

The Synthesis of Symmetrically Octa-substituted Phthalocyanines and Their Physical and Photo-physical Properties

Detao Gao^a (高德涛), Haitao Xu^b (徐海涛),

Tiantang Yan^a (阎天堂) and Bixian Peng^{b*} (彭必先)

^aFaculty of Applied Chemistry, University of Science and Technology of China,
230026, HeFei, Anhui, P. R. China

^bResearch Institute of Physics and Chemistry Technology, Chinese Academy of Science of China,
100101, Beijing, P. R. China

A series of symmetrically substituted phthalocyanines have been synthesized from 3,6-dialkoxypthalonitrile and the corresponding metal salts. All of these complexes are extremely soluble in chloroform. Their melting points vary greatly with their different substituents. Their structures are confirmed by elemental analysis, ¹H NMR, UV-VIS.

INTRODUCTION

Phthalocyanines (Pcs) as newly rising functional dyes have attracted much attention by many scientists for 10-15 years running. Phthalocyanine dyes play an important role in optoelectronic applications such as information recording media,^{1,2} xerography,³ laser printing,⁴ organic conductors,⁵ fuel cells,⁶ solar energy conversion,⁷ organic photoelectrochemical cells,⁸ sensors and goggles,⁹ liquid crystal displays,¹⁰ computers-to-plate,¹¹ catalysts,¹² photosensitizer,¹³ and photodynamic therapy.¹⁴ In the last decade, a lot of effort has been devoted to the synthesis and characterization of new phthalocyanine derivatives applied to compact disks. Phthalocyanines and their derivatives are known to exhibit high durability and better solubility. The synthesis and photo-properties of six metal (Zn, Ga, Ge, Sn, Ru and Pd) 1,4,8,11,15,18,22,25-octabutoxyphthalocyanines were studied by Rihter et al.¹⁵ showing that the relationship between the photo-properties of the metal complexes and the position in the periodic chart of the metals is apparent. The synthesis and aggregation of copper phthalocyanines having different alkoxy substituents were investigated by Huijun Xu & co-workers.¹⁶ In toluene-acetone solution, the existence of aggregations are demonstrated in 1×10^{-5} mol/L to 1×10^{-6} mol/L concentration range. Recently the same group led by HuiJun Xu¹⁷ reported the preparation of 1,4,8,11,15,18,22,25-octa-(isopentyloxy) phthalocyanatocobalt and 1,8,15,22-tetraalkoxy phthalocyanatocobalt and the latter's complex with imidazole. Cook¹⁸ synthesized octa- α -alkoxyphthalocyanines such as (α -RO)₈PcH₂ and (α -RO)₈PcCu and examined the effect of the R length on the solubility and λ_{\max} . Survey and investigation of the content of the above-mentioned

papers led us to know that the emphasis of these papers was placed onto the synthesis and characterization of tetra- or octa- α -OR phthalocyanines where most of R represent normal R, C_nH_{2n+1}, n = 1~12 and whose central metal is copper or cobalt. In this present paper, we synthesized and characterized octa- α -OR phthalocyanine metal, where R is the more branched alkyl groups and whose metal, palladium, is used to design to be novel compounds involved.

RESULTS AND DISCUSSION

The intermediates and the phthalocyanines were synthesized by the route shown in Fig. 1 by the reaction conditions shown in Table 1 and Table 2; the characterization of these compounds are shown in Table 1, Table 2 and Table 3.

Main intermediate

The main intermediate used in the present study is 3,6-dihydroxyphthalonitrile (1). Its molecular weight is 160. The most intensifying *m/z* peak of 160 (Fig. 2) (in accordance with its molecular weight of 160) and the agreement between the calculated and found elemental analysis tell of the fact that the synthesis of this main intermediate is successful.

3,6-di-s-butoxyphthalonitrile (3b)

Fig. 3 gives the MS of 3,6-di-s-butoxyphthalonitrile (3b), one of the typical intermediates of 3,6-dialkoxypthalonitriles. Very good agreement between the calculated and the found elemental analysis data of compound (3b) and the appearance of the largest *m/z* peak in Fig. 3 led us to be convinced that the synthesis of the target compound (3b) is cor-

Table 1. Preparation of the Intermediates (3a~3g)

