

PREPARATION AND PROPERTIES OF TETRA (p-VINYLPHENOXY) METALLOPHthalOCYANINES

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Abstract

This paper describes the preparation and Langmuir-Blodgett (LB) monomolecular film formation of H₂, Cu, Ni, Co, and Zn phthalocyanine compounds with p-vinylphenoxy peripheral substituent on each benzo ring at either 2- or 3- position [i.e., tetra (p-vinylphenoxy) substituted isomer mixture]. These phthalocyanine derivatives form stable LB films at the film pressures greater than 10 dynes/cm. The surface pressure-area isotherms indicate that the phthalocyanine units are densely packed with a cofacial orientation. Schottky cells of [Indium-Tin Oxide/LB film/Al] were prepared and their electronic properties were examined. Much better rectifying properties, diode parameter, break-down potential and mechanical strength were notified by the post-polymerization of LB-layers. On exposing the polymerized films to tetrahydrofuran vapor, the absorption maxima of Q-band shift bathochromically by about 100 nm, being sensitive to diode laser light.

INTRODUCTION

The high thermal stability, semiconducting and catalytic properties of the phthalocyanines have stimulated investigators to attempt the synthesis of polymeric forms in the hope that these would combine the desirable features of the phthalocyanines with the physico-mechanical properties common to all macromolecular compounds. Meanwhile, LB (Langmuir-Blodgett) method for making ultra-thin films has a number of outstanding characteristics not found in any other thin film technology: their thickness can be known to sub-angstrom accuracy; they can be nearly free of defects even in monolayer thickness and they have a highly anisotropic layer structure.

In recent years, there are some reports on the film fabrication of phthalocyanine derivatives by LB technique. However, the utilization of LB technique requires soluble phthalocyanine compounds, (except lithium phthalocyanine) and the rather weak mechanical strength may cause some problems in the application. It is well known that the phthalocyanine ring with alkoxy or aryloxy groups substituted at the periphery appeared promising in improving the solubility^[1,2]. By our experience the post-polymerization of LB materials would play an important role in reinforcing the strength of LB films.

Phthalocyanine compounds have an absorption band at the region of near infrared and lead to wide interests in the potential application of laser disk file memories and organic photoconductors (especially used in laser beam printings). For these purposes, two problems remained: (1) solubility

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should be improved, and (2) the absorption wavelength of phthalocyanine is not consistent with the resonance wavelength of diode laser (mostly 780 and 830 nm).

In the present work the objective is to prepare a series of organic-soluble phthalocyanines with polymerizable vinyl groups, to investigate their versatility for forming stable LB films, to improve their mechanical strength and electric properties of Schottky cell by polymerizing the LB films, and to shift the $\lambda_{\max}$ of these phthalocyanines more to red. Our new findings are that another kind of polymerizable metallophthalocyanine derivatives with good solubility by rather simple synthetic method were prepared, that these phthalocyanine units are densely packed with a cofacial orientation at air-water interface, and that the $\lambda_{\max}$ of them shift more to the red by thermal and solvent vapor treatment.

EXPERIMENTAL

1. Chemicals

All the reagents and solvents used were purified by distillation and dried over molecular sieve 5 Å.

2. Measurements

For the spectroscopies, a JACSO IRA-2 infrared spectrophotometer, a HITACHI 320 electronic spectrophotometer, a JEOL FX-100 NMR spectrometer, and a HITACHI M-80A FD-Mass spectrometer were used. The J-V curves of Schottky cells were measured by a HOKOTO DENKO potentio/galvanostat HA-501 and a function generator HB-104.

3. Preparation of tetra (*p*-vinylphenoxy) metallophthalocyanines [(VPh)₄MPc]

4-(*p*-vinylphenoxy) phthalonitrile

A mixture of 4-nitrophthalonitrile (50 g, 0.29 mol), *p*-vinylphenol (40.80 g, 0.34 mol) and dimethylformamide (DMF, 350 ml) was heated to 60°C under an argon atmosphere. 50.85 ml of 1, 8-diazabicyclo [5, 4, 0] undec-7-ene (DBU, 0.34 mol) was added dropwisely and stirred for 2 hrs. The reaction mixture cooled to room temperature was slowly poured into 1l of cold dilute hydrochloric acid. The aqueous solution was extracted with chloroform (3 × 300 ml), dried with anhydrous sodium sulfate. After reducing the volume by evaporation, the mixture was separated by column chromatography (silica gel, 100 mesh-up, $\phi 10 \times 50$ cm, CHCl_3 : CH_3OH = 50:1), to give 24.65 g of desired product in 34.5% yield.

