Molecular Distortion and Exciton Coupling Effects in β Metal-Free Phthalocyanine

Shinya Matsumoto and Jin Mizuguchi
Department of Applied Physics, Faculty of Engineering,
Yokohama National University
Yokohama, Japan

Abstract

As pointed out in titanylphthalocyanine, molecular distortion (reduction in molecular symmetry) upon crystallization exerts a significant influence on the optical absorption in the near-IR region. The electronic spectra of β metal-free phthalocyanine (MfPc) has been investigated from the standpoint of molecular distortion and exciton coupling effects. Close examination of the crystal structure of MfPc revealed that the molecular symmetry is reduced from D_{2h} to C_i on going from solution to the solid state. Molecular distortion is found to enhance the band splitting in such a way that the longer-wavelength band is more displaced towards longer wavelengths while the shorter-wavelength band is more shifted towards shorter wavelengths. The electronic spectra of MfPc can mostly be interpreted in terms of the distortion of molecular framework. However, some exciton coupling effect is also observed as shown by polarized reflection spectra on single crystals as well as temperature dependence of absorption spectra.

Introduction

Metal-free phthalocyanine (abbreviated to MfPc and shown in the inset of Fig. 1) is a commercial blue pigment which is widely used for paint and automobile industries.[1,2] The first singlet-singlet transition called Q-band is responsible for the coloration in the visible region. Beside its use as a pigment, MfPc has also attracted attention as a photoconductor for laser printers based on GaAsAl laser diodes.[3] Several crystal modifications such as α, β, *x etc.* are known to exist in X-ray powder diffraction diagrams.[1]

In the course of our studies on the mechanism of the near-IR absorption of titanylphthalocyanine (TiOPc), we found that the molecules are heavily deformed on going from solution to the solid state and that the molecular distortion (reduction in symmetry) exerts a profound influence on the optical absorption.[4] An in-depth investigation on the correlation between molecular distortion and optical absorption on the basis of molecular and crystal structures revealed that the band splitting sensitively occurs because the excited state of phthalocyanine compounds is doubly degenerate and this degeneracy can easily be removed by perturbation such as molecular distortion.[4] In fact, the band splitting becomes larger with molecular distortion. In this way, we have successfully interpreted the near-IR absorption of TiOPc as arising from the longer-wavelength band of the split bands.

The above investigation pointed out the importance of molecular distortion in the electronic transition of phthalocyanine compounds, while no investigation has been carried out from the viewpoint of molecular distortion. Our model is in marked contrast to the previous interpretations based on the exciton coupling effect called the Davydov splitting (factor group splitting).[5-7] An attempt was therefore made to characterize the electronic spectra of representative phthalocyanines in terms of the distortion of molecular framework.

The present paper discusses the electronic structure of MfPc from the standpoint of molecular distortion and exciton coupling effects. Attention is also focused on the separation of the effect between molecular distortion and exciton coupling.

Result and Discussions

Solution and Solid-State Spectra

The solution spectrum of MfPc in chloronaphthalene is shown in Fig. 1 together with the solid-state spectrum for β phase in evaporated films. Both spectra give two absorption bands in the visible region due to D_{2h} symmetry.

Crystal Growth and Structure Analysis

The structure analysis for β-MfPc had already been done by Robertson[8] in 1936. His analysis was perfect with an experimental setup at that time, but was not precise enough for the examination of molecular distortion because of the high standard deviation. So the structure was re-determined as described below.[9]

MfPc was purchased from Fluka Chemicals and purified four times by sublimation. The single crystals were then grown from the vapor phase, using a two-zone furnace.[10] A number of lustrous dark blue prisms were obtained after 24 h of vapor growth.

The reflection data was collected by a RigakuAFC7R diffractometer and the structure was solved by direct methods, using SIR92.[11] The crystal data[9] is: monoclinic, $C_{32}H_{18}N_8$, M_r=514.55, $P2_1/a$, a=19.8707(7), b=4.731(7), *c*=121.98(4) Å, *β*=121.98(4)°, *Z*=2. The crystal structure is basically in good agreement with *β*-phase of MfPc reported by Robertson.[8] The ORTEP diagram is shown in Fig. 2.

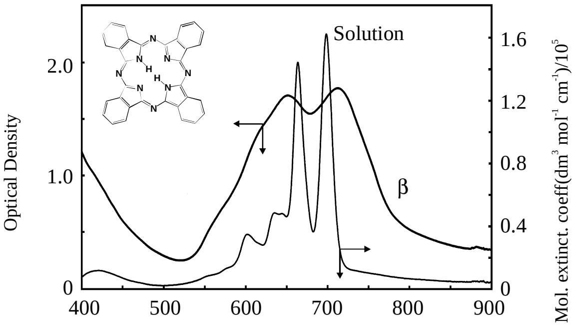


Figure 1. Solution and solid-state spectra of MfPc.

