

Desorption of Water Molecules and its Effect on the Dark Conductivity and Photoconductivity in X-Magnesiumphthalocyanine

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Abstract

Magnesiumphthalocyanine (MgPc) is a blue pigment whose X-phase ($\text{MgPc}/(\text{H}_2\text{O})_2$) is known to exhibit an intense near-IR absorption. The effect of water desorption on the dark conductivity and photoconductivity at elevated temperatures has been investigated in evaporated thin films of the X-phase of MgPc. Both dark conductivity and photoconductivity are found to greatly diminish with the onset of water desorption around 150°C. This is due to the scattering of charge carriers at defects formed by collapse of the vacancies of water molecules. Especially, the photoconductivity is quite sensitive to subtle structural changes due to thermal motion of water molecules in the lattice, even before water desorption. It is therefore crucial to keep the water molecules firmly coordinated to the central metal for the stable operation of MgPc-photoreceptors.

Introduction

X-Magnesiumphthalocyanine (X-MgPc) is known to exhibit an intense near-IR absorption as shown in Fig. 1 when the evaporated film of MgPc is exposed to the vapors of certain organic solvents such as acetone.¹ Because of the near-IR absorption, MgPc has attracted attention as a material for laser printers² and optical disks.³

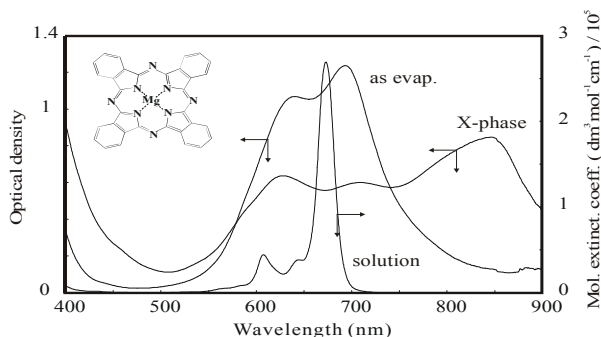


Figure 1. Solution and solid spectra of evaporated MgPc

In our previous investigation,¹ the X phase is found to include two water molecules according to thermal gravimetric analysis and that the water desorption occurs in two steps at 150 and 250°C as shown in Fig. 2: $\text{MgPc}/(\text{H}_2\text{O})_2 \rightarrow \text{MgPc}/\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{MgPc} + 2\text{H}_2\text{O}$. On the basis of this finding, we have interpreted the mechanism of the near-IR absorption of X-MgPc as arising from interactions between transition dipoles based on the molecular arrangement of $\text{MgPc}/(\text{H}_2\text{O})_2$.

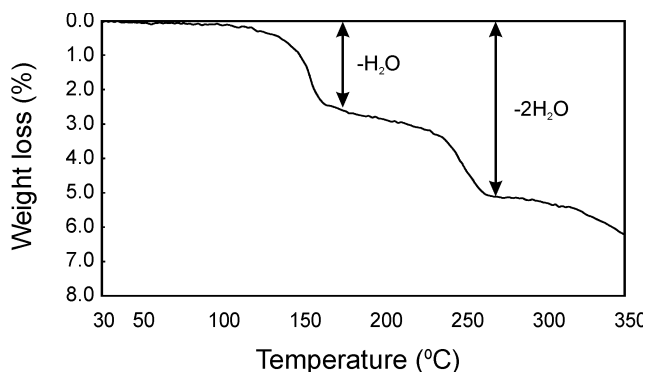


Figure 2. Weight-loss of the X-phase vs temperature.

Similarly, in Y-titanylphthalocyanine (Y-TiOPc),⁴ the presence of water is important for the appearance of the near-IR absorption as well as drastic enhancement of photoconductivity. For this reason, we have investigated the effect of water desorption on the dark conductivity and photoconductivity as well as on the absorption spectra in the X-phase of MgPc.

Experiment

Sample Preparations

The evaporated films of MgPc for measurements of visible absorption spectra, X-ray diffraction diagrams, dark conductivity and photoconductivity were prepared by vacuum evaporation onto plain glass slides or substrates

with interdigital electrodes. The evaporated films of MgPc were exposed to acetone vapor for several hours to bring about a spectral change to give the X-phase. The samples were heated in air at 100, 200 and 300°C for 30 minutes in order to eliminate water molecules from the sample.

