

SYNTHESES AND PROPERTIES OF POLYMERIZABLE METALLOPHTHALOCYANINE DERIVATIVES

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ABSTRACT

Metallophthalocyanine derivatives with polymerizable vinyl groups were synthesized, characterized and polymerized. Preliminary results on their Langmuir-Blodgett (LB) film formation and the electronic properties of (Indium-Tin Oxide/LB-film/Al) Schottky devices were reported.

INTRODUCTION

Low-molecular phthalocyanine compounds have been studied in detail and found extensive industrial application^[1]. The metallophthalocyanine complexes, which have strong absorption band at the visible-near infrared region and stable chemically, are one of the typical semiconductor materials. In addition, the macromolecular compounds possess good mechanical properties and easy to be processed, etc. These features have stimulated investigators to attempt the synthesis of phthalocyanine derivatives with polymerizable group in the hope to combine advantages of both phthalocyanine and macromolecular compounds and to develop more extensive application. In the literature, several types of phthalocyanine polymers have been reported. They are: (1) cofacial polymers in which the phthalocyanine units are connected together through condensation between dihydroxysilicon-, germanium-, or tin-phthalocyanines^[2]; (2) polymers in which the neighboring phthalocyanine rings are linked either with or without a bridge substituent^[3,4]; (3) polymers and copolymers bonded with phthalocyanine compounds^[5]; and so on. According to the process demands based on hybrid materials^[6], for example, by utilization of Langmuir-Blodgett (LB) technique to make MSM [metal/semiconductor (phthalocyanine)/metal] or MIS (metal/insulator/semiconductor) devices, a soluble phthalocyanine monomers must be obtained at first, after the LB film formation, they are polymerized into macromolecule, so it is very clear those phthalocyanine polymers mentioned above are not suitable because of their poor solubility and difficult to be processed. In this paper, the syntheses, characterization, LB film formation, surface pressure-area isotherms of LB film, conditions of polymerization and electronic properties of Schottky devices of 2, 9, 16, 23-tetra[(5'-methacryloxy) butoxy] phthalocyanine and its metal complex are reported.

EXPERIMENTAL

1. Chemicals

All the liquid chemicals and solvents used were reagent grade, they were distilled and further dried over molecular sieve 5A. Other solid chemicals were used as supplied.

2. Characterization and instrumentation

For the spectroscopies, a JASCO IRA-2 infrared spectrophotometer, a HITACHI 320 electronic spectrophotometer, a JEOL FX-100 NMR spectrometer and a HITACHI M-80A FD-mass spectrophotometer were used. Differential thermal analysis (DTA) and thermal gravimetry (TG) were carried out under dry argon atmosphere with a RIGAKU DENKI 8085 DSC-TG apparatus. The data of elemental analysis were offered by the Laboratory of Organic Trace Analysis, RIKEN, Japan.

LB films were obtained with a home-made, computer-controlled Langmuir-Blodgett apparatus. The J - V curves of Schottky devices were measured by a HOKOTO DENKO potentio/galvanostat HA-501 and a function generator HB-104.

3. Syntheses

4-tert-butoxy butanol-1 (**1**): A mixture of 1,4-butanediol (200 ml, 2.25 mol), tert-butyl chloride (65.8 ml, 0.6 mol) and pyridine (49 ml, 0.6 mol) was reacted at 50–90°C for 9 hrs. After cooling, the reaction mixture was slowly poured into water (500 ml). The aqueous solution was extracted with chloroform (3 × 300 ml), and the extract was dried with anhydrous sodium carbonate, then distilled at reduced pressure (2 mmHg) to give 40.0 g of desired product.

