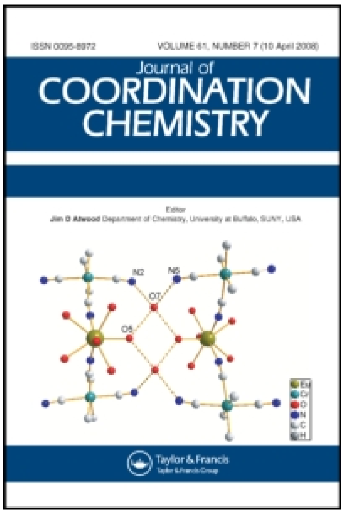

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Electronic States of Zinc Phthalocyanine in Various Films; Its Association Profile

Eiji Kanezaki[a]
[a] Department of Applied Chemistry, Faculty of Engineering, Tokushima University, Tokushima, Tokushima, Japan

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ELECTRONIC STATES OF ZINC PHTHALOCYANINE IN VARIOUS FILMS; ITS ASSOCIATION PROFILE.

EIJI KANEZAKI
Department of Applied Chemistry, Faculty of Engineering,
Tokushima University, 2-1 Minamijosanjima, Tokushima,
Tokushima 770, Japan

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Abstract The x-polymorph of zinc phthalocyanine(ZnPc) is observed both in the absorption spectra of the Langmuir-Blodgett films being compressed to the constant surface pressure and in the photoacoustic spectra of thick sublimed films. This polymorph exhibits the characteristic absorption band in near infrared wavelength region. The molar enthalpy change in the transformation from α- to x-polymorph is estimated to be $\Delta H \cong 0.40$ kJ/mol.

Keywords: X-polymorph, zinc phthalocyanine, Langmuir-Blodgett films, photoacoustic spectra

INTRODUCTION

Although ordinary solids have three-dimensional expansion, thin films are regarded as two-dimensional solids because they have extremely small thickness. Much attention has been paid to nature of films not only from the pure scientific points of view but also from those of applications. One of the reasons is that their properties as a material can be cotrolled easily by the careful procedure in the preparation.[1]

Metal phthalocyanines(MPcs) show polymorphism in the solid state.[2] Each polymorphic form exhibits a quite different absorption spectrum with one another in the visible-near infrared wavelength region. In solid, many MPcs form molecular stacking where molecular planes pile up as cardboards. A different polymorphic form is associates with a different manner of stacking in which intermolecular distance, relative orientation of molecular axes, etc., may be slightly changed. Such structural alterations in each polymorph so perturb the electronic states of MPc molecule as to show unique absorption spectrum. Many MPcs have the intense absorption band in the visible region(Q band), in solutions.[2] The location of the Q band is sensitive to the polymorphic forms in solids.

In vacuum sublimed films of ZnPc, several polymorphic forms are reported, where the x-form has an outstanding property.[2,3] This form has such an intense absorption band in near infrared region that an application is expected to infrared sensitive devices. The author et al. have reported that ZnPc forms a stable solid condensed film at an air-water interface.[4] This film has been transferred successfully onto a solid substrate. From the occupied area per one molecule, it has been concluded that ZnPc molecules in the film have molecular planes being not parallel but declined considerably to the surface of the substrate.

In this paper, absorption spectra and photoacoustic spectra are reported for the two types of film. Some polymorphic forms are found in these spectra, in common. Enthalpy change is estimated for the transformation from α-to x-form.

EXPERIMENTAL

Regent grade of ZnPc(Tokyo Kasei Co. Ltd.) was purified by vacuum sublimation twice. Sublimed films were prepared under 10^{-1} Pa on glass sildes(18 mm x 18 mm) by using the purified ZnPc needlelike crystals. Two kinds of sublimed film were obtained. One had the surface density of 5.40×10^{-5} g cm^{-2}(Thin Film) and the other had 3.00×10^{-4} g cm^{-2}(Thick Film). Though the former was transparent enough to obtain an absorption spectrum with the conventional method, the latter was too opaque for the measurement.