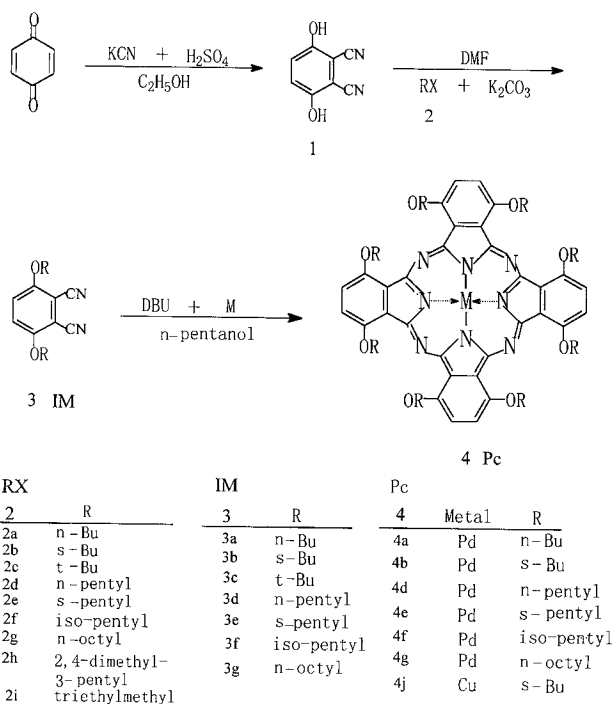
NO.	SM	Formula	Temp	Time	Yield		Calc.(%)			Found(%)		
			(°C)	(hr)	(g)	(%)	C	H	N	C	H	N
3a		C ₁₆ H ₂₀ N ₂ O ₂	80~90	20	5.90	86.4	70.59	7.35	10.29	70.07	7.38	9.57
3b		C ₁₆ H ₂₀ N ₂ O ₂	80~90	20	5.46	80.0	70.59	7.35	10.29	70.59	7.15	10.24
3c	1(4g)	C ₁₆ H ₂₀ N ₂ O ₂	90~100	48	1.05	15.4	70.59	7.35	10.29	69.84	7.82	9.91
3d		C ₁₈ H ₂₄ N ₂ O ₂	80~90	20	6.00	80.0	72.80	8.00	9.33	71.65	8.09	9.04
3e		C ₁₈ H ₂₄ N ₂ O ₂	80~90	20	6.50	86.7	72.80	8.00	9.33	71.55	7.95	9.69
3f		C ₁₈ H ₂₄ N ₂ O ₂	80~90	20	5.50	73.3	72.80	8.00	9.33	72.00	8.05	9.06
3g		C ₂₄ H ₃₆ N ₂ O ₂	80~90	20	7.25	75.5	75.00	9.38	7.29	75.32	9.50	6.96

SM = Starting material.

Table 2. Preparation of the Phthalocyanines (4a~4j)

NO.	SM	Formula	Temp	Time	Yield		Calc. (%)			Found (%)		
			(°C)	(hr)	(g)	(%)	C	H	N	C	H	N
4a	3a	C ₆₄ H ₈₀ N ₈ O ₈ Pd	110~115	20	0.35	15.9	64.32	6.70	9.38	63.91	6.87	9.10
4b	3b	C ₆₄ H ₈₀ N ₈ O ₈ Pd	100~105	20	0.27	11.6	64.32	6.70	9.38	63.95	6.91	8.95
4d	3d	C ₇₂ H ₉₆ N ₈ O ₈ Pd	110~115	20	0.30	13.8	66.16	7.35	8.58	66.14	7.35	8.37
4e	3e	C ₇₂ H ₉₆ N ₈ O ₈ Pd	90~100	20	0.20	9.1	66.16	7.35	8.58	66.28	7.41	8.48
4f	3f	C ₇₂ H ₉₆ N ₈ O ₈ Pd	110~115	20	0.30	13.8	66.16	7.35	8.58	65.50	7.15	8.67
4g	3g	C ₈₀ H ₁₁₂ N ₈ O ₈ Pd	110~115	20	0.32	14.9	67.70	7.90	7.90	68.10	7.50	8.30
4j	3b	C ₆₄ H ₈₀ N ₈ O ₈ Cu	100~105	20	0.40	18.9	66.70	6.95	9.73	65.89	6.70	9.44

SM = Starting material.



M: metal ion IM: intermediate Pc: phthalocyanine

Fig. 1. Synthesis route of the phthalocyanines.

rect, which laid a good foundation for further synthesis.