IR (KBr pellet, cm^{-1}): $\nu_{\text{C}\equiv\text{N}}$ 2200 ν_{vinyl} 1630, $\nu_{\text{C}-\text{O}-\text{C}}$ 1240. ^1HMR (CDCl_3 , δ ppm): 7.74–6.72 (m, 7H, Ar-H); 6.66, 6.54 (d, 1H, $-\text{C}=\text{CH}_2$); 5.79, 5.62, 5.33, 5.22 (d, 2H, $=\text{CH}_2$).

5-(*p*-vinylphenoxy)-1, 3-diiminoisoindoline

A mixture of 4-(*p*-vinylphenoxy) phthalonitrile (20 g, 0.081 mol) and 200 ml of dry methanol was stirred with vigorous ammonia gas bubble for 30 min. Then about 1/100 Eq. amount of sodium metal dissolved in 20 ml of methanol was dropwisely added. With continuous ammonia gas bubble the mixture was reacted for 2 hrs at room temperature, then was brought to reflux for another 3 hrs. The reaction mixture was concentrated by evaporation to about 100 ml, crystallized, filtered, washed with cold methanol. Drying *in vacuo* gave 20.20 g of desired product in 94.7% yield.

Tetra(*p*-vinylphenoxy) phthalocyanine [(VPh)₄H₂Pc]

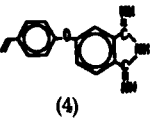
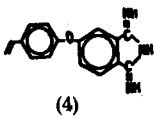
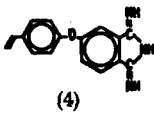
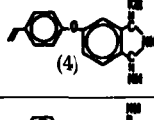
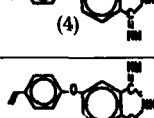
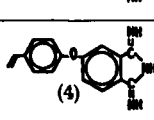
5-(*p*-vinylphenoxy)-1,3-diiminoisoindoline (5 g, 0.019 mol) in 30 ml of 2-dimethylaminoethanol (DMAE) with a small amount of benzoquinone was refluxed for 1.5 hrs. After cooling, the mixture was poured into 400 ml of methanol, collected by filtration, dried, and further

purified by column chromatography. The greenish major elution band was collected, reprecipitated in methanol to give 0.55 g of product in 11.7% yield.

Anal. Calcd for $C_{64}H_{42}N_8O_4$ ($M_w = 986.976$): C, 77.87; H, 4.29; N, 11.35%. Found: C, 76.58; H, 4.29; N, 11.29%. IR (KBr pellet, cm^{-1}): ν_{NH} 3250, $\nu_{C=N-C=N}$ 1600, ν_{Ar-O} 1240, $\nu_{Pc\ ring}$ 1090, 1010, 830, 760. ^1HMR ($CDCl_3$, δ ppm): 7.49–6.80 (m, 12 H, Pc-H); 6.73, 6.63 (d, 1H, $-\overset{||}{C}-$ H); 5.86–5.23 (d, 2H, $=CH_2$). MS: 986 (90, $M^+ - 1$); 959 [100, $M^+ - 1 - (CH_2 = CH -)$].

As for the preparation of corresponding metallophthalocyanines, the procedures were as the same as preparation of $(VPh)_4H_2Pc$ except the existence of transition metal acetate (Ni, Zn, Co) or acetyl acetonate (oxovanadium, oxotitanium, Mn). The reaction conditions and yields were listed in Table 1.