Langmuir-Blodgett(LB) films of ZnPc were prepared on SnO_2 coated glass slides by means of the vertical dipping method.[1] Two kinds of LB film were obtained, also. One was prepared under the surface pressure of 20.7 mN m^{-1} (Compressed LB Film), and the other below 20.7 mNm^{-1}(Uncompressed LB Film). The underlying water(subphase) was a phosphorate buffer solution(pH 8, 15°C) being made from the doubly distilled water.

Absorption spectra were observed by means of a Shimadzu UV-160 Spectrometer being equipped with an infrared sensitive silicon photodiode detector. Photoacoustic spectra were obtained under the non-resonant condition by using the home made system and the photoacoustic cells whose details have been described elsewhere.[5] Light source for the photoacoustic measurement was a 500 W HALOGEN LAMP (USHIO JVC100-500WA).

RESULTS AND DISCUSSION

In Figure 1, photoacoustic spectra of Thin(upper) and Thick(lower) Films are shown. The position of maxima in the spectrum of Thin Film corresponds to that in its conventional absorption spectrum. The maximum at 690 nm(indicated by an asterisk in Figure 1, upper) is an absorption by the α-form(α-band) whereas that at 600 nm by β-form(β-band).[3,6] The appearance of both forms suggests an imperfect polymorphic transformation from the α- to the β-form. The spectral shape of Thick Film almost resembles that of Thin Film except the presence of the band at 830 nm(x-band, indicated by double asterisks in Figure 1, lower). This new band has been assigned to the absorption band by the x-form[6] which appears during the transformation by some excess heating of the α-form[2] for a long time enough to make Thick Film.

Photoacoustic spectroscopy is one of the useful tools to detect the band location in opaque solid samples such as powders, films and so on.[5,7] The thermal diffusion length(μ) which gives the depth limit of an acoustic signal generation from the surface of a sample is formulated as below,[7]

$$\mu = \left[2k/(\rho \cdot C \cdot \omega)\right]^{1/2} \qquad (1),$$

where k, ρ, C, ω are the thermal conductivity, the density, the specific heat of ZnPc and the angular frequency of chopping for an exciting radiation, respectively. The thermal diffusion length in this measurement is calculated as $\mu=8.3 \times 10^{-3}$ cm.[8] The film thickness(t) for Thick Film is estimated as $t=1.6 \times 10^{-4}$ cm. From the relation of $t<\mu$, it is convinced that absorption bands of all photoabsorbing species in Thick Film are detected in the photoacoustic spectrum in Figure 1.[7]

In Figure 2, absorption spectra of Uncompressed(upper) and Compressed(lower) LB films are shown. The location of the prominent maximum in the upper spectrum is almost the same as that of the α-form in the photoacoustic spectrum of Thin Film(Figure 1, upper). Intensity of the β-band reduces to become only a shoulder. This observation indicates clearly that α-form appears predominantly in Uncompressed LB Films. On the contrary, the x-band at 830 nm appears intensely in the Compressed LB Film(Figure 2, lower). In this spectrum, the α-band appears weakly and the β-band only a tiny shoulder, too. Now it is safely concluded that the transformation from α- to x-form takes place when the layer at the air-water interface is compressed to the surface pressure of 20.7 $\mathrm{mN\,m^{-1}}$.

It has been reported that the α-form has a different habit of molecular stacking with that of the β-form.[3,6] Intermolecular forces between the face-to-face neighboring molecules are relatively weak for planar molecules. A displacement of such neighboring molecules in the α-form produces the stacking of the β-form in the direction parallel to the cofacial molecular planes. Thus it is concluded that an application of some kind of pressure or a moderate heating induces the transformation between polymorphic forms in ZnPc. Considering that the transformation from α- to x-form takes place in LB films with such moderate surface pressure, it is tentatively concluded that the x-form also has another molecular stacking which is slightly different from that of α- or β-form, although the exact structure of the x-form is not known.

