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Effect of bromization on the properties of a series of substituted 1,8,15,22-tetra(2,4-ditertbutylphenoxy) phthalocyanines

XIE Wenwei¹, GUO Yanchuan², GAN Changsheng¹, YAN Tiantang¹, PAN Zhongxiao¹ & PENG Bixian²

1. Department of Chemistry, University of Science and Technology, Hefei 230026, China;

2. Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, China

Correspondence should be addressed to Peng Bixian (e-mail: wade8068@163.com)

Abstract A series of 1,8,15,22-tetra(2,4-ditertbutylphenoxy) phthalocyanines [α -(oAr)₄PcM, M₁=(H)₂, M₂=Pd, M₃=Cu, M₄=Zn, M₅=Pb] were synthesized in this study. Each compound was bromized in two kinds of solvent. One is the solvent mixture of 1,1,2-trichloroethane and water, the other is 1,1,2-trichloroethane alone. The effects of solvent, bromine excess added and reaction duration on the bromization reaction were studied. The shift of maximum absorbance wavelength both in solution and in solid thin film was investigated comparatively, discovering that both were bathochromism but the former was more. TG data showed that the temperature of thermal decomposition decreased continuously with the increase of numbers of bromine. Finally, the fragments produced during the bromization of (OAr)₄PcPb in 1,1,2-trichloroethane were characterized by GC/MS. Based on the electronic structure, the possible mechanism of decomposition of these compounds was presented and discussed.

Keywords: phthalocyanines, bromization, maximum absorbance, thermogravimetric analysis.

As a novel kind of functional dyes, phthalocyanines and metallophthalocyanines have been attracting the attention of many scientists for many years. Recently, the chemistry of Pcs has been undergoing a renaissance

because Pcs and many of their derivatives exhibit their properties for potential application in materials science^[1,2].

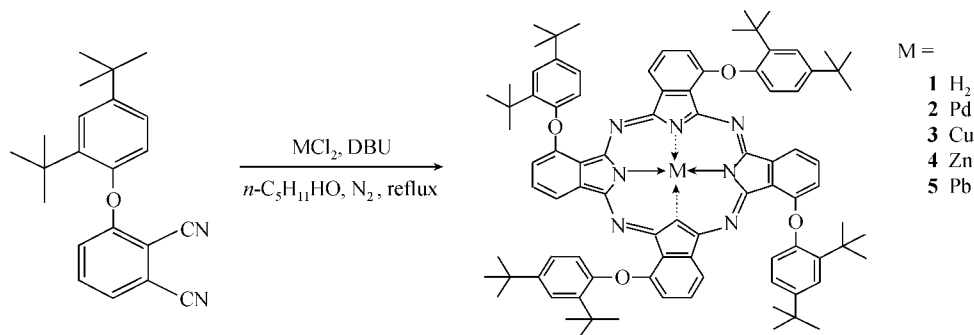
One of the main questions in the field of phthalocyanines research is to modify the molecular structure replacing the benzene-spherical hydrogen atoms by various substituents, thereby allowing a fine-tuning of their physical properties to satisfy the basic performance requirements in various fields. Bromization is one of useful methods besides attaching a wide variety of substituents at the periphery of macrocycle or incorporating different metallic and nonmetallic cations in their resonance cavity. It is very interesting in many areas such as CD-R industry to note that the thermal stabilities will be affected dramatically after bromization^[3]. Wang et al.^[4] reported that the optical absorption of Pcs' Q band would be perturbed after bromization. No detailed results were given in the report. We reported bromization and characterizations of 1,4,8,11,15,18,22,25-octaalkoxyphthalocyaninopalladium^[5], as far as the PcMs other than PcPd are concerned, to our knowledge so far, there are no reports about their bromization at all. All these bromized products are new compounds synthesized to date.

In this report the bromization reaction rate and the depth of bromization were studied. The UV-Vis spectra, the thermal stabilities, and the product decomposition during the bromization process are also presented and discussed.