4-(5'-tert-butoxy) butoxy phthalonitrile (**4**): A mixture of 4-nitrophthalonitrile (NPN, 20.0g 0.12mol), product **1** (16.9ml) and dimethylformamide (DMF, 200 ml) were stirred for 30 minutes under an argon atmosphere. 17.3 ml of 1,8-diazabicyclo-[5.4.0] undec-7-ene (DBU, 0.12mol) was added dropwisely and reacted for 3 hrs at 60°C. After cooling, the reaction mixture was poured into 600ml of cold 6N-HCl solution, and extracted with chloroform (200ml × 3). The organic phase was dried with anhydrous sodium sulfate, filtered, and concentrated by evaporation to the volume of 150ml. After removal of precipitated materials (decomposed imides and unreacted NPN), the solution was further concentrated to about 50ml, and separated by column chromatography (silica gel, 100 mesh-up, 10 × 40cm, CHCl₃), to give 7.84g of desired product.

2,9,16,23-tetra[(5'-tert-butoxy) butoxy] phthalocyanine (**7**): A mixture of product **4** (4.42ml, 0.016mol) and 30 ml of 2-(N, N-dimethylamino) ethanol (DMAE) were stirred for 1 hr at room temperature with ammonia bubbling, followed by reflux for 6 hrs more with continuous ammonia bubbling. After cooling, the reaction mixture was poured into 400ml of water, filtered, dried, separated by column chromatography (silica gel, CHCl₃:CH₃OH = 20:1), to give 2.11g of desired product.

2,9,16,23-tetra[(5'-hydroxy) butoxy] phthalocyanine (**10**): A mixture of product **7** (1.28 g, 0.0012 mol), hydrobromic acid (1.52 g, 0.0056 mol, in acetic acid solution 30% wt), anisole (0.61 ml, 0.0056 mol, to prevent substitution reaction taking place at the phthalocyanine ring) and dichloromethane (50 ml) was stirred at room temperature for 2 hrs. Then the reaction mixture was poured into 100 ml of sodium carbonate-water solution (5% wt). The organic phase was washed with water, and evaporated at reduced pressure to dryness. The crude product was dissolved in DMF (80 ml), 0.4 g of potassium hydroxide (in water solution) was added, and stirred at room temperature for 2 hrs. After concentration at 70°C and reduced pressure, the solution was precipitated in water,

filtered and dried, to give 0.7 g of product. As this product consists of four hydroxy groups, while column chromatography (silica gel) was used for separation, it was absorbed at the top of the column, no suitable eluant was found, so this product was used for next reaction without further purification.

By using triphenylmethyl, benzyl as blocking group for one of the hydroxy of 1,4-butanediol, according to the preparation methods described above for products **1**, **4** and **7**, a series of medium products were obtained: 4-triphenylmethoxy butanol-1 (**2**), 4-benzyloxy butanol-1 (**3**), 4-(5'-triphenylmethoxy) butoxy phthalonitrile (**5**), 4-(5'-benzyloxy) butoxy phthalonitrile (**6**), tetra[(5'-triphenylmethoxy) butoxy] phthalocyanine (**8**), tetra[(5'-benzyloxy) butoxy] phthalocyanine (**9**), after eliminating the blocking group, the same product (**10**) was obtained.

2,9,16,23-tetra[(5'-methacryloxy) butoxy] phthalocyanine (**11**). [(MB)₄H₂Pc]: A mixture of

Table 1 Yields and elemental analysis results of products

Products	Yields (%)	Elemental analysis (%)					
		C		H		N	
		calcd.	found	calcd.	found	calcd.	found
1	45.6	65.71	64.30	12.41	12.37		
2	25.0	83.10	82.72	7.28	7.28		
3	66.0	73.30	72.59	8.95	8.96		
4	24.0						
5	49.9	81.20	81.04	5.72	5.74	6.11	5.87
6	43.1	74.49	73.82	5.92	5.99	9.14	8.69
7	47.6	70.43	70.13	7.57	7.50	10.27	10.34
8	23.5	81.11	78.78	5.82	5.73	6.10	5.77
9	36.8	74.37	74.04	6.08	6.04	9.13	9.23
10	69.0						
11	31.6	67.47	63.34	5.84	6.00	9.84	9.73
12	42.9	64.02	63.95	5.37	5.62	9.33	9.41
13	47.6	64.27	63.83	5.39	5.65	9.37	9.72

