

# Near-IR Absorption in Magnesiumphthalocyanine Complexes

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## Abstract

Magnesiumphthalocyanine (MgPc) is a blue pigment whose X-phase is known to exhibit an intense near-IR absorption. The near-IR absorption of MgPc has been investigated from the standpoints of exciton coupling effects on the basis of the crystal structure. Two kinds of six-coordinate MgPc complexes were grown from solution and their structures were analyzed: MgPc/(H<sub>2</sub>O)<sub>2</sub>·(N-methyl-2-pyrrolidone)<sub>2</sub> (crystal **1**) and MgPc/(2-methoxyethanol)<sub>2</sub> (crystal **2**). In both crystals, two oxygen atoms of the solvent molecule are coordinated to the central Mg atom above and below the molecular plane, forming a distorted *sp*<sup>3</sup>*d*<sup>2</sup> octahedron. Of these crystals, only crystal **1** exhibits a near-IR absorption whose spectral shape is quite similar to that of the X-phase. In addition, the X-phase is also found to contain two water-molecules in the normal ambient atmosphere. The near-IR absorption in both crystal **1** and the X-phase can reasonably be interpreted as arising from exciton coupling effects based on the molecular arrangement of MgPc/(H<sub>2</sub>O)<sub>2</sub>.

## Introduction

Magnesiumphthalocyanine (MgPc) known as a blue pigment possesses several crystal modifications, among which the X-phase exhibits an intense near-IR absorption as shown in Fig. 1.<sup>1-5</sup> Because of this, MgPc has recently attracted attention as a material useful for laser printers<sup>2,3</sup> as well as for optical discs<sup>4</sup> based on GaAsAl laser diodes. Since the elucidation of the near-IR absorption is basic to an understanding of the photoconduction mechanism, an attempt was made to characterize the near-IR absorption of MgPc from the standpoints of molecular distortion and exciton coupling effects on the basis of single crystals.

In the course of our investigation, we encountered two kinds of solvated single crystals of MgPc when recrystallized from *N*-methyl-2-pyrrolidone (MgPc/(H<sub>2</sub>O)<sub>2</sub>·(NMP)<sub>2</sub>; crystal **1**) and 2-methoxyethanol (MgPc/(2-methoxyethanol)<sub>2</sub>; crystal **2**).<sup>6</sup> In both crystals, the MgPc skeleton is found to be slightly deformed (*C*<sub>i</sub> symmetry). However, the band splitting in crystals **1** and **2** due to molecular distortion is too small to cause the near-IR absorption to appear.<sup>7</sup>

The present investigation then aims at clarifying the mechanism of the near-IR absorption of MgPc in terms of exciton coupling effects based on the molecular arrangement.

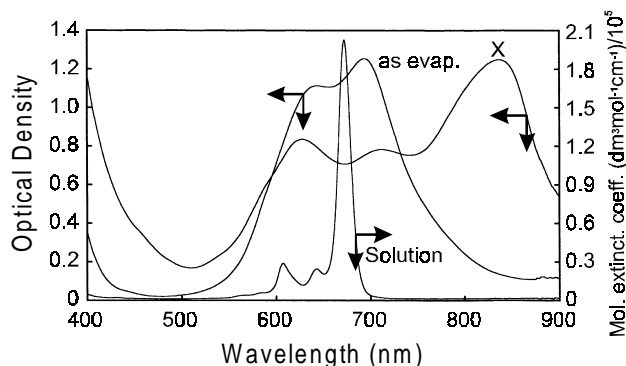


Figure 1 Solution spectrum as well as solid-state spectra of "as evaporated" and the X-phase.

## Results and Discussion

### Structure of Crystals **1** and **2**<sup>6</sup>

In both solvated crystals stated in introduction, two O atoms of the solvent molecules are coordinated to the central Mg atom, forming two kinds of deformed octahedron complexes. The *sp*<sup>3</sup>*d*<sup>2</sup> hybrid structure of the Mg atom accommodates 6 ligands, four of which are the surrounding nitrogen atoms on the molecular plane and two of which are the O atoms above and below the molecular plane. Figs. 2(a) and (b) show the crystal structure of crystals **1** and **2**. The molecules are stacked in a herringbone fashion along the *a*-axis and the *b*-axis for crystals **1** and **2**. In crystal **1**, two kinds of stacking columns are formed side by side: one is the column composed of MgPc/(H<sub>2</sub>O)<sub>2</sub> and the other is based on NMP molecules. Since the interplanar spacing along the *a*-axis is relatively small (3.26 Å), the interaction between translationally-equivalent molecules is expected large. On the other hand, the interaction along the *b*-axis between two translationally-inequivalent molecules is small because of the spacer of the NMP molecules between the MgPc/(H<sub>2</sub>O)<sub>2</sub> columns. In crystal **2**, the situation is quite different. There is only one kind of the stacking column composed of MgPc/(2-methoxyethanol)<sub>2</sub> along the *b*-axis. The interplanar spacing is much larger than that of crystal **1** (7.40 Å), since there are two solvent molecules between MgPc molecules working as the spacer. This indicates that the interaction between two translationally-inequivalent

molecules is much larger as compared with translationally-equivalent molecules in crystal 2.