With the model above, the molar enthalpy change(ΔH) in the

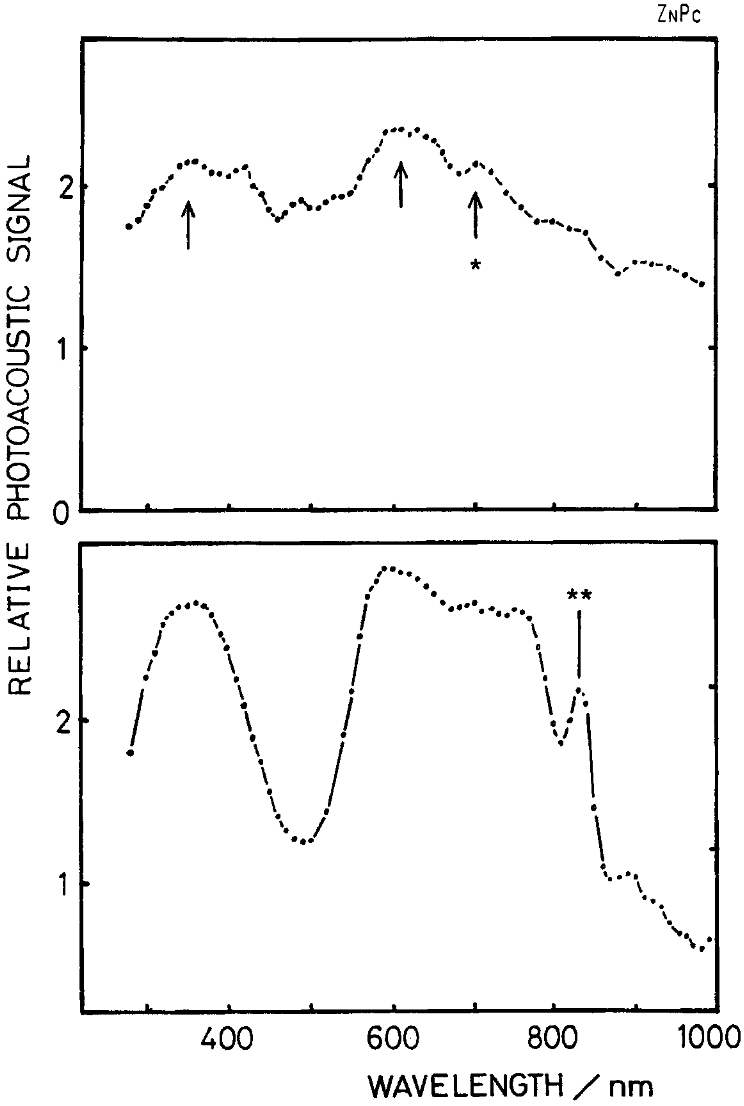

FIGURE 1 Photoacoustic spectra of vacuum sublimed films with the surface density of 5.40 x 10^{-5} g cm^{-2} (upper; Thin Film) and with that of 3.00 x 10^{-4} g cm^{-2} (lower; Thick Film). Arrowed position in the upper spectrum indicates the location of maxima in the absorption spectrum of Thin Film.
Bands with asterisk(s); see text.