product **10** (0.58 g, 0.00067 mol), 4-[N, N-dimethylamino] pyridine (0.82 g, 0.0067 mol), and 30 ml of tetrahydrofuran (THF) was stirred at 0—5°C, 1.31 ml of methacryloyl chloride (0.013 ml, in 10 ml THF) was added dropwisely, and reacted overnight. After concentrated at reduced pressure, the solution was precipitated in water, separated by column chromatograpgy (silica gel, CHCl₃), reprecipitated in methanol to give 0.24 g of desired product.

2,9,16,23-tetra[(5'-methacryloxy) butoxy] phthalocyanato copper (**12**). [(MB)₄CuPc]: A mixture of (MB)₄H₂Pc (0.36 g, 0.00032 mol), a small amount of benzoquinone and 50 ml of THF was bubbled with dry argon gas for 30 min, 4 ml of pyridine and 0.4 g of cuprous chloride was added (in three times), then brought to reflux for 6 hrs. After cooling, the reaction mixture was evaporated at reduced pressure to dryness, dissolved in chloroform, eliminated the undissolved portion by filtration, separated by basic aluminium oxide column chromatograpgy (10 cm length), and further purified by silica gel column chromatography (CHCl₃:CH₃OH = 30:1), to give 0.16 g of desired product.

2,9,16,23-tetra[(5'-methacryloxy) butoxy] phthalocyanato nickel (**13**). [(MB)₄NiPc]: The

Table 2 IR, ¹H-NMR and MS data of products

Products	IR(cm ⁻¹)	¹ H-NMR (CDCl ₃ , δ, ppm)	MS(M/Z)
1	3250(—OH), 2970—2860 (C—H), 1080—1060(—O—)	4.24(1H, —OH), 3.57(2H, —OCH ₂ —), 3.38(2H, —OCH ₂ —) 1.19(9H, —CH ₃)	
2	3230(—OH), 3080—3030 (φ—H), 2950—2870(C—H) 1600(φ), 1350—1310(φ—O), 1100—1050(CH ₂ —O—)	7.46—7.20(15H, φ—H), 3.55 3.10(4H, —OCH ₂ —), 1.94(1H, —OH), 1.62 (4H, —CH ₂)	
3	3280(—OH), 3080—3030 (φ—H), 2930—2850(C—H) 1600(φ), 1120—1060 (O—CH ₂)	7.34—7.23(5H, φ—H), 4.28 (2H, φ—CH ₂), 3.55, 3.48 (4H, —OCH ₂ —), 3.03(1H, —OH), 1.71—1.58(4H, —CH ₂)	
4	2950—2830 (C—H), 2220 (C≡N), 1600—1584(φ), 1367(—CH ₃), 1310—1284 (φ—O), 1095(CH ₂ —O—)	7.72, 7.17(3H, φ—H), 4.09, 3.98(4H, —OCH ₂ —), 1.91, 1.69(4H, —CH ₂ —), 1.17(9H —CH ₃)	
5	3070—2930(φ—H), 2850— 2800(C—H), 2240(C≡N) 1600(φ), 1310(φ—O—), 1100(CH ₂ —O—)	7.68—7.10(15H, φ—H), 4.00, 3.16(4H, —O—CH ₂), 1.95, 1.80(4H, —CH ₂ —)	

(Continued. 2)

