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A NEW POLYMORPH OF METAL-FREE PHTHALOCYANINE

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The spectroscopic characterization of a novel polymorph of metal-free phthalocyanine(τ-form), showing the particular X-ray diffraction peaks, was investigated by comparing the other polymorphs. In this paper, the precise ir spectrum obtained by FTIR and visible absorption spectrum of the τ-form are reported.

Phthalocyanines are known to exist in some polymorphic forms, and their forms are distinguished by X-ray diffractometry and absorption spectra in the visible and infrared regions.[1] Recently a new polymorph of metal-free phthalocyanine, disignated as the τ-form, has been reported.[2] In this paper, the X-ray diffraction patterns and the absorption spectra in visible and infrared regions of the τ-form are reported and have been compared with those of the well known α, β, and X-form.

Every polymorph sample was prepared as follows. The β-form was synthesized by heating o-phthalodinitrile in an inert solvent in the presence of cyclohexylamine or piperidine,[1] and it was washed by repeated solvent extraction techniques. The α-form was obtained from β-form by acid pasting process, i.e., by adding the β-form to 98 percent sulfic acid, followed drowning in water, with hydrolysis of the sulfate and precipitation of the α-form crystal. And it was washed with water and solvent. The new polymorph, called τ-form, was obtained by one of some processes already reported by authors,[2] as follows. Conversion to the τ-form was achieved by wet milling the α-form with grinding aid in an inert solvent rotating above 1000 rpm upon continued heating for 20 hours, and then it was purified by solvent extraction. And an analysis of the τ-form by a Hitachi mass spectrometer model M-80A, did not yield any other organic compounds except metal-free phthalocyanine. Also an inorganic analysis of it yielded the impurities in parts per million: Fe, 400-800; SiO_2, 150-400; and others, 20-100.

Powder diffraction patterns was recorded by a Rigaku Denki diffractometer model Rotaflex 200 employing CuKα radiation. The results are shown in Fig. 1 and Table 1. The visible absorption spectrum was observed under the condition of the suspension in tetrahydrofran. The result is shown in Fig. 2. It indicates that the τ-form has a singularly strong absorption peak above 800 nm.

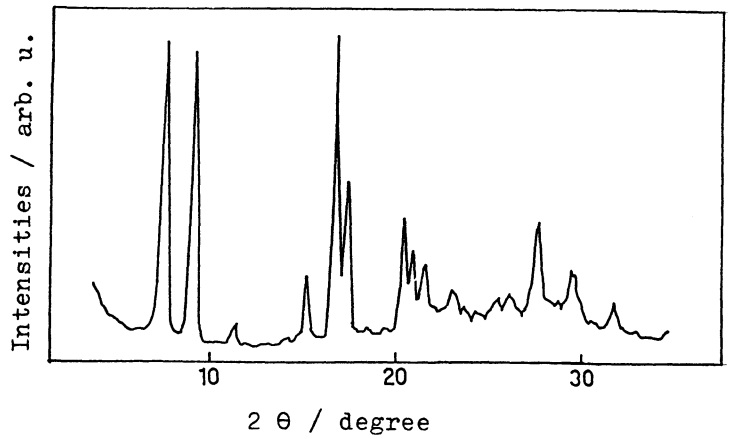

Fig. 1. X-Ray diffraction patterns.

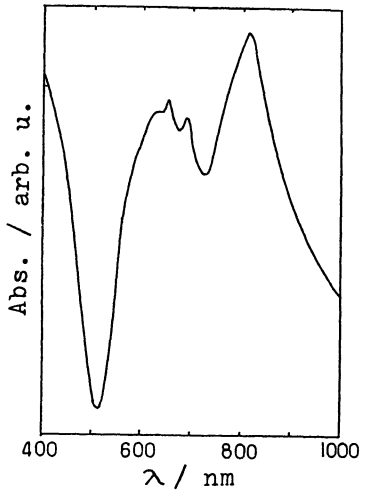

Fig. 2. Visible absorption spectrum.

Table 1. Diffraction angles[a] of the and X-form[b]

τ	7.6(s)	9.2(s)	16.8(s)	17.4(s)	20.4(m)	20.9(m)	21.5(m)	27.5(m)	[c]	29.4(m)
X	7.5(s)	9.1(s)	16.7(m)	17.3(m)			22.3(w)		28.5(w)	

a) Intensities of the diffraction lines are qalitatively described as weak(w), medium(m), or strong(s). b) Quoted from Ref. 3. c) Read from Ref. 4.

Ir spectrum was observed with Nihon Denshi Fourier transform infrared spectrometer (FTIR) model JIR-100. The differences of polymorphs have been usually investigated by comparing with the spectra in the region between mainly 700-800 cm^{-1}, and the distinct spectra above 1600 cm^{-1} have scarcely been obtained by the conventional ir spectroscopy.[1, 3] Contrary, the precise analysis of the spectra by FTIR was available to distinguish the polymorphs especially in the region above 1600 cm^{-1}, though their assignments have not been yet investigated sufficiently. The spectrum of the τ-form is shown in Fig. 3 and Table 2. Also, the resulting spectra and a summury of main absorption frequencies in the region where the most significant differences among the four polymorphs are observed, are given in Fig. 4 and Table 3.