1 Experimental

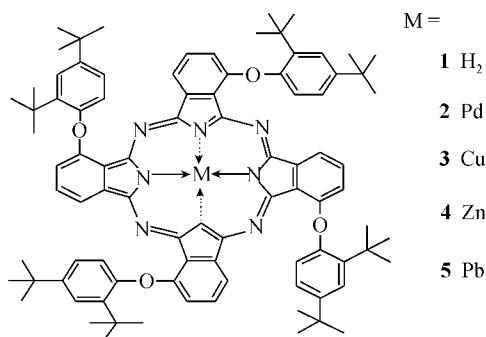
3-(2,4-ditertbutylphenoxy) phthalodinitrile was synthesized by methods described elsewhere. DBU (1,8-diazabicyclo [5.4.0] undec-7-ene, Aldrich) and all other chemicals were commercially available. UV-Vis spectra were recorded on a Hitachi 2001 using cells of pathlength 1 cm. Elemental analyses were obtained with Carlo Erba1106 and Flash EA112. Thermogravimetric measurements were carried out on a PERKIN-ELEMER TGA-1. GC/MS were obtained with Trio 2000. Fast atom bombardment (FAB) spectra were recorded on a Zab-SpecE spectrometer. Spin-coated films were fabricated on KV-4A spin coater.

(i) Preparation of phthalocyanines



Scheme 1

All of compounds were prepared by the methods described by Brewis, M. et al.^[6] with minor modifications. In a typical procedure, 3-(2,4-ditertbutylphenoxy) phthalodinitrile (5 g, 15 mmol) was added to the solution of 0.7 g (4 mmol) of palladium chloride and catalyst amount of DBU in a dry 1-pentanol (8 mL). Then solution was heated to reflux under a nitrogen atmosphere. The process of reaction was monitored with the aid of TLC. When 3-(2,4-ditertbutylphenoxy) phthalodinitrile consumed completely, the mixture was cooled, the solvent mixture of methanol and water (80 mL, 4 : 1 *V/V*) was added. After additional stirring for 0.5 h, the precipitate was filtered, and then washed through with methanol until the filtrate looked nearly colorless. The crude product was purified by silica gel column chromatography using chloroform as the eluting solvent. It was then evaporated by rotating evaporator under reduced pressure to give 2 g of green solid of **2** in 36.1% yield, then it was evaporated. The rest of other compounds were prepared by similar procedures.



The data of elemental analysis are given in Table 1. Complex **5** was new compound.

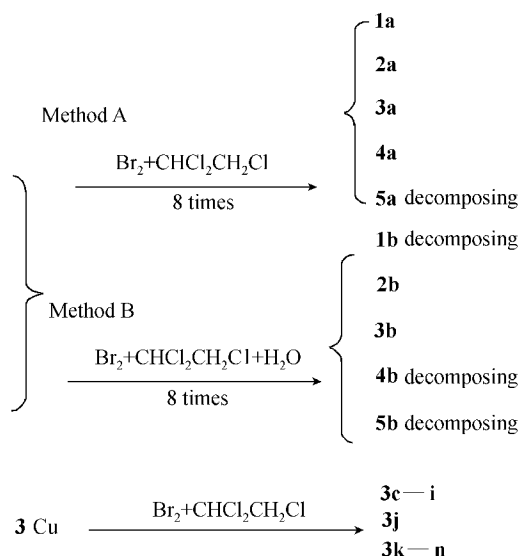
Table 1 Data of elemental analysis of **1—5**

Product	Pc ^{a)}	Elemental analysis		
		C% (Found)	H% (Found)	N% (Found)
		79.10	7.30	8.25
1	PcH ₂	(79.17)	(7.28)	(8.43)
2	PcPd	72.95 (72.61)	7.09 (6.74)	7.46 (7.81)
3	PcCu	74.36 (74.88)	6.12 (6.95)	8.59 (8.05)
4	PcZn	74.21 (74.82)	6.94 (6.95)	7.44 (8.04)
5	PcPb	68.58 (68.72)	6.12 (6.30)	7.49 (7.29)

a) The phthalocyanine is abbreviated to Pc.