Products	IR(cm^{-1})	$^1\text{H-NMR}$ (CDCl_3 , δ , ppm)	MS(M/Z)
6	3070—3020($\phi\text{-H}$), 2930—2840(C—H), 2230($\text{C}\equiv\text{N}$), 1600(ϕ), 1320—1292($\phi\text{-O}$), 1100—1090($\text{CH}_2\text{-O}$)	7.67—7.15(8H, $\phi\text{-H}$), 4.51(2H, $\phi\text{-CH}_2\text{-}$), 4.08, 3.55(4H, $\text{-OCH}_2\text{-}$), 1.94, 1.77(4H, $\text{-CH}_2\text{-}$)	
7	3280(NH), 2950—2860(C—H), 1610($\text{C}=\text{N}-\text{C}-\text{N}$), 1360(-CH_3), 1080, 1030—1015, 940—920, 820, 755(Pc ring)	7.52—6.97(12H, Pc—H), 4.20, 3.68(16H, $\text{-OCH}_2\text{-}$), 2.13(16H, $\text{-CH}_2\text{-}$), 1.39(36H, $\text{-CH}_2\text{-}$), —4.59(2H, =NH)	
8	3340(NH), 3060—3030($\phi\text{-H}$), 2940—2860(C—H), 1615($\text{C}=\text{N}-\text{C}=\text{N}$), 1070, 1050—1030, 900, 822, 750(Pc ring)	7.59—7.22(72H, $\phi\text{-H}$, Pc—H), 4.26, 3.34, 3.32(16H, $\text{-OCH}_2\text{-}$), 1.59(16H, $\text{-CH}_2\text{-}$) —3.20(2H, =NH)	
9	3260(NH), 3050—3000($\phi\text{-H}$), 2940—2860(C—H), 1610($\text{C}=\text{N}-\text{C}=\text{N}$), 1110, 1010, 928, 820, 745(Pc ring)	8.02—7.04(32H, $\phi\text{-H}$, Pc—H), 4.67(8H, $\phi\text{-CH}_2\text{-}$), 4.05, 3.98, 3.75(16H, $\text{-OCH}_2\text{-}$), 2.02(16H, $\text{-CH}_2\text{-}$), —4.95(2H, =NH)	
11	3260(NH), 2930—2840(C—H), 1715($\text{C}=\text{O}$), 1675($\text{C}=\text{C}$), 1610($\text{C}=\text{N}-\text{C}=\text{N}$), 1090, 1005, 935, 820, 745(Pc ring)	8.22—6.91(12H, Pc—H), 6.28, 5.70(8H, $\text{H}_2\text{C}=\text{C}$), 4.46, 4.16(16H, $\text{-OCH}_2\text{-}$), 2.11(16H, $\text{-CH}_2\text{-}$), —4.40(2H, =NH)	1139 (M^+)
12	2930—2860(C—H), 1720($\text{C}=\text{O}$), 1675($\text{C}=\text{C}$), 1610($\text{C}=\text{N}-\text{C}=\text{N}$), 1093, 950, 820, 750(Pc ring)	6.21, 5.65(8H, $\text{CH}_2=\text{C}$), 4.31, 3.50(16H, $\text{-OCH}_2\text{-}$), 2.18—1.65(16H, $\text{-CH}_2\text{-}$), 1.29(12H, -CH_3)	
13	2930—2860(C—H), 1720($\text{C}=\text{O}$), 1675($\text{C}=\text{C}$), 1610($\text{C}=\text{N}-\text{C}=\text{N}$), 1093, 1005, 820, 750(Pc ring)	6.27, 5.70(8H, $\text{CH}_2=\text{C}$), 4.39, 3.50(16H, $\text{-OCH}_2\text{-}$), 2.09(16H, $\text{-CH}_2\text{-}$), 1.35(12H, -CH_3)	

reaction conditions and operation procedures refer to that of product **12**.

The yields and the results of elemental analysis of each product are listed in Table 1. IR, ^1H -NMR and MS data are listed in Table 2.