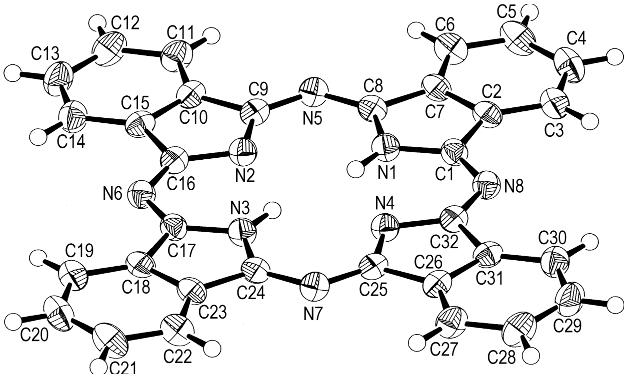


Figure 2. ORTEP diagram of β-MfPc.

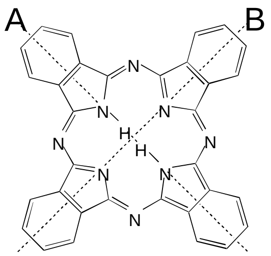
Table 1. Molecular distortion in *β*-MfPc and the optimized geometry.

		Dihedral (deg)	
Plane 1	Plane 2	X-ray (β phase)	Opt. geo.(solution)
N1,N2,N3,N4	phenyl C2…C7	1.86	0
N1,N2,N3,N4	phenyl C10…C15	2.32	0
N1,N2,N3,N4	phenyl C18…C23	-1/86	0
N1,N2,N3,N4	phenyl C26…C31	-2.32	0
Molecular symmetry		C_i	D_{2h}

Molecular Distortion and its Influence on the Optical Absorption Spectra

In order to quantify the extent of molecular distortion, we measured the angles between the plane of the four central nitrogen atoms (N1, N2, N3 and N4: plane 1) and the plane of each phenyl ring (plane 2). If all these angles are equal to zero, this is taken as D_{2h} symmetry. The angles are listed in Table 1 together with those of the optimized geometry (MNDO Hamiltonian in MOPAC93[12]) which corresponds to the conformation in solution. It is apparent that the molecule in *β*-phase is slightly distorted and possesses the C_i symmetry; whereas the optimized structure is entirely planar and is characterized by D_{2h} symmetry.

Table 2. The calculated absorption bands for *β*-MfPc as well as for the optimized geometry.



		Calculated		Observed (Figure 1)	
		λ_{max}(nm)	*f*	λ_{max}(nm)	Mol. extinct. coeff. ($dm^3mol^{-1}cm^{-1}/10^5$) or optical density
Solution[a] (D_{2h})	A:	630.8	0.693	664.0	1.44
	B:	646.6	0.727	698.5	1.64
		$\Delta\lambda$ = 15.8 (387 cm^{-1})		$\Delta\lambda$ = 34.5 (744 cm^{-1})	
β phase[b] (C_i)	B:	690.3	0.837	651.5	1.712
	A:	744.5	0.773	712.0	1.778
		$\Delta\lambda$ = 54.2 (1055 cm^{-1})		$\Delta\lambda$ = 60.5 (1304 cm^{-1})	

[a] in Cl-naphthalene. [b] Evaporated film

The influence of the present molecular distortion is best evaluated by molecular orbital (MO) spectroscopic calculations using the x, y, z coordinate sets of the X-ray structure.[9] The bands calculated by the INDO/S Hamiltonian[13] are given in Table 2 together with the experimental values observed for solution and evaporated films. The transition moments A and B as well as their direction are set out in the inset. The effect of molecular distortion is clearly recognized in the calculation for the *β*-phase (C_i: 690.3/744.5 nm) as compared with that in solution (D_{2h}: 630.8/646.6 nm). The band splitting as given by the difference in energy between transitions A and B is about 1055 cm^{-1} in *β*-phase and this is much larger than the value of 387 cm^{-1} in solution. The difference of 668 cm^{-1} is therefore attributed to the effect of molecular distortion. This tendency is qualitatively in good agreement with experiment as shown in Fig. 1 and Table 2, indicating that the band splitting is larger in the solid state (1304 cm^{-1}) than in solution (744 cm^{-1}).

Polarized Reflection Spectra

In order to study the effect of exciton coupling on the absorption band, polarized reflection spectra shown in Fig. 3 were measured on the (001) plane of a single crystal by means of a microscope-spectrophotometer (UMSP80; Carl Zeiss) (Fig. 3). A prominent reflection band appears around 730 nm for polarization perpendicular to the *b*-axis, accompanied by another dispersion peaking at 650 nm. An intense reflection band as well as a broad band are also observed around 715 and 645 nm, respectively, for polarization parallel to the *b*-axis. It is apparent that the position of the reflection maximum is different, depending on the polarization direction, either parallel or perpendicular to the *b*-axis. This is typical of the Davydov splitting known as the interaction between transition moments and indicates the involvement of exciton coupling in the optical process.