(ii) Bromization of phthalocyanines

As far as solvent is concerned, the bromization reaction can be divided in two ways of which one is in 1,1,



Scheme 2

2-trichloroethane (named method A) and the other is in solvent mixture of 1,1,2-trichloroethane and water (named method B). Complexes **1—5** were bromized using both methods obtained corresponding compounds. In addition, in order to examine the depth of the bromization reaction complex **3** was bromized in different excess of bromine, such as 2 times, 3 times, and 4 times. And samples of the reaction mixture (ca. 5 mL) were withdrawn at different intervals and checked systematically.

General procedures for the bromization of **1—5** are given in the following.

Method A: A mixture of 9 mL of 1,1,2-trichloroethane, 0.6 g (0.4 mmol) of **2** was heated at 55—60°C. Then 0.51 g (3.2 mmol) dissolved in 5 mL of 1,1,2-tri-

chloroethane was added dropwise to maintain the temperature between 55—60°C. The mixture was additionally stirred for 4 h at the same temperature. Then the mixture was cooled and poured into 30 mL of saturated aqueous sodium bisulfate. The organic fraction was isolated, washed with water (40 mL × 2), and dried with anhydrous potassium chloride. The solvent was removed by reduced pressure. The crude product was dissolved in chloroform and purified by silica gel column chromatography using chloroform as eluent. It was then evaporated solvent to give 0.14 g of **2a**.

Method B: A mixture of 9 mL of 1,1,2-trichloroethane, 3 mL of water, and 0.6 g (0.4 mmol) of **2** was heated at 55—60°C. The rest of procedures was similar to

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method B.

2 Results and discussions

(i) Direct comparison of methods A and B. Complexes **1** and **4** can be bromized successfully by use of method A, but decomposed by use of method B. Complexes **2** and **3** showed high thermal stabilities. Both can be bromized by use of either method A or B. However, complex **5** decomposed completely by use of both methods A and B. The reason would be discussed below.

(ii) Bromization rate and depth. Bromization of complex **3** was performed at different excess of bromine in order to examine the bromization rate and depth. The data of elemental analysis for complexes **3c—n** are given in Table 2.

Table 2 Data of elemental analysis of **3c—n** and the number of bromine atoms

Product	Reaction time/min	Elemental analysis (Found)			Number of bromine atoms
		C(%)	H(%)	N(%)	
3c	5	67.42	6.46	6.10	2.23
3d	10	66.35	6.17	6.37	2.53
3e	30	65.43	6.10	6.32	2.79
3f	60	65.26	6.05	6.13	2.88
3g	90	64.21	6.10	6.32	3.19
3h	150	64.06	5.88	6.26	3.21
3i	300	63.22	5.69	5.79	4.23
3k	15	59.25	5.68	6.21	3.84
3l	30	58.01	5.24	5.67	5.36
3m	150	57.55	5.80	5.93	5.61
3n	300	56.93	5.09	5.58	5.80

Fig. 1 shows the relationship between bromization reaction time and carbon percentage. Note that the content of carbon decreased dramatically at the beginning, then it took about 30 min, and then the reaction gradually reached the equilibrium. Afterwards, there was nearly no change in the carbon percentage. It also indicated that the number of attached bromine atoms was rapidly enhanced with the continuation of bromization.

(iii) FAB MS spectra characterizations of complex **3m**. There is no information about bromophthalocya-

nines with phenoxy substituent in the literature. The FAB MS spectra are given in Fig. 2. The molecular peak for the **3m** appeared at $m/z = 1708.4$, indicating that each phthalocyanines molecule has four bromine atoms (Calcd. molecular weight 1708.9). The data of elemental analysis and FAB MS spectra proved the success of synthesis.