Table 1 Preparation of $[(VPh)_4MPc]$

Feed		Conditions			product	yield (%)
indoline (molar ratio)	metal	temp. (°C)	period	solvent		
 (4)	$CuCl$ (1.2)	reflux	2	DMAE	$(VPh)_4CuPc$	13.2
 (4)	$Ni(OAc)_2$ (1.2)	reflux	2.5	DMAE	$(VPh)_4NiPc$	40.3
 (4)	$Zn(OAc)_2$ (1.2)	reflux	2	DMAE	$(VPh)_4ZnPc$	56.7
 (4)	$Co(OAc)_2$ (1.2)	reflux	2	DMAE	$(VPh)_4CoPc$	
 (4)	$VO(acac)_2$ (1.2)	reflux	2	DMAE	$(VPh)_4VOPc$	39.1
 (4)	$Mn(acac)_2$ (1.2)	130	3	Sulfolane	$(VPh)_4MnPc$	10.9
 (4)	$TiO(acac)_2$ (1.2)	130	3	Sulfolane	$(VPh)_4TiOPc$	18.6

4. LB film and Schottky cell preparation

The LB films were obtained with a computer-controlled home-made Langmuir-Blodgett apparatus. 200 μ l of (VPh)₄MPc-chloroform solution (about 1 mg/ml) was dropped carefully on a nano-pure grade freshly distilled water sub-phase (ca. pH = 6) of 21°C in a Teflon trough (26 × 39 cm). After the complete evaporation of solvent, the 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 Ω /sq.) cut into 2.5 × 5 cm were repeatedly well washed with freshly distilled methanol and chloroform, dried and immediately used. In order to make Schottky cells of [ITO/LB-film/Vacuum deposited Al of ca. 200 Å thickness], 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 and tetrahydrofuran (THF) vapor treatment

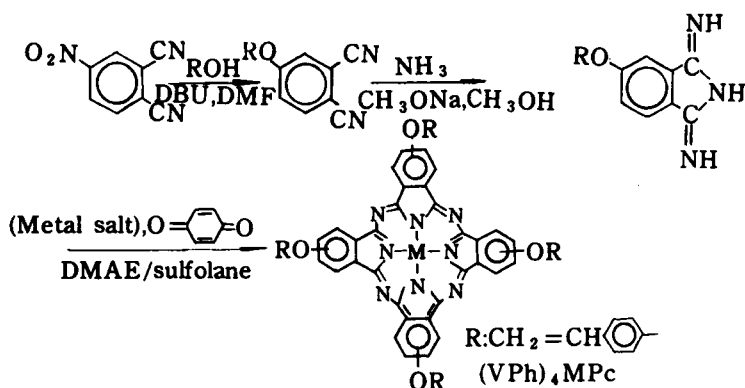
The polymerization of LB films was carried out under inert atmosphere at 100°C for 18 hrs. Judging from the amount of soluble (un-polymerized) part, more than 96% of monomer units are revealed to be cross-linked.

As to the treatment by THF vapor, the (VPh)₄MPc films with or without post-polymerization were stood in a saturated THF vapor for a given period at room temperature.

RESULTS AND DISCUSSION

1. Preparation

The preparation scheme of (VPh)₄MPc is as follows:



We once succeeded in the synthesis of another type of polymerizable phthalocyanines, tetra[methacryloxy-butoxy] metallophthalocyanine (MB)₄MPc, but the synthesis was rather difficult and resulted at lower total yield because of the longer synthetic route^[3]. From the starting material of alcohol compound to the final product of (MB)₄MPc, it took six steps of reaction with the total yield less than 1%. However, following the reaction scheme shown above, to obtain the (VPh)₄MPc only three steps were needed. Although the total yield of (VPh)₄H₂Pc is about 4% due to the partial polymerization during the reaction, it was higher than 10% in the case of (VPh)₄MPc.

2. Surface pressure–area (FA) isotherms and LB films

Monomolecular films of the (VPh)₄MPc compounds, where M = H₂, Cu, Ni, Co and Zn were obtained by spreading chloroform solution of them at the air–water interface. The FA isotherms of (VPh)₄MPc are presented in Fig.1.