Phthalocyanine synthesis

Phthalocyanine (4b) in the metal-free form is a completely new compound. Its ¹H NMR spectral data are given in Fig. 4 as a typical example. As assignment of different peaks is indicated in Fig. 4; the ¹H NMR spectroscopy data of all of the Pc dyes prepared in the present study is given in Table 3. Terekhov¹⁹ investigated the effect of a series of concentration (10⁻²~10⁻⁵ mol/L) and temperatures (mostly 40~70 °C) on the chemical shift of the internal proton of metal-free Pc and the chemical shift of aromatic protons of metal Pcs; it is shown that there is a strong concentration dependence for the linear alkynyl Pcs, but that the ¹H NMR chemical shift of the aromatic protons of the more branched compound, such as tert-butylethynyl Pc, is only slightly concentration dependent. This observation was explained by the fact that the bulky tert-butylethynyl groups prevent aggregation far better than the linear alkynyl groups. A compromise is made in the present study to use the concentration of 4.0~4.5 × 10⁻⁴ M in CHD₃ for all the ¹H NMR studies. The ¹H NMR and elemental analysis data demonstrated the correct synthesis of all the phthalocyanines from 4a~4j, whose palladium complexes except 4a are all new compounds. However, with the increase of

Table 3. ^1H NMR Spectroscopy Data of Dyes

Dyes	^1H NMR Spectroscopy Data					
4a	7.10-7.57 (m, 8H)	4.89 (t, 16H)	2.23 (m, 16H)	1.26 (m, 16H)	1.09 (t, 24H)	
4b	7.12-7.56 (m, 8H)	4.72 (m, 8H)	2.27 (d, 24H)	1.63 (m, 16H)	1.03 (t, 24H)	
4d	7.01-7.52 (m, 8H)	4.87 (t, 16H)	2.24 (m, 16H)	1.60 (m, 16H)	1.49 (m, 16H)	1.00 (t, 24H)
4e	7.20-7.65 (m, 8H)	4.84 (t, 16H)	2.21 (m, 16H)	1.88 (m, 16H)	1.63 (m, 16H)	1.47 (m, 16H)
	1.36 (m, 16H)	1.28 (m, 16H)	0.87 (t, 24H)			
4f	7.60 (m, 8H)	4.95 (t, 16H)	2.17 (m, 16H)	2.06 (m, 8H)	1.15 (d, 48H)	
4g	7.05-7.53 (m, 8H)	4.70 (m, 8H)	2.28 (d, 24H)	1.55 (m, 16H)	1.23 (m, 16H)	1.01 (t, 24H)
4j	7.14-7.48 (m, 8H)	4.75 (m, 8H)	2.45 (d, 24H)	1.59 (m, 16H)	1.07 (t, 24H)	

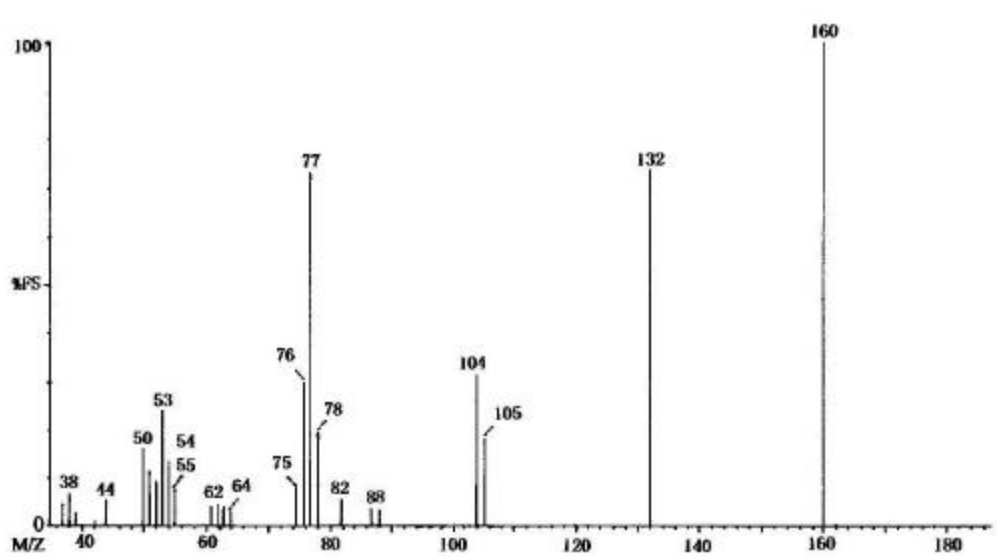


Fig. 2. The mass spectra of the starting material (1).

the branching of the alkyl group, the reaction between the 3,6-dihydrophthalonitrile and the branched alkyl halide agent is becoming more and more difficult. When the alkyl halide, such as tri-ethylmethyl bromide and 2,4-dimethyl-3-pentyl bromide is used, no corresponding 3,6-dialkoxy phthalonitrile was found in the reacted mixture under our conditions tested in the present study. This is probably due to the extremely high steric hindrance caused by these two alkyl halides, in dictating that obstacles in synthesis of some $(\text{RO})_8\text{Pc}$ where R is highly branched groups is very difficult to be overcome.