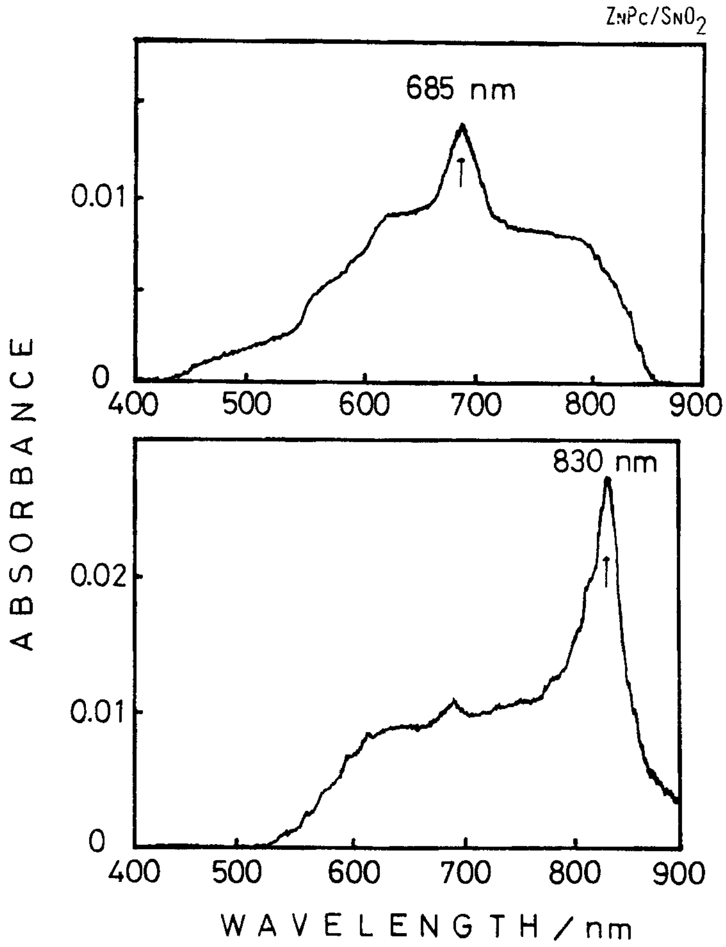

FIGURE 2 Absorption spectra of single Uncompressed (upper) and Compressed(lower) LB Films on SnO_2 layer. Arrowed positions indicate the location of the absorption maxima which are expressed in wavelength above them.

transformation from the α- to the x-form is formulated as,

$$\Delta H = \frac{1}{2}\Pi \cdot L \cdot \Delta x \cdot \cos\theta \cdot N_0 \qquad (2),$$

where Π, L, Δx, θ, N_0 are the surface pressure which induces the transformation, the width of molecular front edge which is perpendicular to the direction of the surface pressure at the air-water interface, the molecular displacement due to the transformation, the angle between the molecular plane and the interface respectively. The calculated enthalpy change is ΔH=0.40 kJmol^{-1},[10] which is smaller than the reported value of ΔH=(10.7±0.1) kJmol^{-1} in the transformation from the α- to the β-form of CuPc.[11] Although the discrepancy may be elucidated by an intramolecular deformation being associated inevitably with polymorphic transformations, the small enthalpy change may be related to the tendency of the five coordination of zinc atom.[12]

Finally, it is concluded that the polymorphic transformation which is observed in sublimed films is also detected in LB films by the application of the moderate surface pressure at the air-water interface. A possibility is proposed to detect such transformations by means of an application of the proper surface pressure to solid condensed film at the interface. This method need not heat samples, therefore, it would be suitable to apply a compound which forms stable solid condensed film at the interface but decomposes on heating. Futhermore, this method would clarify the classic problem of association in condensed phases of many macrocyclic molecules.

REFERENCES

1. G. L. Gaines, Jr., Insoluble Monolayers at Liquid-Gas Interfaces (Interscience, New York, 1966).
2. F. H. Moser and A. L. Thomas, The Phthalocyanines (CRC Press, Florida, 1983), Vol. I.
3. F. Iwatsu, T. Kobayashi and N. Ueda, J. Phys. Chem., 84, 3223 (1980).
4. E. Kanezaki, H. Yamanouchi and T. Sadamoto, to be published.
5. E. Kanezaki, Chem. Phys. Lett., in press.

6. A. M. Hor and R. L. Loutfy, *Thin Solid Films*, *106*, 291(1983); J. H. Sharp and M. Lardon, *J. Phys. Chem.*, *72*, 3230(1978).
7. A. Rosencwaig and A. Gersho, *J. Appl. Phys.*, *47*, 64(1976).
8. With values of $k=2.2 \times 10^{-3}$ cal cm^{-1} s^{-1} K^{-1}, $\rho=1.84$ g cm^{-3} and $C=0.55$ cal g^{-1} K^{-1}, respectively.
9. W. R. Scheidt and W. Dow, *J. Amer. Chem. Soc.*, *99*, 1101(1977).
10. With values of $\Pi=20.7$ mNm^{-1}, $L\cong 15 \times 10^{-10}$ m, $\Delta x\cong 0.5 \times 10^{-10}$ m,[9] $\theta=30°$ and $N_0=6.02 \times 10^{23}$ mol^{-1}, respectively.
11. J. H. Beynon and A. R. Humphries, *Trans. Faraday Soc.*, *51*, 1065(1955).
12. D. S. C. Black and N. E. Rothnie, *Aust. J. Chem.*, *36*, 2395 (1983).