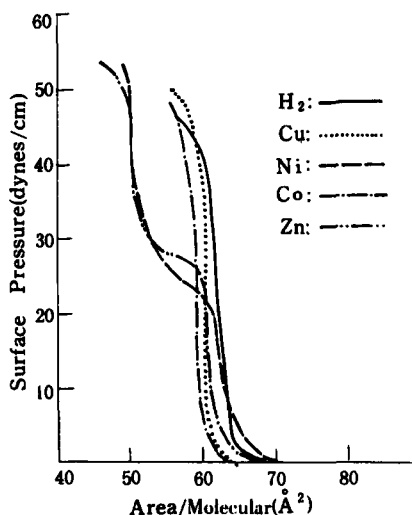


Fig. 1 Surface Pressure–Area Isotherms of (VPh)₄MPc

Each phthalocyanine compound was discovered to form stable, reproducible films. Two features of the resulting FA curves are: (1) the limiting molecular areas of (VPh)₄MPc were almost the same regardless with the central metal ions (61 Å²–66 Å²), and (2) the complexes of Ni and Zn showed “two slopes” type isotherms which also be found in the alkoxy substituted phthalocyanines^[4]. Snow et al.^[1] found that an X-ray powder diffraction spectrum of tetracumylphenoxy phthalocyanine consists of a single sharp reflection at a 3.4 Å spacing. They concluded that the 3.4 Å is the “thickness” of the molecule while packed by face-to-face orientation. According to X-ray analysis the diagonal distance across the molecule of unsubstituted phthalocyanine is 13.2 Å. An approximate calculation including two additional p-vinylphenoxy groups leads to 28.1 Å. Thus a planar view of the molecule is a square of side 19.9 Å. The calculated area per molecule is consistent with the formation of a monolayer with the faces of the molecule edge-onto the water surface. In this configuration the average area on the water surface per molecule would be 67.7 Å² (19.9 × 3.4 Å). As the limiting molecular areas of 5-samples from FA curves were in between 60–70 Å², it is reasonable to assume that the molecules of (VPh)₄MPc are densely packed with a cofacial orientation perpendicular to the air–water interface.

Judging from the transfer ratio (the area lost from the water-borne film during LB deposition divided by the substrate geometric area onto which the film is to be deposited, the first a few layers of LB films of (VPh)₄MPc were found to be so-called Z type (when the substrate went up, the transfer ratio $\simeq$ 1, when the substrate went down, the transfer ratio $\simeq$ 0), and then turned to Y type. The transfer ratio of Y type membrane was essentially unity in both up-and down-modes. No defect larger than 0.1 μm was found from the observation of LB-films of 10 to 60 Y-layers by a differential interference contrast optical microscope at the magnification of 400.

By comparison the X-ray diffraction pattern of polymerized LB film of (VPh)₄MPc with virgin

ones, no new diffraction peak was observed, except the intensity of original diffraction peak (at $2\theta \approx 6^\circ$) gradually decreased during the course of polymerization. The polymerization seemed to cause the change of film structure from the crystalline-rich to amorphous.

3. Schottky cells

Schottky cells consist of a metal-semiconductor contacts, because of their importance of rectifying properties and as tools in the analysis of other fundamental physical parameters, Schottky cells have been studied extensively^[5].

The open circuit voltage (V_{oc}), short circuit current density at 10 volt (J_{10V}), rectifying ratio ($R.R.$), diode parameter ($D.P.$), break-down voltage ($B.V.$) of Schottky cells of [ITO/virgin or polymzd. (VPh)₄MPc LB-film/Al] and break-down pressure ($B.P.$) were listed in Table 2.

Table 2 Parameters of [ITO/LB-film/Al] of (VPh)₄MPc Schottky cells

Films	(VPh) ₄ Pc layers		Thickness ^{a)} (Å)	V_{oc} (volt)	J_{10V} (mA/cm ²)	$R.R.$	$D.P.$	$B.V.$ (volt)	$B.P.$ ^{b)} (mg)
Virgin	H ₂	20	240	c	—	—	—	—	11
	H ₂	40	465	0.65	d	32	2.1	4.5	—
	H ₂	80	950	0.72	2.3	80	1.9	e	12
	Cu	20	260	c	—	—	—	—	—
	Cu	40	490	0.82	d	40	2.0	3.9	15
	Cu	80	1020	0.85	3.6	230	1.8	e	12
Polym.	H ₂	20	230	c	—	—	—	0.6	23
	H ₂	40	450	0.72	1.8	65	1.9	e	—
	H ₂	80	930	0.72	2.2	360	1.8	e	32
	Cu	20	250	0.88	2.5	40	1.9	e	33
	Cu	40	480	0.92	2.8	120	1.7	e	27
	Cu	80	975	0.86	2.6	530	1.7	e	—

a) Measured by a Sloan (Santa Barbara, CA, USA) Dek-Tak IIA surface profilometer.

b) Pressure required to scratch the film by a stylus, radius 100 μm , scanning at 1 cm/min.

c) break-down before reaching to 0.5 V or short-circuit.

d) break-down before reaching to 10 V.

e) no break-down at 10 V.