Melting point-structure dependence

The melting points datum for the intermediates and the phthalocyanines are shown in Table 4. From Table 4, we observed that the melting points decreased with the increasing of branching degree of the substituent group (for example: 3a, 3b, 3c). Also, the melting points descend with the addition of the number of carbon atoms of the substituent group (for

instance: 3a, 3d, 3g). These two cases above confirmed that the melting point is greatly affected by the nature of the substituent group which influences the self-assembly and the arrangement of the phthalocyanine molecules. It is worth noting that when the group is changed from primary (n-Bu), through secondary (s-Bu) to tertiary (t-Bu), the melting point of corresponding $(\alpha\text{-OR})_8\text{PcPd}$ drops from 158.5~160 °C to 80~81.5 °C. This implies that the substituent structure modification can be one of the powerful measures to tune the susceptibility of the CD-R dye used.

Electronic spectroscopy-structure dependence

Table 4 and Fig. 5 give the electronic spectral datum for the phthalocyanines obtained in two kinds of solvents. In general, the absorption peaks of all seven kinds of phthalocyanines obtained in propanol/butanol (1/9) are blue-shifted in comparison with the absorption peaks gained in chloroform. The molar extinction coefficients of the phthalocyanines acquired in propanol/butanol (1/9) are much lower

than the molar extinction coefficients obtained in chloroform. When the number of the carbon atom in the linear alkyl is increased from *n*-Bu, through *n*-pentyl to *n*-octyl, the λ_{\max} of corresponding $(\alpha\text{-OC}_4\text{H}_9)_8\text{PcPd}$, $(\alpha\text{-OC}_5\text{H}_{11})_8\text{PcPd}$ and $(\alpha\text{-OC}_8\text{H}_{17})_8\text{PcPd}$ is 734, 736 and 736 nm, respectively, without essential difference. The same tendency is also observed by MJ Cook,¹⁸ showing a nearly constant λ_{\max} of $(\alpha\text{-OR})_8\text{PcPd}$, 734–738 nm upon the transition of OR from OEt

to OC_5H_{11} . When the branching degree is increased from 4d to 4e and 4f, the λ_{\max} of corresponding $[\text{a-O}(\text{n-C}_5\text{H}_{11})]_8\text{PcPd}$, $[\text{a-O}(\text{s-C}_5\text{H}_{11})]_8\text{PcPd}$ and $[\text{a-O}(\text{isoC}_5\text{H}_{11})]_8\text{PcPd}$ remains as 733, 734 and 734 nm, respectively. This means neither linear alkyl length nor the branching degree can tune to a large extent the λ_{\max} under the conditions in present study. The reason is simple. No matter how the structure of the alkyl group is modified, the effect of the modified R group on the $\pi\text{-}\pi^*$ tran-

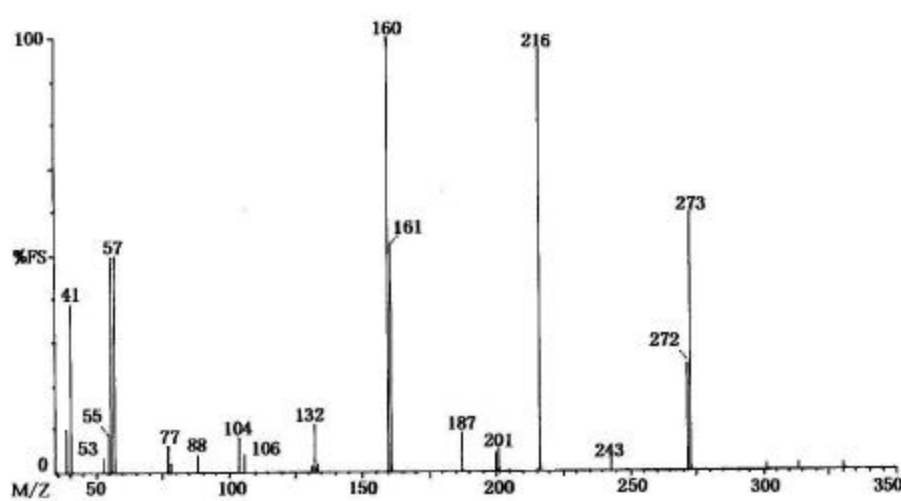


Fig. 3. The mass spectra of the intermediate (3b).