According to those results, X-ray diffraction pattern of the τ-form resembles to that of the X-form.[4] However, it indicates distinctively different features in the region above 20 degrees. Especially, the diffraction lines of the τ-form at 20.4, 20.9, 21.5, 27.5, and 29.4 appeared stronger and clearer than the typical peak, 22.3, of the X-form. These differences above 20 degrees may be caused the difference of growing state or its direction, or the area rate of crystal planes that may influence the various properties. While, the crystal structures of phthalocyanines have been investigated and the structure of the α and β-form have been determined,[5, 6] however, thestructures of the polymorphs like as the τ, X, R,[7] or ε-form[8] which exist the middle energy states between the α and β-form have not been decided, though the assumption was proposed that the X-form has a dimetric structure.[3] One of difficulties to determine these crystal structures may be that these usually showed only quite broad diffraction lines, which were caused by crystal imperfection or minute particles. Therefore, as the τ-form which is considerably near perfect crystal including few dislocations and defects,

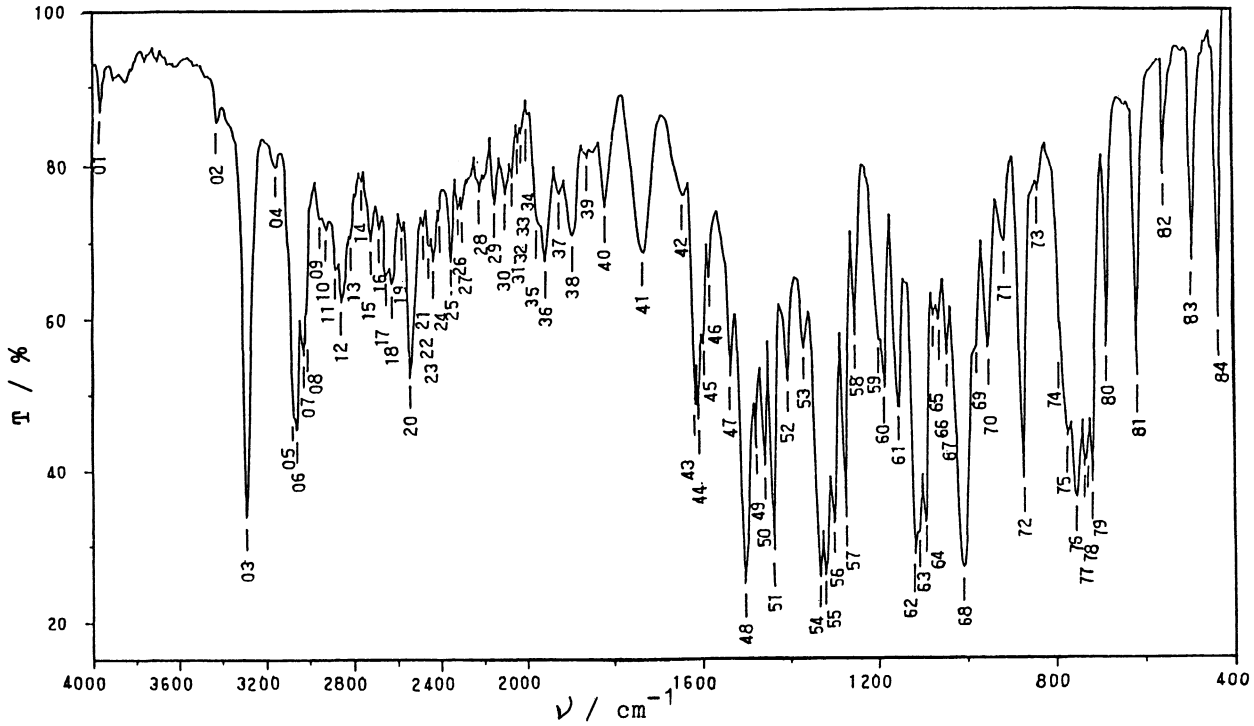

Fig. 3. Infrared spectrum of the τ-form observed by FTIR.

Table 2. Absorption frequencies[a] of the τ-form[b]