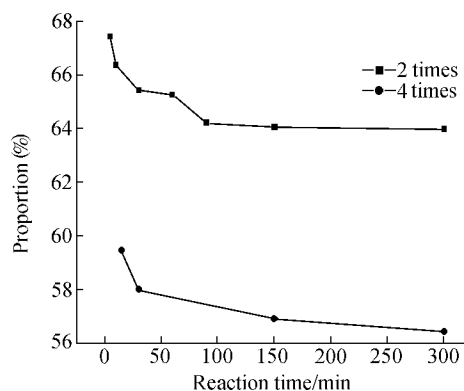


Fig. 1. Plots of proportion vs. reaction time for **3**.

The fact that in MS spectra the fragments which appeared at $m/z = 1629.3$, 1550.6, 1471.4 and the neighboring gap was about 80 demonstrated that three attached bromine atoms dropped off step by step. The bromine atom dropped off earlier than other substituents. The relatively less intense fragment 1471.4 indicated that it was difficult for the last bromine atom to drop off. The reason may be that the whole molecule was relatively stable when three bromine atoms dropped off. In such a case the whole molecule was a large π conjugation system, so it was difficult for the last bromine atom to drop off at the same energy level. In addition, there were no signals under $m/z = 1360$, demonstrating that the precursor was very stable on the other side.

(iv) Effect of bromization on the UV-Vis spectra (in the solution). The maxima absorption for the complexes synthesized in this study in chloroform are presented in Table 3.

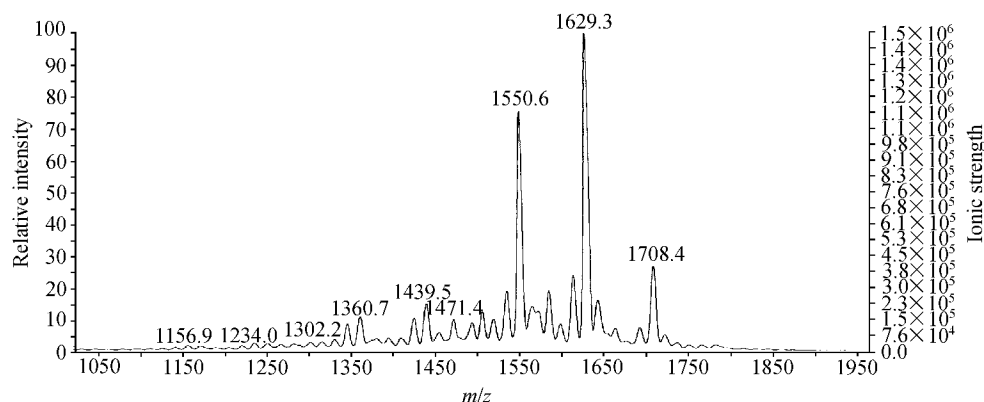


Fig. 2. The FAB MS spectra of **3m**.

Table 3 λ_{\max} in chloroform

Product	Pc	λ_{\max}/nm	$\epsilon \times 10^{-5}/\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$	$\Delta\lambda/\text{nm}$
1	PcH ₂	728, 696	2.545	
2	PcPd	691	1.434	
3	PcCu	710	3.256	
4	PcZn	706, 755 ^{b)}	2.894	
5	PcPb	750	4.489	
1a	PcH ₂ Br	727	2.567	1
2a	PcPdBr	713	3.246	21
3a		729	2.864	19
3c		713	2.553	3
3d		715	1.998	5
3e		717	2.785	7
3f		718	2.312	8
3g		718	2.691	8
3h		718	2.147	8
3i		718	2.845	8
3j	PcCuBr	720	2.612	10
3k		721	2.546	11
3l		721	2.487	11
3m		723	2.698	13
3n		723	2.179	13
4a	PcZnBr	723, 776 ^{a)}	3.256	17, 11

a) New peak appearing after purification; b) not disappearing after bromization^[7,8].