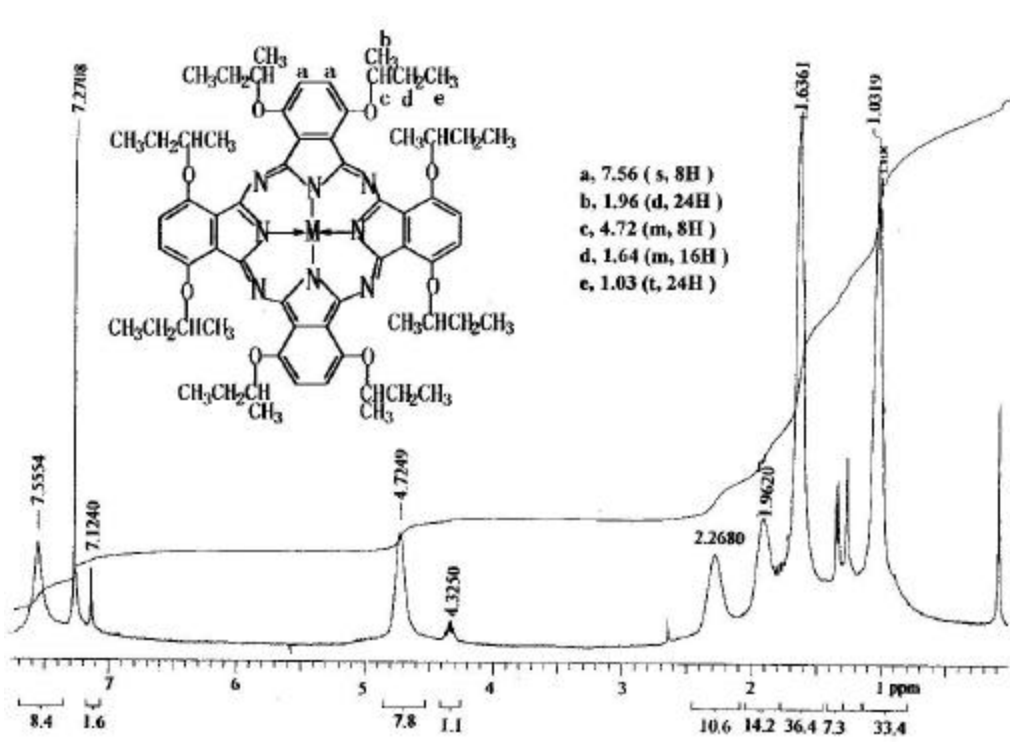


Fig. 4. The ^1H NMR spectra of the phthalocyanine (4b).

Table 4. Physical and Photo-physical Properties Data for the Intermediates and Phthalocyanines

IM	mp. (°C)	Pcs	mp. (°C)	Solubility (g/l)		λ_{\max}/nm ($10^{-4}\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)	
				in CHCl_3	In propanol\ butanol (1\9)	In CHCl_3	In propanol\ Butanol (1\9)
3a	183~184.5	4a	158.5~160		0.111	734 (33.4)	727 (14.6)
3b	109~110	4b	315.5~317	30	0.054	733 (15.9)	729 (5.33)
3c	82.5~83.5	4d	109.5~110.5	↓	0.061	736 (19.9)	727 (9.53)
3d	164~165	4e	264~265		0.077	734 (13.9)	732 (16.1)
3e	70~71.5	4f	205~207			736 (20.84)	727 (13.3)
3f	178~179	4g	80~81.5	40	0.061	736 (16.9)	728 (10.0)
3g	145~146.5	4j	319~320.5		0.074	754 (14.7)	749 (10.9)

IM = intermediate.

sition of conjugated system is limited. (The molar extinction coefficients, however, are greatly influenced by both of the factors mentioned above. For example, in chloroform, the molar extinction coefficients (ϵ) decreased with the addition of the carbon atom number of the substituent groups (for instance: 4a, 4d, 4g) and also decreased with the increasing of the branching degree of the substituent groups (for example: 4a, 4b; 4d, 4e). The two examples confirmed that the sub-

stituent groups have an effect on the vibration strength of the phthalocyanine molecules.

Thermal losses-structure dependence

Fig. 6 and Table 5 give the thermal loss data for the phthalocyanine (4b, 4d, 4f); during the thermal loss process, the transition temperature of dyes is one of the important characteristic parameters of functional dyes used in CD-R manufacture. The peripheral substituent OR containing 4~5 atoms of carbon is mostly used in practice to improve the solubility of phthalocyanine. It is shown that Pc having OC_5H_{11} has a higher transition temperature than that having OC_4H_9 ; their difference can be up to 24~33°C.

