

기능성 프탈로시아닌 물질의 제조 및 대전방지/UV차단 특성

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Preparations and Antistatic/UV Blocking Properties of Dual Functional Phthalocyanine Materials

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Abstract : A new route to phthalocyanine complexes were developed to synthesize these products by fusion in the absence of solvent. This new method of synthesis without using solvent has advantages over the conventional synthetic methods since there are no risk of explosion and formation of harmful vapor from organic solvent. Reaction of PcFe with axial ligands such as PcFe(4-VP)₂[Pc: Phthalocyanine, 4-VP: 4-Vinylpyridine] and PcFe(VIM)₂[VIM: 1-Vinylimidazole] afforded powderlike, pure dark greenish blue colored products. The resulted products are soluble in CH₂Cl₂ and found to be complexes of the type PcFeL₂. Spectral properties were studied with ATR-FTIR and UV/Vis. Thermal and electrical characterization was also performed. Phthalocyanine complexes exhibit useful properties such as UV/Vis blocking, antistatic characteristics and excellent thermal stability and we anticipate various applicability in numerous products.

초 록 : PcFe(4-VP)₂[Pc: Phthalocyanine, 4-VP: 4-Vinylpyridine]와 PcFe(VIM)₂[VIM: 1-Vinylimidazole]의 제조를 재래 식 방법인 유기용제 사용에 따른 폭발 및 유해증기 발생 위험성을 차단하기 위해 무용제 방식으로 ligand인 4-VP와 VIM을 반응매체로 하여 PcFe를 밀폐용기에서 용융시키는 새로운 방법을 도입, 제조하여 분말상 진청특색의 물질을 제조하였다. 이들 물질은 CH₂Cl₂에 가용성인 PcFeL₂형태의 물질이다. 제조된 물질을 ATR-FTIR, UV/Vis, DSC/TGA, Surface Resistivity Meter를 이용하여 분석한 결과 film 상태에서 UV/Vis 차단 특성이 뛰어난과 동시에 대전 방지특성을 나타내며 또한 내열성이 우수한 물질이 제조되어 사용 및 응용이 가능할 것으로 사료된다.

Key Words : phthalocyanine, antistatic, UV blocking

1. Introduction

As we are becoming ever more aware of health and advanced safety system, there is great demand for functional materials which improve the quality of workers' life. Safety-related materials such as flame-retardant materials, high performance product combining lightweight and high strength, and sensors for detecting defects in the safety system etc., have received increasing attention due to these functional roles.

These materials have continued to evolve in response to the multidisciplinary aspect of the related technology.

Phthalocyanine(Pc) complexes are widely used in numerous safety-related areas due to their rich and varied chemistry and outstanding physico-chemical properties¹⁾. The application of Pc using the conductive characteristics can be found not only as the antistatic materials used in reducing the risk of explosion of the explosive gas²⁾ but as the semiconductor materials to prevent the formation of defects³⁾ and the vanishment of valuable data. Pc has been used in various areas controlling the health hazard such as the

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disposable biosensor to monitor the cholesterol level of the operator⁴⁾, photodynamic therapy(PDT) which involves the use of dye combined with irradiation of light to cause cell⁵⁻¹⁰⁾ and tissue destruction in specific regions of living organisms, polarizing filter for eye protection¹¹⁾, gas sensing material to monitor the hazardous gas¹²⁻¹⁵⁾ and solvent¹⁶⁾, and UV-care products for protecting the skin against ultraviolet rays^{17,18)}.

In addition, Pc are widely used as corrosion resistant material¹⁹⁾, disk brake pad for high speed train²⁰⁾, pressure-sensitive tape for aerodynamic testing, luminophor-sensor to detect pressure pattern for airflight safety²¹⁻²³⁾, pressure-sensitive tape for preventing the formation of defects in precision mold²⁴⁾. They have also been used in a range of catalytic applications²⁵⁾ such as suppressing the chemical reaction or explosion of electrochemically active polymers for rechargeable batteries²⁶⁾, and used as ultrahigh pressure(0.5GPa) detecting sensor²⁷⁾, sensitizer in the dye-sensitized solar cell²⁸⁾ and gas sensing materials such as NO₂²⁹⁾.

However, in spite of their various applicability in numerous products, MPc has lower reactivity and solubility which limit their use in preparation of thin films, coating, and gelation process. In order to enhance the solubility of MPc, MPc complexes were prepared by introduction of ligands with functional groups onto phthalocyanine ring or multilayer formation using a reactive substrate and axial ligand.