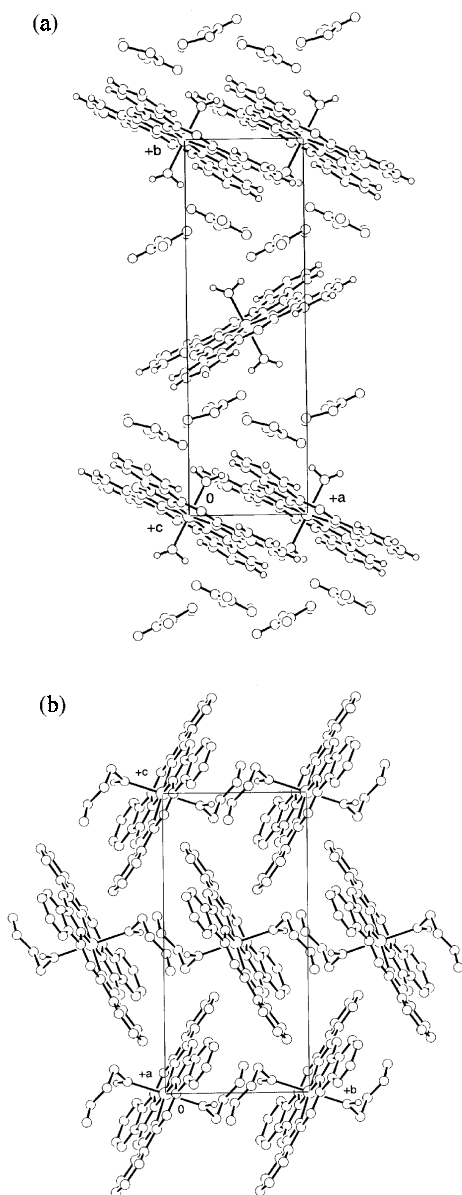


Figure 2. Projection of the crystal structure: (a) the (a,b) plane (crystal 1) and (b) the (b,c) plane (crystal 2).

### Polarized Reflection Spectra

Figs. 3(a) and 3(b) show the polarized reflection spectra measured on single crystals for crystals 1 and 2, respectively. In crystal 1, two prominent bands appear around 625 and 690 nm for polarization perpendicular to the *a*-axis. In addition, an intense reflection shoulder is also observed around 752 nm in the near-IR region. On the other hand, the shoulder in the near-IR region becomes an intense band around 765 nm for polarization parallel to the *a*-axis while the two intense bands in the visible region almost disappeared.

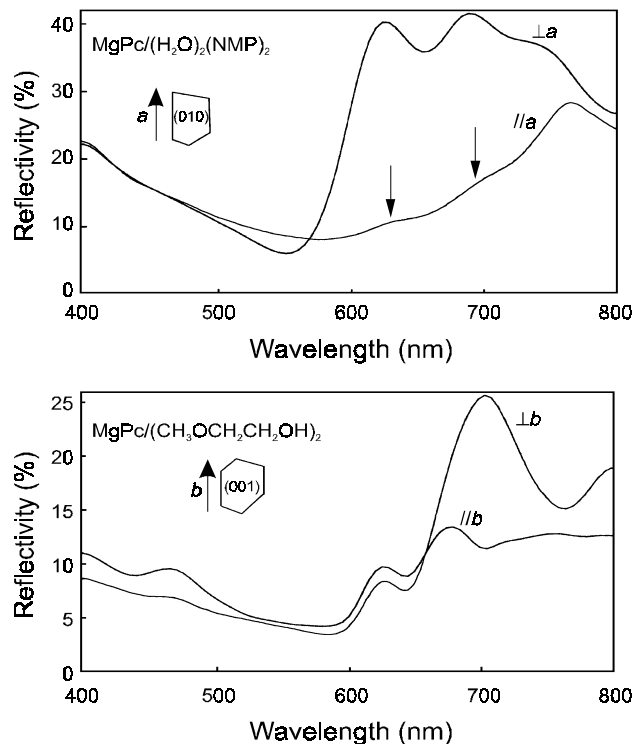


Figure 3 Polarized reflection spectra: (a) measured on the (010) plane for crystal 1 and (b) on the (001) plane for crystal 2.