In our symmetrically alkoxy-substituted phthalocyanine, there are totally eight alkoxy substituents. It is very interesting to examine how these 8 substituents decompose during the thermal loss process. The following parameters such as G_1 (% 4OR/[OR] $_8$ PcPd, R = C_4H_9 , C_5H_{11}), G_2 (% 8OR/[OR] $_8$ PcPd, R = C_4H_9 , C_5H_{11}), the found thermal loss ΔY (%) and the transition temperature range are summarized in Table 5 for comparison and discussion. It is obvious that ΔY (%) is very close to G_1 , not G_2 . It implies that only 4 substituents of OR were decomposed within the temperature range indicated in Table 5. It seems that the other 4 alkoxy groups probably continue to decompose alone or together with the Pc macrocycle while the temperature continues to increase.

EXPERIMENTAL SECTION

General Method

UV-visible absorption spectra were measured on a Hitachi 557 UV-visible spectrometer. Mass spectra were performed on a VGTRIO-2000 and VG platform IIESI. NMR spectra were recorded on a VARIAN GEMINI-300. Thermal

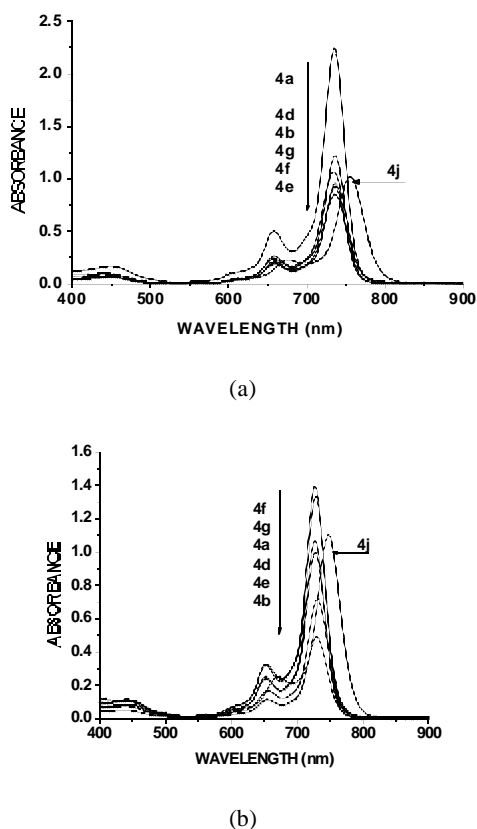


Fig. 5. (a) The absorption spectra of phthalocyanines chloroform. (b) The absorption spectra of phthalocyanines in propanol\
butanol (1\9).

Table 5. Thermal Losses Data for Phthalocyanines (4b, 4d, 4f)

NO.	Onset Temperature (°C)	Temperature range (°C)	Wt. %		
			G ₁ (4OR)	G ₂ (8OR)	ΔY
4b	346.19	300~420	24.46	48.92	25.19
4d	370.00	300~425	26.67	53.34	27.50
4f	379.07	320~450	26.67	53.34	29.05

G₁: (% 4OR/[OR]₈ PcPd, R = C₄H₉, C₅H₁₁), G₂: (% 8OR/[OR]₈ PcPd, R = C₄H₉, C₅H₁₁), ΔY (%): the found thermal loss in Fig. 6.

losses were performed on a PERKIN-ELMER TGA-1.

Preparation of 3,6-dihydroxyphthalonitrile (1)²⁰

In a vessel equipped with a stirrer, 32.4 g (0.3 mol)

p-quinone was suspended in 750 mL anhydrous ethanol and was stirred at 20 °C for 30 min. Then a 70 mL solution of H₂SO₄ in ethanol (2.5 M) was charged and 100 g of a solution of 23.5 g of KCN in water was added dropwise into the vessel