No.	cm^{-1}	No.	cm^{-1}	No.	cm^{-1}	No.	cm^{-1}	No.	cm^{-1}	No.	cm^{-1}	No.	cm^{-1}	No.	cm^{-1}	No.	cm^{-1}
01	3967	11	2879	21	2484	31	2067	41	1733	51	1437	61	1155	71	914	81	617
02	3421	12	2854	22	2454	32	2040	42	1641	52	1404	62	1119	72	872	82	555
03	3291	13	2816	23	2434	33	2025	43	1615	53	1367	63	1111	73	838	83	494
04	3153	14	2765	24	2407	34	1998	44	1606	54	1333	64	1093	74	789	84	432
05	3074	15	2721	25	2347	35	1969	45	1596	55	1321	65	1074	75	773		
06	3061	16	2683	26	2315	36	1957	46	1581	56	1302	66	1065	76	752		
07	3028	17	2652	27	2296	37	1926	47	1535	57	1276	67	1045	77	735		
08	3014	18	2629	28	2216	38	1894	48	1502	58	1252	68	1009	78	730		
09	2953	19	2580	29	2146	39	1861	49	1477	59	1196	69	980	79	717		
10	2926	20	2542	30	2098	40	1818	50	1456	60	1186	70	953	80	685		

a) The errors are less than ±1 cm^{-1} in the 400-2000 cm^{-1} region and they are ±2 cm^{-1} in the region above 2000 cm^{-1}. b) Each number of Table 2 corresponds to the indicated one in Fig. 3.

the possibility of structure determination of it may be expected in the near future.

The results of X-ray diffractometry and precise ir spectrum and visible absorption spectrum are estimated to indicate that the τ-form produced by the particular method above mentioned, is a novel polymorph. Detailed and further studies are underway about reported results.

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References

1) F.H. Moser and A.L. Thomas, "Phthalocyanine Compounds," Reinhold Publishing Co. New York (1963).

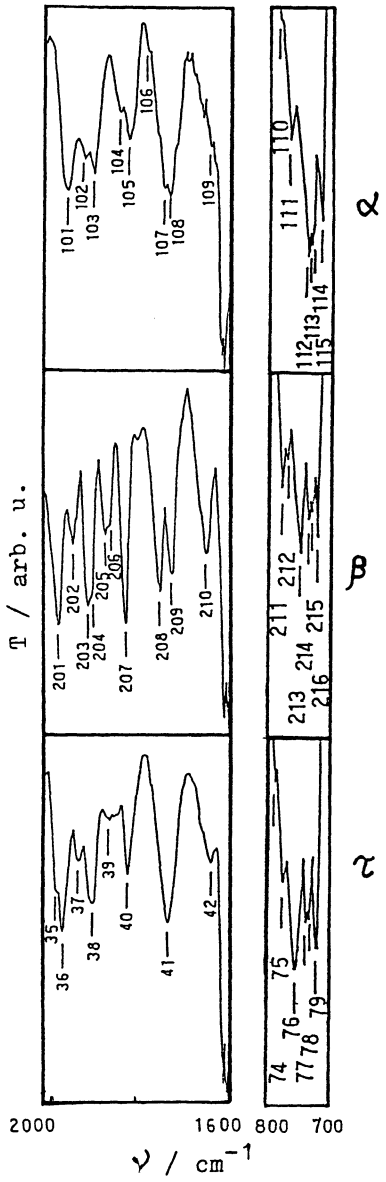

Table 3. Absorption frequencies[a] in the region of 700-800 cm^{-1}, 1600-2000 cm^{-1} and 3300 cm^{-1} for α, β, τ, and X[b] polymorphs

α		β		τ		X
No.	cm^{-1}	No.	cm^{-1}	No.	cm^{-1}	cm^{-1}
	3291		3275	3	3291	3302
		201	1969	35	1969	
				36	1957	
101	1949					
		202	1936			
				37	1926	
102	1915					
		203	1904			
103	1894	204	1896	38	1894	
		205	1867			
		206	1858	39	1861	
104	1834					
105	1817	207	1824	40	1818	
106	1778					
		208	1751			
107	1738					
108	1730	209	1726	41	1733	
109	1637-41	210	1650	42	1641	
110	785			74	789	784
		211	780			
		212	770	75	773	772
111	764					
		213	751	76	752	755
112	738					
113	735	214	736	77	735	734
114	730	215	730	78	730	
115	714	216	720	79	717	720

a) Each numder corresponds to the number indicated in Fig. 4. b) Quoted from Ref. 3.

Fig. 4. Infrared spectra of the α, β, and τ-form in the region of 700-800 cm^{-1} and 1600-2000 cm^{-1}.

2) S. Takano, M. Sawada, and I. Kumano(Toyo Ink), Japan Kokai Tokkyo Koho JP 5813757 (1983); A. Kakuta, H. Oka, S. Suzuki, K. Araya, Y. Mori, H. Morishita, S. Takano, M. Sawada, and I. Kumano(Hitachi, Toyo Ink), Eur. Pat. Appl. EP 93331 (1983).
3) J.H. Sharp and M. Lardon, J. Phys. Chem., 72, 3230 (1968).
4) J.F. Byrne(Xerox), U.S.Patent 3357989 (1967).
5) J.M. Robertson et al., J. Chm. Soc., 1935, 615; 1936, 1195, 1736; 1937, 219.
6) M. Ashida, N. Ueda, and E. Suito, Bull. Chem. Soc. Jpn., 39, 2616 (1966).
7) F.L. Pfeiffer(American Cyanamid), U.S. Patent 3051721 (1962).
8) B.I. Knudsen(KVK), U.S. Patent 3160635 (1964).

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