The reflection spectra for crystal 2 exhibit no near-IR absorption. An intense band appears around 704 nm together with a small band around 625 nm for polarization perpendicular to the *b*-axis. Polarization parallel to the *b*-axis gives similar reflection bands around 625 and 667 nm, although the longer-wavelength band lies at a shorter wavelength by about 37 nm as compared with that for polarization perpendicular to the *b*-axis (704 nm). This difference is attributed to the Davydov splitting induced by two translationally-inequivalent transition dipoles.

Judging from the above polarized reflection spectra, the two visible bands appear in common in both crystals while the near-IR absorption is additionally present only in crystal 1. Furthermore, polarization parallel to the *a*-axis in crystal 1 greatly enhances the near-IR absorption but almost quenches the visible bands. These facts suggest that the near-IR absorption arise from exciton coupling effects.

On the basis of exciton coupling model, the reflection spectra can qualitatively be well interpreted by the molecular arrangement in crystals 1 and 2. As mentioned in the previous section, the interaction between two translationally-equivalent molecules along the stacking axis is larger in crystal 1 than in crystal 2; whereas the interaction between two translationally-inequivalent molecules is larger in crystal 2 than in crystal 1. This could suggest that the spectral shift plays the dominant role in crystal 1 rather than the Davydov splitting, while the Davydov splitting is the major effect in crystal 2 rather than the spectral shift. In fact, the near-IR absorption that

corresponds to a large spectral shift towards longer wavelengths appears only in crystal **1** (Fig. 3(a)); whereas the Davydov splitting is uniquely observed in crystal **2** (Fig.3(b)).

### Computations for the Exciton Displacement Energies in Crystals **1** and **2**

The exciton displacement energies are calculated for 8 neighboring molecules for crystals **1** and **2** on the basis of the following equation<sup>8</sup>:  $\Delta E = |\mu|^2 (1-3\cos^2\theta) / r^3$ , where  $r$  and  $\theta$  denote the distance and angle between two transition dipoles ( $\mu$ ). The distance  $r$  and angle  $\theta$  were obtained from the crystal structure for each crystal. The transition moment  $\mu$  in crystals **1** and **2** were calculated on the basis of the X-ray x, y, z coordinate sets using the INDO/S Hamiltonian. The results calculated for crystal **1** is set out in Table 1. The AA or BB denotes the coupling of transition moment A (or B) of one MgPc molecule with transition moment A (or B) of the neighboring one. The molecular sites are designated in fractional coordinates. The minus or plus sign of  $\Delta E$  denotes the bathochromic or hypsochromic shift displacement. In crystal **1**, five pairs are found to contribute to the bathochromic shifts, leading to the total displacement energy of about  $2730 \text{ cm}^{-1}$ . Especially, the molecular pairs along the stacking axis (denoted in bold in the figure) give large contribution to the bathochromic shift. On the other hand, the calculation in crystal **2** results in the hypsochromic shift of about  $2070 \text{ cm}^{-1}$ .

**Table 1. 8 neighboring molecules around the molecule at (000) and their displacement energies for crystal 1**

Transition moment	Site	Number of equivalent Molecules	$r$ (Å)	$\theta$ (°)	$\Delta E$ (cm <sup>-1</sup> )
AA	<b>(1,0,0)</b>	<b>2</b>	<b>6.860</b>	<b>50.80</b>	<b>-854</b>
	(0,0,1)	2	13.000	54.85	2
	(1,0,1)	2	13.367	28.14	-770
	(1,0,-1)	2	15.920	78.48	300
BB	<b>(1,0,0)</b>	<b>2</b>	<b>6.860</b>	<b>51.14</b>	<b>-686</b>
	(0,0,1)	2	13.000	38.01	-478
	(1,0,1)	2	13.367	63.77	210
	(1,0,-1)	2	15.920	23.68	-456
Total		16			<b>-2730</b>

### Near-IR Absorption in Crystal **1** and the X-phase

Fig. 4 shows the superposition of the two polarized reflection spectra for crystal **1** (Fig. 3(a)). The present averaged spectrum is strikingly similar to that of the X-phase shown in Fig. 1. It should also be remembered that the near-IR absorption in crystal **1** is due to exciton coupling effects based on the molecular arrangement of MgPc/(H<sub>2</sub>O)<sub>2</sub>(NMP)<sub>2</sub>, in which MgPc/(H<sub>2</sub>O)<sub>2</sub> and (NMP)<sub>2</sub> independently form their own stacking columns along the  $a$ -axis (Fig. 2(a)). In addition, we are aware that the single

crystal grown from the vapor phase rapidly polycrystallizes in the normal ambient atmosphere probably due to moisture from the air<sup>6</sup>. These facts prompted us to assume that the X-phase includes water-molecules in the form of MgPc/(H<sub>2</sub>O)<sub>2</sub> when the sample is vapor-treated with acetone and that the near-IR absorption arises from exciton coupling effects based on the molecular arrangements of MgPc/(H<sub>2</sub>O)<sub>2</sub>. For this reason, we have carried out a thermogravimetric analysis (TGA) on evaporated films of the X-phase in order to justify the present assumption.