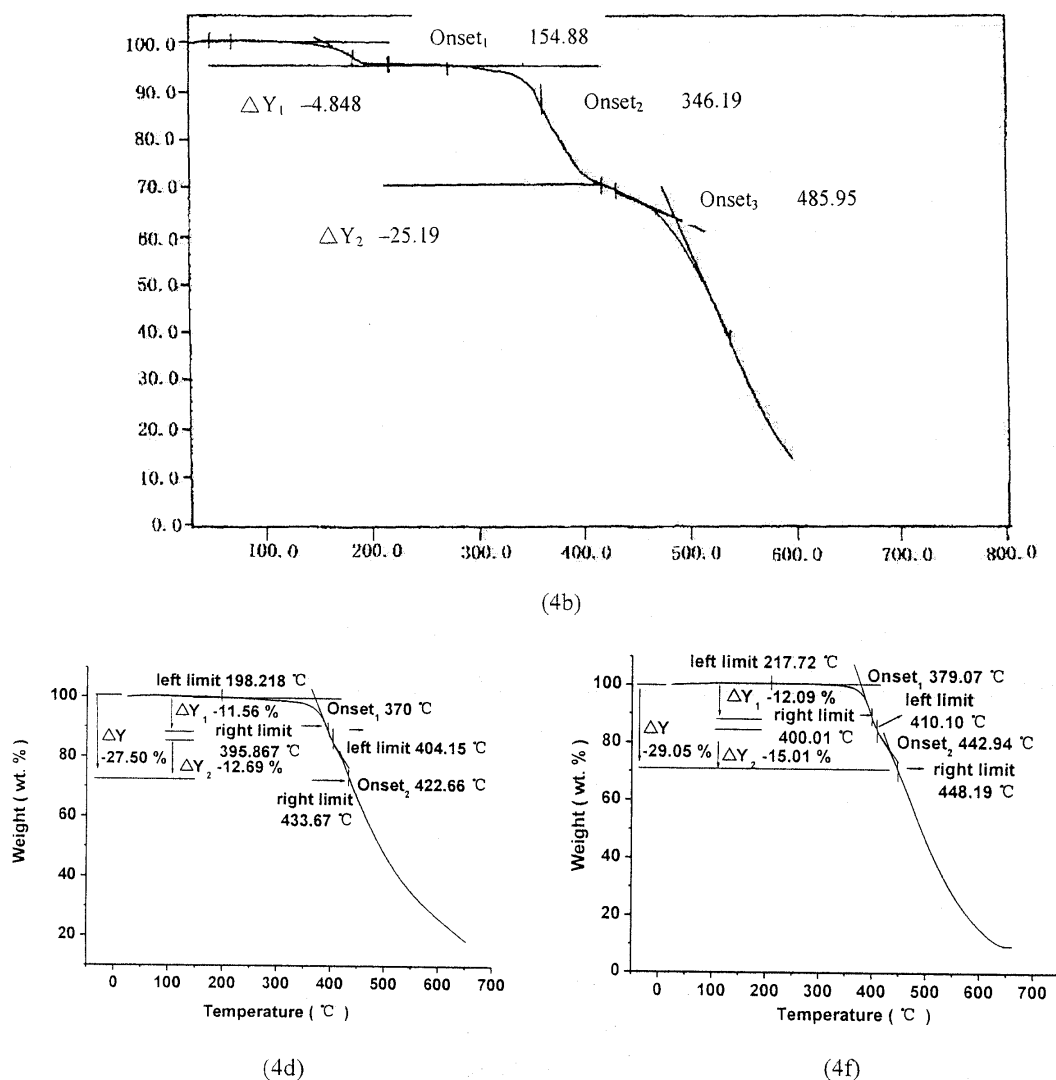


Fig. 6. The picture of thermal losses of the phthalocyanine.

within 45 min. The resulting solution was stirred for 3 hours at 20 °C. The mixture was concentrated under reduced pressure to distill most of the solvent. Then 70 mL solution of H₂SO₄ (2.5 M) was added dropwise into the vessel, and the mixture was stirred for 30 min. The mixture was poured into 500 mL distilled water and filtered; the residue was washed with distilled water until it became neutral. Yield: 17.5 g (73%). Mp. 229~230 °C. MS (Fig. 2). Anal. C₈H₄N₂O₂, Calcd.: C, 60.00; H, 2.50; N, 17.50. Found: C, 59.96; H, 2.71; N, 17.19. MS (Fig. 2).

Preparation of 3,6-dialkoxypthalonitrile (3a~3i)²¹

Preparation of 3,6-di-*s*-butoxyphthalonitrile (3b)

In a vessel equipped with a stirrer, a reflux condenser and a nitrogen inlet tube, 4 g (25 mmol) of the above-obtained phthalonitrile (1), 25 mL of dried dimethyl-formamide (DMF) and 17 g (120 mmol) of anhydrous potassium carbonate were charged, followed by heating to 60 °C in a nitrogen atmosphere. 30 min later, 9.4 g (70 mmol) *s*-butylbromide was added, followed by heating to 80 °C and stirring for 20 hours. The resulting mixture was poured into 250 mL of distilled water and filtered; the residue was washed with distilled water until it became neutral. Yield: 5.46 g (80%) Anal. (Table 1). MS (Fig. 3).