4. LB film preparation

A given amount ($\sim 200\ \mu\text{m}$) of $(\text{MB})_4\text{MPc}$ -chloroform solution (typically 1 mg/ml) was cast on a nano-pure grade freshly distilled water sub-phase (ca. pH = 6) of 21°C in a Teflon trough ($26 \times 39\ \text{cm}$). After waiting the complete evaporation of casting solvent, surface pressure-area (FA) isotherms were measured by a couple of a Wilhelmy plate and a moving Teflon barrier at the compression speed of 14.6 mm/min. The Langmuir-films kept at the given surface pressure were transferred to the substrate either by the vertical dipping (VD) or horizontal lifting (HL) methods at the substrate up-down speed of 1 mm/min. The substrate plates. ITO (indium-tin oxide Nesa glass, $10\ \Omega/\text{sq.}$) cut into $2.5 \times 5\ \text{cm}$ were repeatedly well washed with freshly distilled methanol and chloroform, dried and immediately used. In order to make Schottky device of $[\text{ITO}/\text{LB film}/\text{Al}]$, about 3 mm width of longer edge of ITO was etched and this part was used for the Ag-paste contact with Al top electrode. As the Langmuir film was not transferred on the bare glass surface, the non-etched ITO area was used for the determination of transfer ratio.

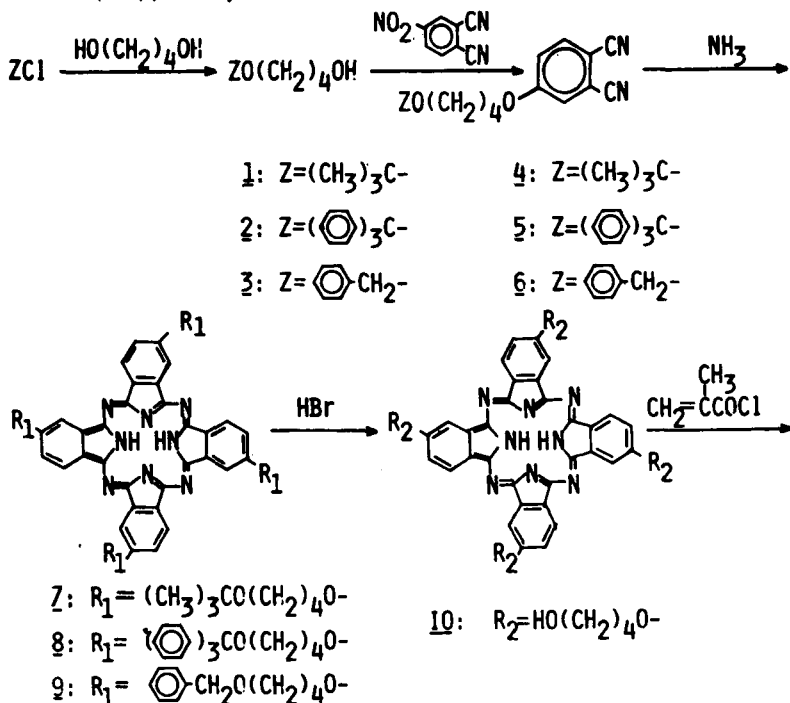
5. Polymerization

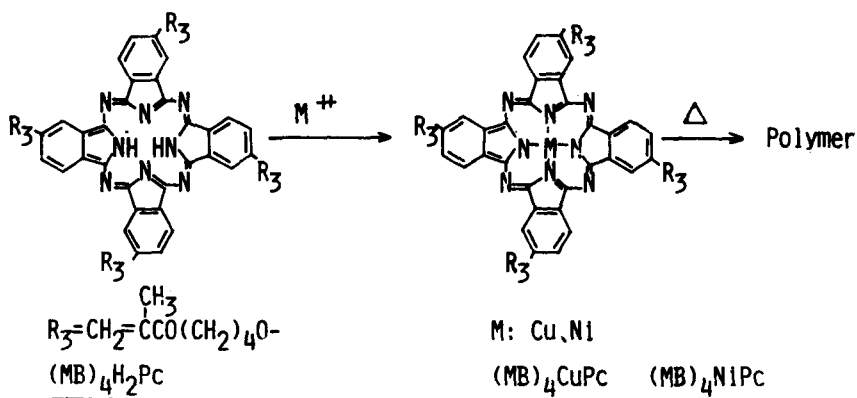
The polymerization of LB films was carried out under inert atmosphere at 70°C for 12 hrs. Judging from the amount of soluble (un-polymerized) part, more than 96% of monomer units are revealed to be cross-linked.