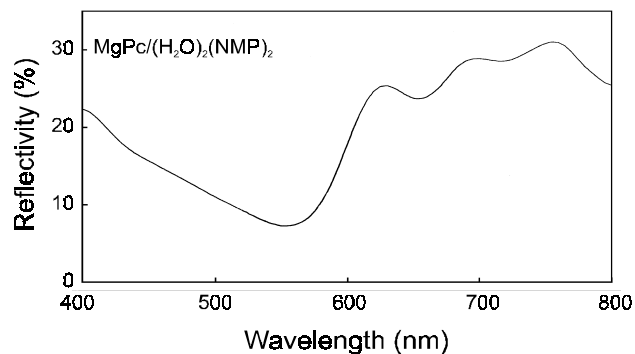


Figure 4. Averaged reflection spectrum of crystal **1**.

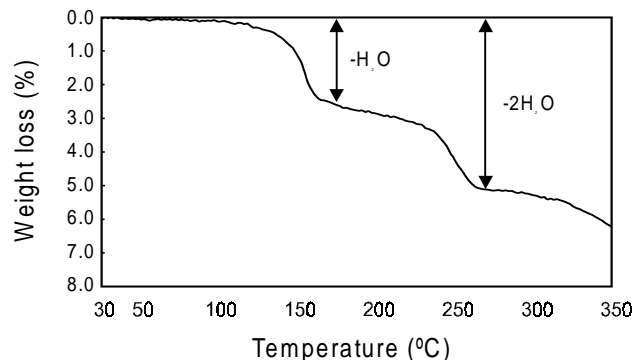


Figure 5. Weight-loss of the powdered sample of the X-phase as a function of temperature.

Fig. 5 shows the weight-loss of powdered X-phase as a function of temperature. The weight-loss apparently occurs in two steps at about 160 and 260 °C and these correspond exactly to the weight-loss of one molecule (H<sub>2</sub>O/MgPc (H<sub>2</sub>O)<sub>2</sub> = 3.14 %) and two molecules (6.28 %). This experiment evidently indicates that the X-phase is composed of MgPc/(H<sub>2</sub>O)<sub>2</sub> and that the near-IR absorption is ascribed to the molecular arrangement of not MgPc alone but MgPc/(H<sub>2</sub>O)<sub>2</sub>. Furthermore, the X-ray diffraction analysis revealed that the interplanar spacing of the X-phase along the stacking axis (3.32 Å) is very close to that of crystal **1** (3.26 Å).

## Conclusions

- Crystal **1** exhibits an intense near-IR absorption around 765 nm and this mechanism can be interpreted as arising from exciton coupling effects based on the molecular arrangement of MgPc/(H<sub>2</sub>O)<sub>2</sub>(NMP)<sub>2</sub>.
- The X-phase of MgPc is found to comprise MgPc/(H<sub>2</sub>O)<sub>2</sub>. The near-IR absorption can be explained in the same fashion as that of crystal **1**.
- Coordination of water-molecules to MgPc is ascribed to the inherent nature of magnesium atom characterized by deliquescent properties.

## References

1. A. M. Hor and R. O. Loutfy, *Thin Solid Films* 1983, 106, 291.
2. R. O. Loutfy, A. M. Hor, G. DiPaola-Baranyi and C. K. Hsiao, *J. Imag. Sci.* 1985, 29, 116.
3. N. C. Khe and M. Aizawa, *Nippon Kagaku Kaishi* 1986, 393 (in Japanese).
4. T. Daidoh, H. Matsunaga and K. Iwata, *Nippon Kagaku Kaishi* 1988, 1090 (in Japanese).
5. H. G. Kubota, J. Muto and K. M. Itoh, *J. Mat. Sci. Lett.* 1996, 15, 1475.
6. S. Matsumoto, A. Endo and J. Mizuguchi, *Z. Krist.* in print.
7. A. Endo, S. Matsumoto and J. Mizuguchi, submitted to *J. Phys. Chem*
8. M. Kasha, *Spectroscopy of the Excited State*, Plenum Press (1976) p.337.

## Biography

Jin Mizuguchi received B. Sc. in chemistry from Sophia Univ. in 1970, Dr. of Sc. from Univ. of Tokyo in 1982 and Venia Docendi from the Univ. of Bern in 1994. He worked at Sony Corporation Research Center from 1970 to 1985. In 1985, he moved to Ciba-Geigy AG in Switzerland and was involved in electronic characterization of organic pigments together with electronic applications. In 1995, he was nominated for professor for materials science at Yokohama National Univ.