Preparation of 3,6-di-*t*-butoxyphthalonitrile (3c)

In a vessel equipped with a stirrer, a reflux condenser and a nitrogen inlet tube, 4 g (25 mmol) of 3,6-dihydroxyphthalonitrile (1), 25 mL of dried dimethyl-formamide (DMF) and 17 g (120 mmol) of anhydrous potassium carbonate were charged, followed by heating to 60 °C in a nitrogen atmosphere. 30 min later, 9.4 g (70 mmol) *t*-butylbromide was added, followed by heating to 90~100 °C and stirring for 48 hours. The resulting mixture was poured into 250 mL of distilled water and filtered; the residue was washed with distilled water until it became neutral. Yield: 1.05 g (15.4%) Anal. (Table 1).

Preparation of 3,6-di-(2,4-dimethyl-3-pentoxy)-phthalonitrile (3h)

In a vessel equipped with a stirrer, a reflux condenser and a nitrogen inlet tube, 2 g (12.5 mmol) of 3,6-dihydroxyphthalonitrile (1), 12 mL of dried dimethyl-formamide (DMF) and 8.5 g (60 mmol) of anhydrous potassium carbonate were charged, followed by heating to 60 °C in a nitrogen atmosphere. 30 min later, 6.2 g (35 mmol) 2,4-dimethyl-3-pentyl bromide was added, followed by heating to 90~100 °C and stirring for 48 hours. The resulting mixture was poured into 120 mL of distilled water and filtered; no residue was ob-

tained, the filtrate was deep green.

Preparation of 3,6-ditrimethylethylphthalonitrile (3i)

In a vessel equipped with a stirrer, a reflux condenser and a nitrogen inlet tube, 2 g (12.5 mmol) of 3,6-dihydroxyphthalonitrile (1), 12 mL of dried dimethyl-formamide (DMF) and 8.5 g (60 mmol) of anhydrous potassium carbonate were charged, followed by heating to 60 °C in a nitrogen atmosphere. 30 min later, 6.2 g (35 mmol) trimethylethyl bromide was added, followed by heating to 90~100 °C and stirring for 48 hours. The resulting mixture was poured into 120 mL of distilled water and filtered; no residue was obtained, the filtrate was deep green.

Other intermediate products were synthesized with 4.00 g of 3,6-dihydroxyphthalonitrile (1) in the same way, and their respective yields and elemental analysis data are shown in Table 1.

Preparation of palladium 1,4,8,11,15,18,22,25-octa-alkoxyphthalocyanine (4a~4j)²²

Preparation of palladium 1,4,8,11,15,18,22,25-octa-(*s*-butoxy)phthalocyanine (4b)

In a vessel equipped with a stirrer, a reflux condenser and a nitrogen inlet tube, 2.00 g (7.5 mmol) of 3,6-di-*s*-butoxyphthalonitrile (b), 20 mL of pentanol, 1.14 g (7.5 mmol) DBU were charged, followed by heating to 100~105 °C in a nitrogen atmosphere. At the same temperature, 0.34 g (1.9 mmol) of PdCl₂ were added, followed by reaction at 100~105 °C for 20 hours. After the completion of the reaction, the reaction mixture was cooled and insoluble matter was removed by filtration. The filtrate was concentrated under reduced pressure to distill off the solvent. The residue was purified by column chromatography on silica gel using petroleum ether: ethanol (30:1) as eluent, whereby 0.27 g of the target compound was obtained. Yield: 11.60%, ¹H NMR (Table 3). Anal. (Table 2).

Preparation of copper 1,4,8,11,15,18,22,25-octa-(*s*-butoxy)phthalocyanine (4j)

In a vessel equipped with a stirrer, a reflux condenser and a nitrogen inlet tube, 2.00 g (7.5 mmol) of 3,6-di-*s*-butoxyphthalonitrile (b), 20 mL of pentanol, 1.14 g (7.5 mmol) DBU were charged, followed by heating to 100~105 °C in a nitrogen atmosphere. At the same temperature, 0.19 g (1.9 mmol) of CuCl were added, followed by reaction at 100~105 °C for 20 hours. After the completion of the reaction, the reaction mixture was cooled and insoluble matter was removed by filtration. The filtrate was concentrated under reduced pressure to distill off the solvent. The residue was

purified by column chromatography on silica gel using petroleum ether: ethyl alcohol (30:1) as eluent, whereby 0.40 g of the target compound was obtained. Yield: 18.90%. ¹H NMR (Table 3). Anal. (Table 2).

Other phthalocyanines were synthesized with 2.00 g of their respective starting materials in the same way, and their yields and elemental analysis data are in Table 2; their ¹H NMR data are shown in Table 3.

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Key Words

Phthalocyanines; Phthalonitrile.

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