In general, the influence of bromization on the UV-Vis electronic spectrum absorbance can be affected from two ways: one is absorbance wavelength shift and the other is the shape of absorbance. The decomposition of Pc during the bromization process is accompanied always with the shift of absorbance wavelength. However, Pc1 (metal-free Pc) behavior is very unique, though there is almost no absorbance wavelength shift, the shape of absorbance changes remarkably, which can be seen from Figs. 3 and 4.

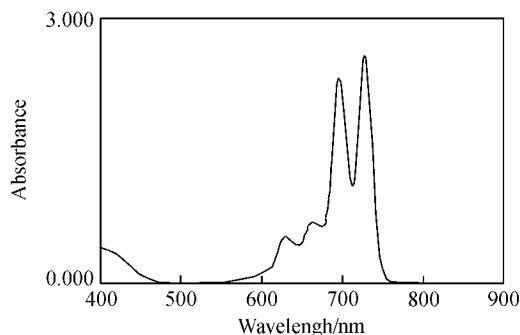


Fig. 3. Electronic absorption spectra of **1**.

From comparison between Fig. 3 and Fig. 4 it can be seen that after bromization reaction two distinguished absorption bands by which empty Pc is featured have been combined into a broad one. It is probable that as a result of cooperative influence of the super-conjugated effect of

the bromine atom and the conjugated influence of the macromolecule ring, the excited state is increased in degeneracy, therefore enabling the primitive two splitting bands combined to be a single and broad one. In other case where the cavity of Pc is full, due to the mutual interaction between the centered metal and bromine atom, Pc macromolecule is sustained in its original geometry, the force led to no change in the electron transition type.

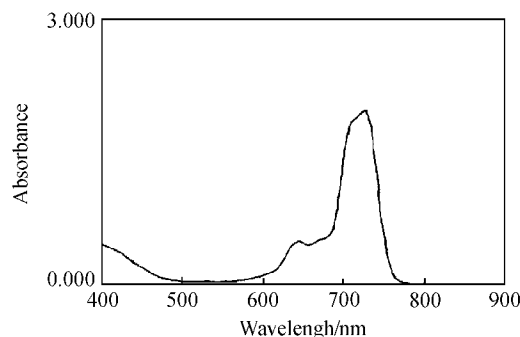


Fig. 4. Electronic absorption spectra of **1a**.

From Tables 2 and 3, it can also be seen that the different metal-centered Pc behaves quite differently under the various conditions of bromine excess added. Taking PcCu **3** as an example, whose question on the bromization rate was studied in detail. From Fig. 5, it is clear that when the bromine excess is comparatively small (i.e. only 2 times of excess), longer reaction time is required to attain an equilibrium state. When the bromine excess is increased up to 3—8 times of excess, the process proceeds very fast. The reaction will be finished only after the addition of the last droplet of bromine to the flash. When the bromine excess is arranged in order from lower to higher (2, 3, 4, and 8 times), their corresponding λ_{\max} are 718, 720, 723, and finally 729 nm. Such a wide range of λ_{\max} shift will benefit to having more room to tune with the wavelength of the semiconductor laser source.

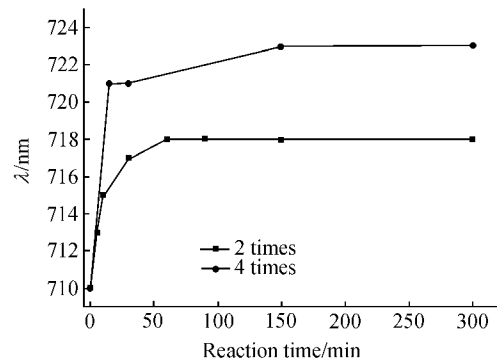


Fig. 5. Plot of absorbance vs. reaction time at different quantum bromine.

(v) Effect of bromization on the UV-Vis spectra (in

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the solid film). The thin film was fabricated by spin-coating. All of films were prepared from chloroform solution whose concentration approximated $0.02 \text{ g} \cdot \text{cm}^{-1}$. The substrate in each case was a clean, but otherwise untreated, glass microscope slide. Spin-coating was achieved at 1800 r/min. And then all the films were dried for 1 h at 90°C . The maximum absorbances are given in Table 4.