RESULTS AND DISCUSSION

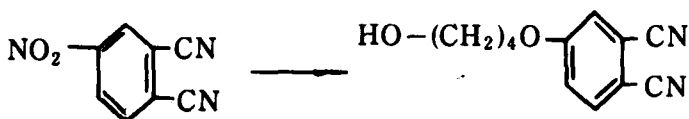
1. Syntheses

The scheme of $(\text{MB})_4\text{MPc}$ syntheses is as follows:



Fig.1 Synthesis scheme of $(\text{MB})_4\text{MPc}$

As already known, nucleophilic substitution reaction can be taken place between 4-nitrophthalonitrile and alcohol. At first, the following reaction was tried:



The reaction conditions i.e., temperature, period, catalysts, such as: DBU, K_2CO_3 were changed. The phenomena of these reactions were almost the same: the reaction mixture turned to green after about one hour latter, many components were found from testing by thin layer chromatography (TLC), the main product was greenish solid, which was difficult to purify and determine due to its poor solubility. However, a small amount of 4-(5'-hydroxy) butoxy phthalonitrile was synthesized (yield < 1.0%). Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$: C, 66.65; H, 5.59; N, 12.95. Found: C, 65.99; H, 5.53; N, 12.62. Infrared spectrum (KBr pellet, cm^{-1}): $\nu_{\text{O-H}}$ 3275 (s), $\nu_{\phi-\text{H}}$ 3075 (w), $\nu_{\text{C-H}}$ 2930–2870 (s), $\nu_{\text{C}\equiv\text{N}}$ 2240 (m), ν_{ϕ} 1600 (s), $\nu_{\phi-\text{H}}$ 1320 (s), $\nu_{\text{CH}_2-\text{O}}$ 1100–1095 (s). $^1\text{H-NMR}$: 7.70, 7.27, 7.20 (3H, $\phi-\text{H}$), 4.12 (2H, CH_2-O), 3.85 (2H, CH_2-O), 1.95, 1.77 (4H, $-\text{CH}_2-$), 1.58 (1H, OH, treated with D_2O , disappeared). It seems necessary to block one side of hydroxy group of 1,4-butanediol, so the above reaction route was chosen.

Tert-butyl, triphenylmethyl and benzyl were used to be blocking group respectively. For the reaction of tritylchloride and 1,4-butanediol, the majority of the product was symmetrical both side substituted one (in 60% yield), which was treated with trifluoroacetic acid, another portion of 4-(5'-triphenylmethoxy) phthalonitrile could be obtained (in about 30% yield). while benzyl was used as blocking group, during the reaction of deblock, the benzyl could not be eliminated completely. In comparison with each other, tert-butyl used as blocking group got better results than others.

Usually, diiminoisoindoline was a very good intermediate for synthesis of phthalocyanine, but in the synthesis of diiminoisoindoline, on the one hand, the deblock reaction took place due to the presence of NaOCH_3 , on the other hand, the product failed in next reaction to form phthalocyanine, thus in the case of preparation of $(\text{MB})_4\text{MPc}$, phthalonitrile was used directly.