In this paper, we report the synthesis, structure and properties of MPc complexes incorporating axial ligands such as 4-VP(4-vinylpyridine) and VIM(1-vinylimidazole). The absorption spectra were measured with FT-IR and UV/Vis and thermal characterization was also performed. The increase in solubility and antistatic property as measured by surface resistivity will also be discussed.

2. Experimental

2.1. Preparation

The crude PcFe(Aldrich) were purified by vacuum sublimation under the condition of 10⁻⁶ torr and 260°C. 4-vinylpyridine(Aldrich) and 1-vinylimidazole(Aldrich) were used after vacuum distillation. The PcFe(4-VP)₂ and PcFe(VIM)₂ were synthesized without solvent

following published procedure of Kang et al.¹⁾ with slight modification to include excess axial ligands the quantity of which is 30times as large as PcFe under a stream of nitrogen for 12hr at 110°C.

The products were purified by washing with MeOH until colorless and subsequently dried for 24hr at 70°C, which were then dissolved with dichloromethane(CH₂Cl₂) and purified by passing through SiO₂(neutral) bed. The final products were obtained by vacuum drying (10⁻³torr) for 12hr at 70°C.

2.2. ATR-FTIR

ATR-FTIR(Perkin-Elmer, Spectrum GX-1) measurement system was used for identification of PcFe, PcFe(4-VP)₂, and PcFe(VIM)₂ in the range 600~2000cm⁻¹.

2.3. UV/Vis

UV/Vis absorption spectra of solutions of PcFe(4-VP)₂, and PcFe(VIM)₂ dissolved in CH₂Cl₂ and films of PcFe(4-VP)₂, and PcFe(VIM)₂ deposited onto optically flat fused quartz substrates were recorded on spectrophotometer(Hewlett Packard, 8452A) in the spectral range from 190~800nm.

2.4. Thermal Analysis

Thermogravimetric analysis(TGA) and differential scanning calorimetry(DSC) were performed on Mettler Toledo, TGA/SDTA 851e and Mettler Toledo 833e thermal analysis systems, respectively at a heating rate of 10°C/min under N₂ atmosphere in the 25~550°C range.

2.5. Surface Resistivity

Conductivity of thin film grown on PET substrate was measured using standard two probe techniques (Surface Resistivity Meter(Monroe, 262A)).

3. Results and Discussion

A new route to phthalocyanine complexes were developed to synthesize these products by fusion in the absence of solvent. This new method of synthesis without using solvent has advantages over the conventional synthetic methods since there are no risk of explosion and formation of harmful vapor from

organic solvent.

Reaction of PcFe with axial ligands such as 4-VP and VIM afforded powderlike, pure dark greenish blue colored PcFe(4-VP)₂, and PcFe(VIM)₂ in 23.8% and 19.8% yield, respectively. The resulted products are soluble in CH₂Cl₂ (solubility: 1g/1L) whereas purified PcFe are not soluble in this solvent. The solubility of these products can be exploited for coating and film formation application.

3.1. ATR-FTIR

Fig. 1(a) shows the ATR-FTIR spectra of purified reference PcFe(a), PcFe(4-VP)₂(b), PcFe(VIM)₂(c), respectively. As seen in Fig. 1(b) and (c) there are absorption peaks at 725, 752, 773, 912, 1070, 1094, 1116, 1164, 1288, 1326, 1420, 1610cm⁻¹; and 718, 750, 772, 912, 1068, 1091, 1115, 1162, 1282, 1325, 1418, 1609cm⁻¹, respectively. Complexes of the type [PcFeL₂] such as PcFe(4-VP)₂(b), PcFe(VIM)₂(c) have similar IR spectra to that of reference PcFe(a).