Characteristic visible spectra are dramatically different from that in the solution. The absorbance of the Q bands in the solid film broadened and was red shift of about 5 nm because of the strong aggregations between neighboring molecules. Four general types of Pc arrangement have been observed in spin-coated films and these are cofacial (face to face), herringbone, edge-to-edge and isolated^[9]. Each of the four basic types of arrangement displays a characteristic visible absorption spectrum determined by the nature and extent of the intermolecular excitation coupling between the aromatic cores of neighboring Pc molecules. Because of the large steric hindrance of phenoxy substituent, the type of arrangement of phthalocyanines in this study would be edge-to-edge to reduce the hindrance. The results were not consistent with the fact in the literature^[10]. The reason may be that it was not phenoxy-substituted phthalocyanine, but alkoxy substituted phthalocyanine.

Table 4 λ_{max} in chloroform

Product	Pc	$\lambda_{\text{max}}/\text{nm}$, in solution	$\lambda_{\text{max}}/\text{nm}$, in solid film	Red-shift/nm
1	PcH ₂	728,696	731,700	3, 4
1a	PcH ₂ Br	727	734	7
2	PcPd	691	694	3
2a	PcPdBr	713	718	5
3	PcCuBr	710	716	6
3a		729	735	6
3c		713	716	3
3d		715	717	2
3e		717	720	3
3f	PcCuBr	718	722	4
3g		718	724	6
3h		718	724	6
3i		718	720	2
3j		720	726	6
3k		721	727	6
3n		723	728	5
4	PcZn	706,755	712,760	6, 5
4a	PcZnBr	723,776	722,780	-1, 14

(vi) Effect of bromization on the thermogravimetric results. Thermal stabilities are very important in many application fields. The TG curves of complexes **3**, **3j** and **3m** are given in Figs. 6, 7 and 8. As a whole, they all have sharp weight loss with the increase of temperature. And decomposing temperature will become lower with the increase of more bromine atoms. But the decomposing

rate proceeds smoothly. Complex **3** began to decompose at the point of 237.1°C . From 237.1°C to 517.10°C , the

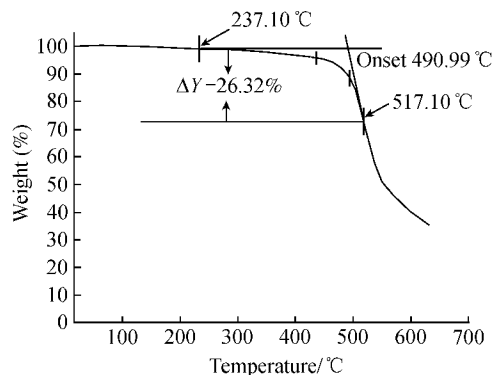


Fig. 6. The TG spectra of **3**.

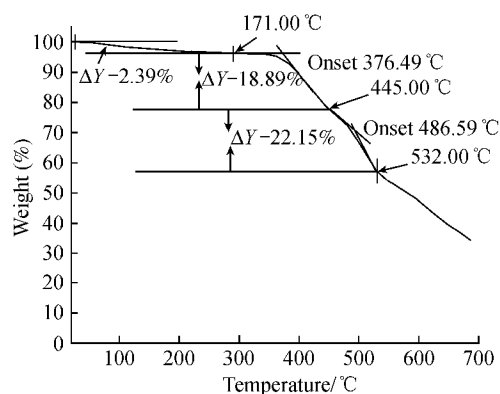


Fig. 7. The TG spectra of **3j**.