It can be seen that the polymerized LB-film is not scratched even at 33 mg-pressure while the virgin one is destroyed at 15 mg-pressure, in other words, the mechanical strength of polymerized LB-film increases by one-fold over un-polymerized one.

Due to better mechanical strength, the electrical properties of Schottky cells of polymerized LB-films are also improved. Especially the break-down voltage is over 10 V, and the rectifying ratio is two times as large as un-polymerized one. Such improvement in the electronic properties may be attributed by (1) moderate migration of Pc rings during the heat-polymerization which minimized pin-hole defects of LB layers, and (2) better mechanical strength which may prevent the Al-top layers to creep into the deep position of LB layers.

Fig. 2 shows the J-V characteristics of [ITO/Polymerized (VPh)₄H₂Pc (40-layers)/Al] Schottky cell in dark (Fig. 2a) and under illumination at 0.4 mW/cm² of white light [400–800 nm, Fig. 2(b)]. The open circuit voltage, short circuit current density and fill factor were determined to be 0.61 V, 17 μ A/cm² and 0.33 respectively.

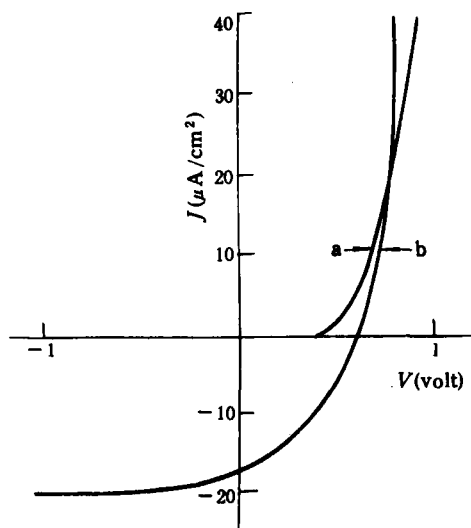


Fig. 2 J-V Characteristics of ITO/Polymerized (VPh)₄H₂Pc (40 layers)/Al Schottky Cell in dark (a, scanning at 2 mV/sec) and under illumination at 0.4 mW/cm² of white light (b)

4. UV/VIS spectra

There are some reports on changing the absorption spectra of unsubstituted phthalocyanines by a ball-milling process^[6], by heat treatment^[7], or by solvent treatment^[8,9]. The similar solvent-induced shift of $\lambda_{\max}$ is also observed for our phthalocyanine films by exposing them to organic solvent such as THF, CHCl₃, methanol, benzene and so on.

Fig. 3 shows the UV/Vis spectra of ((VPh)₄ZnPc (a) as CHCl₃ solution, and (b) as cast-film on a quartz plate (thickness about 0.1–0.2 μ m). From Fig. 3 (a), the spectrum consists of a very strong narrow absorption band appeared at 680 nm [$\log(\epsilon_{\max})$ 5.1 l/mol.cm] accompanied by a weaker vibrationally band at 70nm shorter wavelength, which is typical Q-band of metallophthalocyanines due to π - π transition. There was no sign of molecular association until the concentration upto 10⁻⁴ mol/l. In Fig. 3 (b), the major difference is that the stackmer dominates the spectrum. This is due to the formation of molecular association during the film casting, as the almost saturated solution (ca.10⁻² mol/l) was used. The same situation appeared at the UV/Vis spectra of LB-films.

Fig. 4 shows UV/Vis spectra of polymerized (VPh)₄ZnPc films (cast-film, thickness about 0.1–0.2 μ m) (a) non-treated, (b) exposed to THF vapor for 6 hrs, (c) exposed to THF vapor for 18 hrs. It is quite clear that after the treatment with THF vapor, the absorption band was broadened. When (VPh)₄VOPc was used the result became more outstanding. As compared in Fig.5(a) and (b), the 10 min-exposure of un-polymerized (VPh)₄VOPc film to THF vapor broadened the absorption spectrum, although it was not good enough to synchronize the irradiation wavelength of diode lasers. Unfortunately, the prolonged exposure of this film for 5 hrs [Fig. 5(c)] only yielded marked decrease of the absorption intensity, because the solvation, migration and therefore the "patch"-like aggregate formation during exposure diminished the optically active area. The polymerized and