2. UV/VIS spectra of $(\text{MB})_4\text{MPc}$

The UV/VIS spectra of $(\text{MB})_4\text{H}_2\text{Pc}$, $(\text{MB})_4\text{CuPc}$, and $(\text{MB})_4\text{NiPc}$ were listed in Table 3

Table 3 UV/VIS spectra of (MB)₄MPc

Compounds	λ_{max} (nm) (log ϵ)						
(MB) ₄ H ₂ Pc	703 (5.36)	665 (5.30)	642 (4.98)	605 (4.77)	385 (4.81)	342 (5.16)	287 (4.97)
(MB) ₄ CuPc							
		682 (5.23)	613 (4.66)	380 (4.46)	339 (4.92)	287 (4.75)	275 (4.75)
(MB) ₄ NiPc							
		667 (5.18)	608 (4.66)	380 (4.54)	332 (4.80)	300 (4.87)	286 (4.88)

The UV/VIS spectra is one of the important and useful methods to distinguish between metallophthalocyanines and metal-free phthalocyanines, especially during the metalation reaction, it seems more convenient than IR and ¹H-NMR to examine how is the reaction going on? Metal-free phthalocyanine compounds consist of two strong absorption bands at 650—700 nm, which is so—

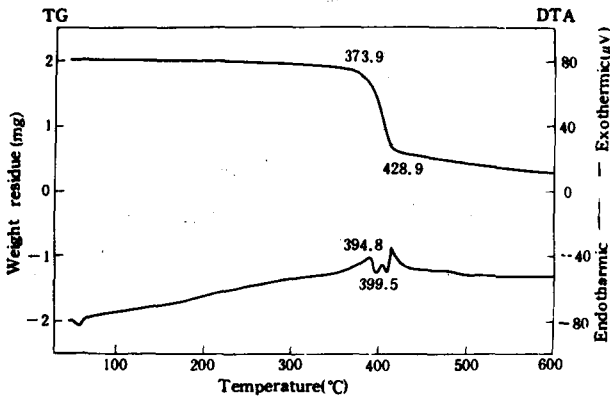


Fig.2 TG-DTA curves of (MB)₄H₂Pc

Table 4 TG-DTA of (MB)₄MPc

Substances	T_i^* (°C)	T_{end}^{**} (°C)	Δm^{***} (%)	DTA_{max}^{****} (°C)	
(MB) ₄ H ₂ Pc	373.9	428.9	36.5	394.8	399.5
(MB) ₄ CuPc	390.8	437.9	22.7	418.8	432.0
(MB) ₄ NiPc	365.8	440.5	35.7	403.5	417.8

* T_i : temperature of the starting of the greatest weight loss by decomposition; ** T_{end} : temperature of the ending of the greatest weight loss by decomposition; *** Δm : weight loss in % up to T_{end} ; **** DTA_{max} : temperature of endothermic or exothermic peak maxima.

called Q-band, and the intensity is approximately equal. Once the two inner hydrogen atoms are substituted by metal ion, along with the disappearing of these two bands, a new strong absorption band appears in between of them as a result of deviation from D_{2h} to D_{4h} symmetry^[7].

3. Thermal analysis

In Fig.2 are shown the typical thermo-gravimetric and differential thermal analysis (TG-DTA) of polymerizable phthalocyanine compounds, the data are listed in Table 4.

From Table 4, it can be seen that these phthalocyanine compounds are starting to decomposition at 370–390°C with the weight loss in the range of 23–37%, the temperatures of decomposition are almost the same as alkoxy substituted ones, which are lower than unsubstituted phthalocyanines.

4. Surface pressure-area (FA) isotherms

Monomolecular films of $(MB)_4H_2Pc$, $(MB)_4CuPc$ and $(MB)_4NiPc$ were obtained by spreading chloroform solution of them at the air-water interface. Figure 3 shows their surface pressure-area isotherms. The limiting molecular area of $(MB)_4H_2Pc$ ($92 \text{ \AA}^2$) is larger than that one of *n*-octanoxy substituted phthalocyanine ($62 \text{ \AA}^2$), their side chain length are almost the same. Meanwhile, the limiting molecular areas of $(MB)_4CuPc$ and $(MB)_4NiPc$ are up to $150 \text{ \AA}^2$ and $120 \text{ \AA}^2$, respectively. This may be due to the interaction between ethylene group or ester group at the side chain and the central metal of nearby phthalocyanines, which makes each phthalocyanine molecule at relative loose state, and leads to significant increase of the limiting molecular area.