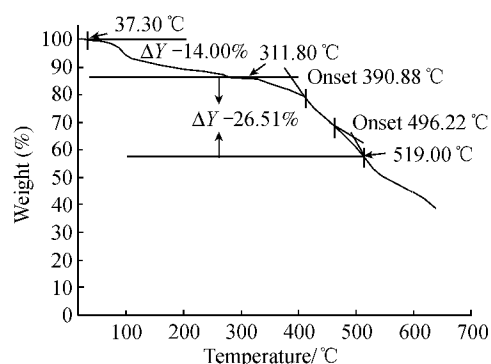


Fig. 8. The TG spectra of **3m**.

corresponding maximum weight loss was going up to 26.32% which implies to the loss of eight tertbutyl groups located in the phenoxy substituent (25.91%).

For complex **3j**, it can be seen from Fig. 7 that there is a little weight loss (2.38%) under 171.00°C . The total weight loss is about 18.87% from 170.00°C to 445.00°C . In such a process, the bromine atoms may be dropped off. And then the weight loss of 22.15% occurred, corre-

sponding to the loss of tertbutyl groups located in the phenoxy substituent (22.18%).

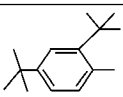
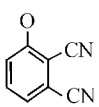
With the increase of the bromine atoms, three different weight loss phases became more clear for complex **3m**. In the first phase the weight loss was similar to complex **3j**, with the characteristic decomposing behavior of bromine atoms. The weight loss (14.00%) was consistent with the above-indicated FAB results, i.e. 14.06% (3Br) dropped from the main moiety. Increasing temperature further enabled the last bromine atom and tertbutyl group to be decomposed gradually. But the decomposing order between the last bromine atom and the tertbutyl group did not distinguish clearly so the TG curve has no obvious tuning-point. The found total weigh loss is about 26.51%, coinciding with the loss of one bromine atom and eight-tertbutyl group (25.79%)

From the above analysis it is reasonable to conclude that the thermal stabilities of Pcs were determined by two factors: one is bromine atom and the other is substituent group. So we can selectively design phthalocyanines molecules to satisfy the special need in practice.

3 Decomposition in the process of bromization

During the bromizing process, some Pcs will decompose, the extent of which depends on the central atom. There are nearly no decomposing compounds with absorbance above 400 nm, indicating that the large π conjunctive structure has destroyed completely. The decomposing compounds were detected by the GC/MS. The main fragments are listed in Table 5.

Table 5 The fragments of the decomposing product of **5** by GC/MS

No.	Retention time/min	Peak area	<i>m/z</i>	Possible structure
I	23.286	94208	191(100%), 175,163,147,133, 115,107,91,77,65,51,39	
II	28.337	41728	149(100%), 122,104,76,51,39	

Other fragments contain 1,1,2-trichloroethane and its analogues and some chloro-bromoethane whose chloro group in 1,1,2-trichloroethane is replaced by bromo group. Temperature region: 60—270°C, temperature rate: 10°C/5 min, column: 20 m × 0.25 mm.

In the GC/MS spectra there was only a low molecular weight fragment. This demonstrated that different central atoms had a large effect on the stabilities of Pc. Because there are 18 π electrons in the conjunction system, the interaction between the central atom and the macro-structure may be very strong. Obviously, the nature of the central atom and the density of π electrons determined such interaction. The valence electron structure of the different atoms is listed in Table 6.

From the above-mentioned, it is known that there is large difference in the thermal stabilities of phthalocyanines with different central atoms. There exists a rela-

Table 6 The valence electron structure of (H)₂, Pd, Cu, Zn, and Pb

Product	Pc	Central atom	Valence electron structure
1	PcH ₂	(H) ₂	1s ²
2	PcPd	Pd	4d ¹⁰ 5s ⁰
3	PcCu	Cu	3d ¹⁰ 4s ¹
4	PcZn	Zn	3d ¹⁰ 4s ²
5	PcPb	Pb	6s ² 6p ²

tively small force between phthalocyanine and lead ion which the d orbit is full and contractive and also has a large steric hindrance. So it is easy to decompose in the bromization reaction whatever medium is. Complexes **2** and **3** are very stable because palladium and copper ion have unoccupied d orbital. However, complex **4** would decompose in a tuff medium. The reason may be that d orbit was occupied fully although it is possible to change its shape.

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