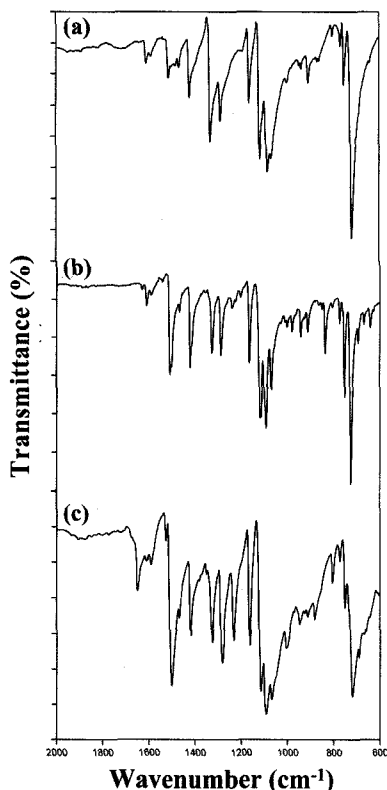


Fig. 1. ATR-FTIR spectra of PcFe(a), PcFe(4-VP)₂(b), PcFe(VIM)₂(c).

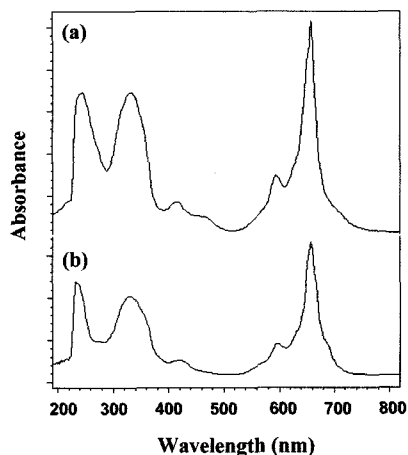


Fig. 2. UV/Vis spectra of resulted products PcFe(4-VP)₂(a), PcFe(VIM)₂(b).

However, PcFeL₂ complexes also exhibit additional bands in their IR spectra arising from the axial ligands that are not present in the PcFe spectra. The IR spectra of complexes with axial 4-VP(b) and VIM(c) ligands have characteristic new bands at 837, 980, 1240, 1502 cm⁻¹; and 881, 1233, 1501, 1649cm⁻¹, respectively.

3.2. UV/Vis and Blocking Properties

The recorded absorption measurements in the UV/Vis region show two well defined absorption bands of PcFe(4-VP)₂ and PcFe(VIM)₂ in the visible region (Q-band) and in the UV spectral region(B-Band).

A close examination of strong Q-band and B-band of PcFe(4-VP)₂ in CH₂Cl₂ appears in the region at 656, 332 nm, respectively. Q-band and B-band of PcFe(VIM)₂ in CH₂Cl₂ appear at 656nm, 330nm, respectively. The appearance of strong Q-band and B-band of these resulted products indicates that PcFe complexes were prepared by introduction of these ligands.

Details of the absorption bands observed in the UV/Vis spectra of films of PcFe(4-VP)₂, and PcFe(VIM)₂ deposited onto optically flat fused quartz substrates are shown in Fig. 3 and Table 1.

Table 1. UV/Vis spectra bands

Products	Band	Remarks
PcFe(4-VP) ₂	244 332 414 464(sh) 594 656	CH ₂ Cl ₂
PcFe(4-VP) ₂	218 340 418 466(sh) 610 672	Film
PcFe(VIM) ₂	234 330 420 596 656	CH ₂ Cl ₂
PcFe(VIM) ₂	220 342 424 616 678	Film

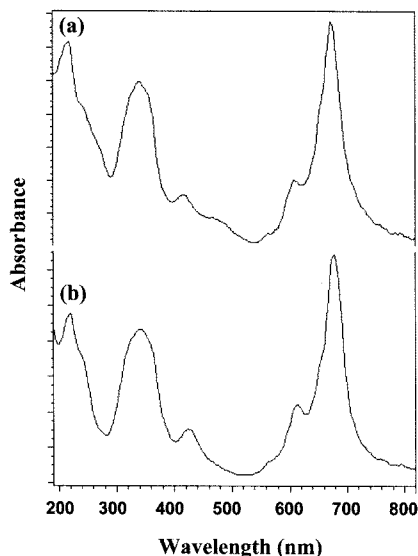


Fig. 3. UV/Vis spectra of films of PcFe(4-VP)₂(a), PcFe(VIM)₂(b) deposited onto quartz.

The absorption bands of PcFe(4-VP)₂ film appear in the region at 672nm which revealed 16nm bathochromic shift of strong Q-band and in the region at 218nm which revealed 26nm blue shift of B-band of PcFe(4-VP)₂ in CH₂Cl₂ respectively. Also, the absorption bands of PcFe(VIM)₂ film appear in the region at 678nm which revealed 12nm bathochromic shift of strong Q-band and in the region at 220nm which revealed 14nm blue shift of PcFe(4-VP)₂ in CH₂Cl₂ respectively. These shift might be attributed to the solvent effect. The strong absorption bands of films of PcFe(4-VP)₂ and PcFe(VIM)₂ deposited on quartz indicate that ultrahigh UV protection property has been provided in these films.