5. Schottky devices

The open-circuit voltage (V_{oc}), short circuit current density at 10 V (J_{10v}), rectifying ratio ($R.R.$) and ideality factor (n) of Schottky devices of [ITO/ $(MB)_4H_2MPc$ LB-films/Al] are listed in Table 5.

Table 5 Electric parameters of [ITO/ $(MB)_4H_2Pc$ LB-films/Al] of Schottky devices

Compounds	Thickness (Å)	V_{oc} (V)	J_{10v} (mA/cm ²)	$R.R.^*$	n
$(MB)_4H_2Pc$	44	—	—	—	—
	92	—	—	—	—
	136	0.25	—	—	—
	252	0.54	—	48	ca.2
$(MB)_4H_2Pc$ polymer	40	0.73	0.92**	$2.8 \cdot 10^2$	1.7
	84	0.82	2.45	$3.4 \cdot 10^2$	1.7
	120	0.84	2.56	$3.6 \cdot 10^2$	1.65
	240	0.84	2.48	$3.7 \cdot 10^2$	1.65

* at 1 V; ** at 4 V.

The mechanical strength of polymerized LB-film of $(MB)_4H_2Pc$ increases markedly, by using a stylus, radius $200 \mu\text{m}$, scanning under 25 mg-pressure at 1 cm/min, no scratch was observed while the virgin was destroyed at 10 mg-pressure.

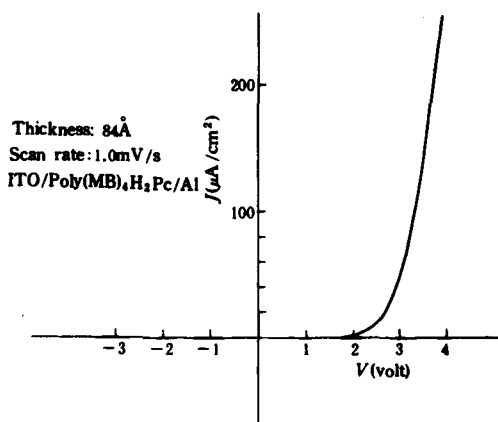
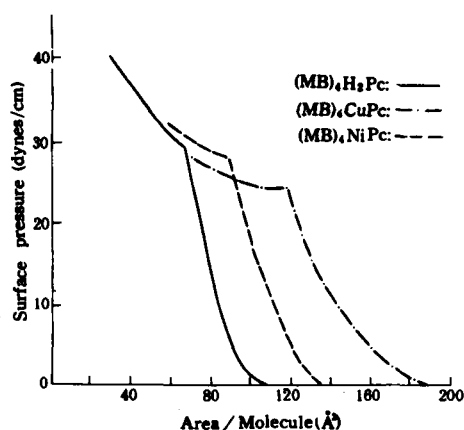


Fig.3 Surface pressure-area isotherms of $(\text{MB})_4\text{H}_2\text{Pc}$, Fig.4 J - V curve of Schottky device of poly- $(\text{MB})_4\text{H}_2\text{Pc}$ $(\text{MB})_4\text{CuPc}$ and $(\text{MB})_4\text{NiPc}$

From Table 5, it is very clear that the electric properties of Schottky devices of [ITO/polymerized LB-film of $(\text{MB})_4\text{H}_2\text{Pc}/\text{Al}$] are getting better, the V_∞ increases by 0.3 V; there are no J_{10v} data for the Schottky devices with the virgin LB-film, because they have been destroyed before 10 V; and R.R. also increases by one order of magnitude. Figure 4 shows the J - V characteristics of [ITO/ $(\text{MB})_4\text{H}_2\text{Pc}$ polymer/Al], obviously, better rectifying properties can be seen.

Keywords:

Metallophthalocyanine; Vinyl monomer; Langmuir-Blodgett film; Schottky device

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