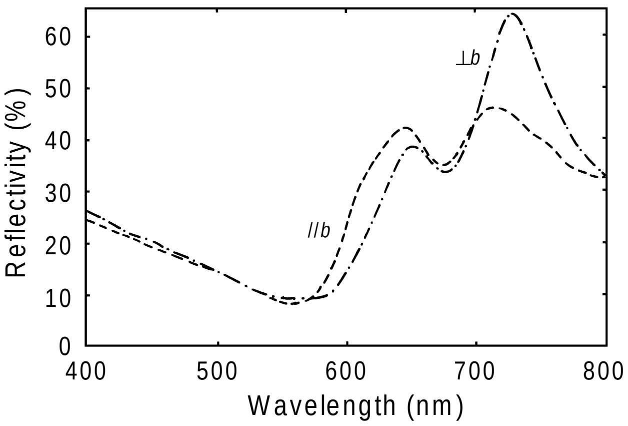


Figure 3. Polarized reflection spectra measured on the (001) plane of a single crystal of β-MfPc.

Temperature Dependence of Absorption Spectra

Lattice contraction as well as molecular distortion are expected more enhanced on lowering the temperature. So the enhanced intermolecular interaction due to lattice contraction or enhanced molecular distortion may induce some change in optical absorption. To investigate this effect, the temperature dependence of absorption spectra has been measured in an evaporated film of *β*-MfPc in the temperature range between 12 and 293 K. The result is shown in Fig. 4.

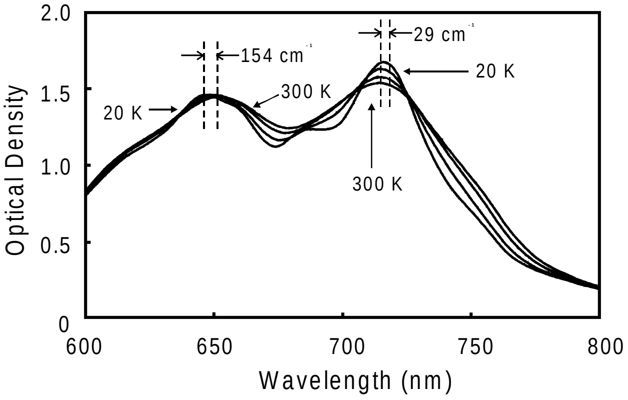


Figure 4. Temperature dependence of absorption spectra in an evaporated film of β-MfPc.

A rather significant temperature dependence is clearly observed around 650-800 nm. It is of interest to note that the shorter-wavelength band is more displaced towards shorter wavelengths on lowering the temperature; whereas the longer-wavelength band is more shifted towards longer wavelengths. However, the extent of the spectral shift is asymmetric. If we assume that the molecule is more distorted on lowering the temperature, more band splitting will result in a symmetrical way as shown in Fig. 5(a). That is, the band splitting occurs by an equal amount towards shorter or longer wavelengths. In experiment, however, the spectral shift is larger at the shorter wavelength-band than the longer-wavelength band. This can be explained, as follows, in terms of exciton coupling effects in the electronic transition as observed in the polarized reflection spectra (Fig. 3).

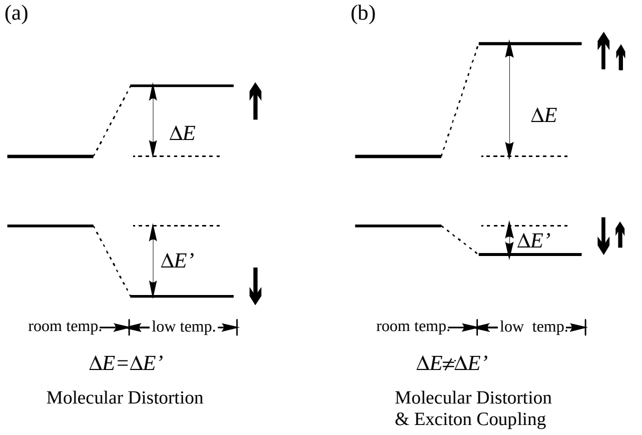


Figure 5. Energy diagram for the temperature effect: (a) due to molecular distortion and (b) due to molecular distortion plus exciton coupling effect.

Conclusions

The electronic spectra of *β*-MfPc has been characterized from the standpoint of molecular distortion. The reduction in molecular symmetry from D_{2h} to C_i is recognized on going from solution to the solid state. Molecular distortion is found to enhance the band splitting in such a way that the longer-wavelength band is more displaced towards longer wavelengths while the shorter-wavelength band is more shifted towards shorter wavelengths. The electronic spectra of MfPc can mostly be interpreted in terms of the distortion of molecular framework. However, some exciton coupling effect is also observed in the optical transition as shown by polarized reflection spectra as well as temperature dependence of absorption spectra.

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Biography

Shinya Matsumoto received his B. Eng. and M. Eng. in chemistry from Osaka Prefecture University. After that, he joined SHARP Corporation and was engaged in the development of liquid crystal displays. In 1997, he left SHARP Corporation and came back to the university in order to pursue more fundamental investigations. He is currently in the graduate course for materials science at Yokohama National University. His research interest includes electronic characterization of organic pigments together with their electronic applications. He is a member of the Imaging Society and the Chemical Society of Japan.