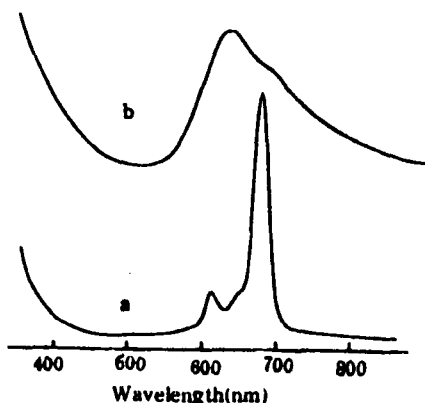


Fig.3 UV/VIS Spectra of $(VPh)_4ZnPc$
(a) in chloroform (b) casting on quartz plate

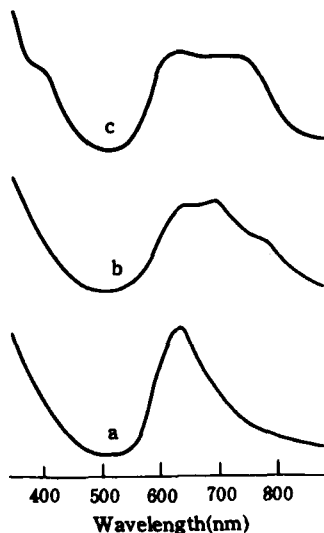


Fig.4 UV/VIS Spectra of $(VPh)_4ZnPc$ Films after
polymerized at $100^\circ C$, 18 h. (a) non-treated (b) exposed
to THF, 6 h

non-exposed film showed exactly same UV / Vis spectrum as in Fig. 5 (a), but it turned into Fig. 6(a) after 5 hrs exposure to the THF vapour. Further prolonged exposure for 25 hrs yielded the very wide absorption bands covering the irradiation wavelength of diode laser [Fig.6(b)] without any apparent decrease of absorption intensity. No more spectral change was observed after this. Such spectral change was not brought about by the formation of "inclusion compound" of Pc ring-solvent molecule, because the spectrum of Fig. 6(b) was unchanged after evacuated for 3 days at room temperature or at $80^\circ C$. Therefore the authors consider that the solvent-induced spectral change was due to some kind of stackmer formation by the moderate migration of Pc rings. But it should be very local motion, because no specific X-ray patterns were observed for the sample of Fig. 6(b).

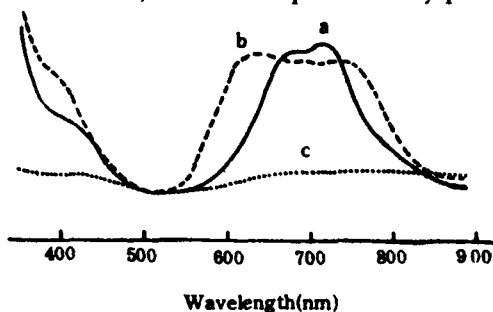


Fig. 5 UV/VIS Spectra of $(VPh)_4VOPc$ films
(a) original (b) exposed to THF 10 min
(c) exposed to THF 5 h, at room temperature

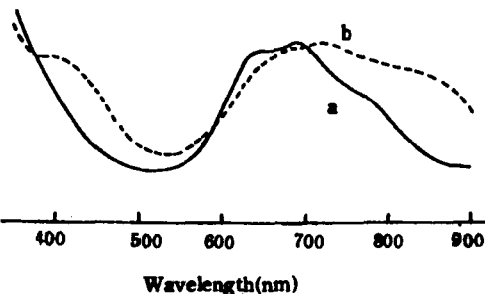


Fig. 6 UV/VIS Spectra of $(VPh)_4VOPc$ films after
Polymerized at $100^\circ C$, 10 h. (a) exposed to THF 5 h
(b) exposed to THF 25 h, at room temperature

CONCLUSION

In this paper, a new kind of polymerizable metallophthalocyanines were prepared by a simple method. They form stable Langmuir monomolecular layers. The mechanical strength and the

electrical properties are improved by polymerization of LB films. With the solvent vapour treatment the diode laser-sensitive phthalocyanine films are obtained. Its stability is also improved by the polymerization.

Keywords:

Metallophthalocyanine; Vinyl monomer; LB film; Schottky cell

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