3.3. Thermal Analysis

Fig. 4 and Table 2 show thermogravimetric analysis (TGA) and differential scanning calorimetry(DSC) analysis of the resulted product. TGA showed that the onset(initial decomposition temperature) were 156°C and 161°C for PcFe(4-VP)₂, PcFe(VIM)₂ respectively, which indicate that these products are thermally stable and can be used in the temperature range up to 150°C. The theoretical weight loss of PcFe(4-VP)₂ is 27% which is 2 molar equivalent of weight loss of 4-VP. Experimental value of weight loss of PcFe(4-VP)₂ was 26.3%. Agreement between calculated and

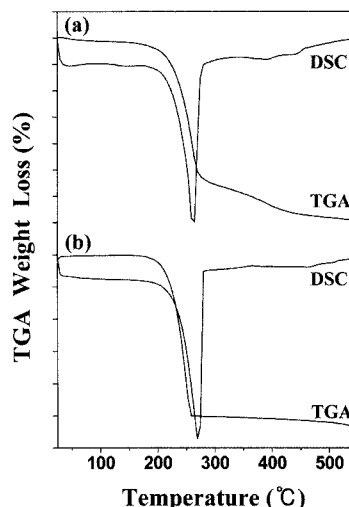


Fig. 4. TGA curves of PcFe(4-VP)₂(a), PcFe(VIM)₂(b).

Table 2. TGA/DSC data of PcFe(4-VP)₂, PcFe(VIM)₂

	Thermal degradation temp. range(°C)	Mass loss calc'd/experimental(%)	DSC-data (Tmax, °C)
PcFe(4-VP) ₂	156-287	27.0/26.3	262
	287-480		392(sh)
PcFe(VIM) ₂	161-260	24.9/25.1	272

experimental data is satisfactory. Similar results were obtained for the weight loss of PcFe(VIM)₂ theoretical and experimental data were 24.9% and 25.1%, respectively. These data strongly suggest that these products include two axial ligands.

3.4. Antistatic Properties(Surface Resistivity)

Conductivity of PcFe(4-VP)₂ and PcFe(VIM)₂ thin film grown on PET substrate was measured and sheet resistance was $\sim 10^{11} \Omega/\text{sq}$.

This value is much higher than that measured for virgin PET film ($\sim 10^{16} \Omega/\text{sq}$), suggesting that these thin films can be used in the antistatic coating.

4. Conclusion

The present study presents a new route to phthalocyanine complexes such as PcFe(4-VP)₂ and PcFe(VIM)₂ and the following conclusion can be drawn:

- 1) Phthalocyanine complexes such as PcFe(4-VP)₂ and PcFe(VIM)₂ have similar IR spectra to each other with little influence from the axial ligand. Their bands

contain contributions mostly from the atoms in the Pc ring near to the metal. However, these complexes also exhibit additional bands in their IR spectra arising from the axial ligands that are not present in the PcFe spectra, suggesting that these products are complexes of the type PcFeL₂.

2) The recorded absorption measurements in the UV/Vis region show two well defined absorption bands in the visible region Q-band and in the UV spectral region B-Band, which can be attributed to the solvent effect.

UV/Vis spectra of films of PcFe(4-VP)₂, and PcFe(VIM)₂ deposited onto fused quartz substrates also show UV/Vis blocking characteristics. These observations strongly support that phthalocyanine complexes can be used as powder and solvent type as well.

3) TGA showed that the initial decomposition temperature were 156 °C and 161 °C for PcFe(4-VP)₂, PcFe(VIM)₂, respectively, which indicate that these products are thermally stable and can be used as coating material in the temperature range up to 150 °C.

4) Conductivity of PcFe(4-VP)₂ and PcFe(VIM)₂ thin film grown on PET substrate were measured and sheet resistance was $\sim 10^{11} \Omega/\text{sq}$, suggesting that these thin films can be used in the antistatic coating.

In summary, phthalocyanine complexes exhibit useful properties such as UV/Vis blocking, antistatic and thermally stable characteristics and we anticipate that they can be applied to a variety of application.

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