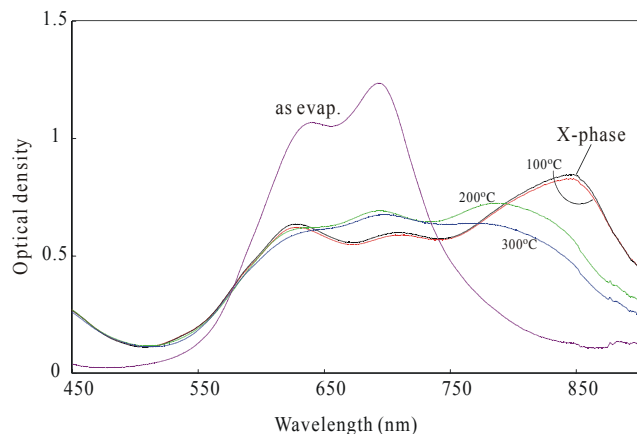


Figure 3. Abs. spectra of MgPc at various temperatures.

Results and Discussion

Spectral Changes as a Function of Temperature

Figure 3 shows the changes in absorption spectra for variously treated samples. As evaporated, MgPc exhibits a typical absorption spectrum with two absorption bands in the visible region peaking at 630 and 695 nm. Then, vapor treatment brings about the near-IR absorption which is typical of the X-phase ($\text{MgPc}/(\text{H}_2\text{O})_2$). No significant change in spectral shape is recognized for the sample heated at 100°C. However, at 200°C where the first water molecule has already been desorbed (Fig. 2), the absorption maximum around 850 nm is displaced toward shorter wavelengths, accompanied by reduction in absorption intensity. The present tendency is more enhanced at 300°C where the water molecules have completely been removed.

Structural Changes as a Function of Temperature

Fig.4 shows the X-ray diffraction diagrams as a function of temperatures. As evaporated, only halo diffraction diagram due to the glass substrate is recognized and is indicative of an amorphous phase. Then, a small diffraction peak appears around $2\theta = 7.5^\circ$ caused by vapor treatment (*i.e.* the range for long-periodicity) while no change was observed in the 2θ range between 15 and 30° (*i.e.* the range for short-periodicity) even at higher temperatures. The present state remains unchanged even at 100°C where no noticeable change in the absorption spectrum was recognized either (Fig. 3). After that, an additional peak appears around $2\theta = 6.5^\circ$ at 200°C where the first water molecule has already been desorbed (Fig. 2), accompanied by a change in the absorption spectrum (Fig. 3). The present diffraction peak grows up further while the peak around $2\theta = 7.5^\circ$ disappears completely at 300°C. The

crystalline state at 300°C is of complete absence of water molecules.

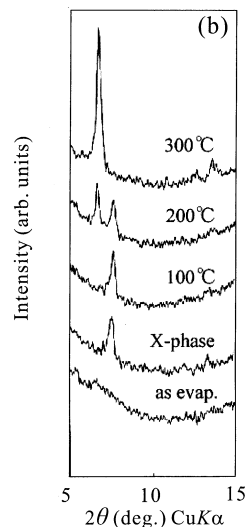


Figure 4. X-ray diagrams of MgPc at various temperatures.

However, the diffraction peak around $2\theta = 6.5^\circ$ cannot be assigned to the crystal structure of water-free MgPc analyzed on single crystals.⁵

Temperature Dependence of Dark Conductivity and Photoconductivity

The temperature dependence of dark conductivity is shown in Fig. 5. No significant change in dark conductivity can be seen in the temperature range between room temperature and 100°C.

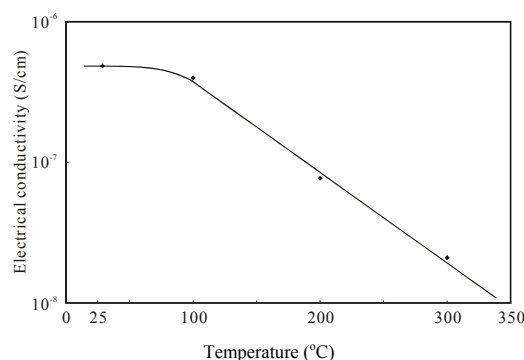


Figure 5. Temperature dependence of dark conductivity of vapor-treated MgPc (X-phase).

