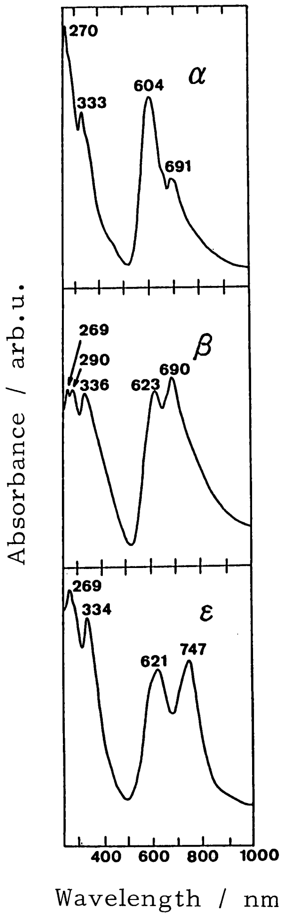


Fig. 3. Electronic absorption spectra of NiPcs dispersed in chloroform.

morphs. The wavelength of the C-H out-of-plane vibrations are located between those of α- and β -NiPc. The electronic absorption spectrum shows a new absorption peak, which appears at 747 nm. These results suggest that the ε -form would be a new crystal phase of NiPc.

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