Then, the electrical conductivity begins to decrease with an onset temperature of around 100°C and further decreases remarkably with increasing temperature.

Figure 6 shows the photoconduction spectra measured in the temperature range between room temperature and 300°C. The photoconduction spectrum of the X-phase appears almost in accordance with the absorption spectrum shown in Fig. 3 and is greatly enhanced as compared with

that of the sample “as evaporated”. The photoconductivity is then appreciably reduced at 100°C, although no change in absorption spectrum (Fig. 3), the molecular arrangement (Fig. 4) and dark conductivity (Fig. 5) is recognized. In other words, the optical absorption as well as subsequent formation of excitons are assumed to remain unchanged. However, the contribution to the photoconductivity is almost one-eighth of the X-phase. The photoconductivity is finally quenched at 200 and 300°C in the half and complete absence of water molecules, respectively. Here again, the optical absorption is not greatly decreased at these temperatures.

Vacancies Due to Desorption of Water Molecules and Their Subsequent Collapse in the Crystal Lattice

Upon desorption of water molecules at elevated temperatures, it is likely that there formed a number of vacancies of water molecules. Therefore, it is important to clarify whether these lattice vacancies remain as they are, just in the case of ionic crystals such as silver halides, or can be collapsed, leading to the rearrangement of molecules.

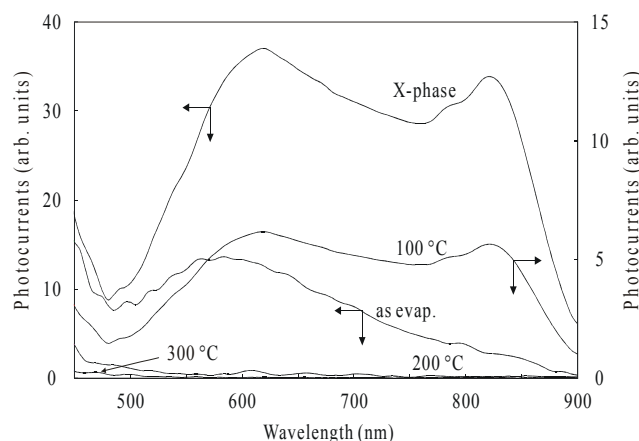


Figure 6. Photoconduction spectra of vapor-treated MgPc (X-phase) at various temperatures.

In the temperature range between room temperature and 100°C, no change in dark conductivity as well as optical absorption and molecular arrangement are observed, although the water molecules are expected to move back and forth in the lattice at these temperatures. On the other hand, the photoconductivity is sensitively influenced by thermal motion of water molecules. Above 150°C, the first water-molecules are desorbed, resulting in the formation of vacancies. Then, a collapse of the vacancies (in other words, rearrangement of molecules) follows in the range between 150 and 200°C as shown by the appearance of a new diffraction peak around $2\theta = 6.5^\circ$ at 200°C (Fig. 4). We see clearly this transition from the X-phase to a new phase in the form of two diffraction peaks around $2\theta = 6.5$ and 7.5° . Finally, the molecules rearrange themselves completely around 300°C as characterized by one single diffraction peak around 6.5° . These vacancies as well as the

crystal defects due to collapsed vacancies work as scattering centers for charge carriers, *i.e.* both electrons and holes as revealed from our preliminary FET measurements. This is well reflected in the temperature dependence of dark conductivity (Fig. 5) in which the conductivity decreases abruptly above 100°C.

Like the dark conductivity, the photoconductivity of the X-phase is sensitive to the desorption of water molecules as shown in Fig. 5. Particularly, the photoconductivity is even decreased at 100°C to one-eighth of the value at room temperature and is then completely quenched above 200°C. The present photoconductivity-quenching is presumably caused mostly by scattering of the photocarriers, just as in the case of dark conductivity.

Near-IR Absorption

The near-IR absorption has already been clarified as arising from interactions between transition dipoles where the translational periodicity plays an important role for exciton migration (*i.e.* delocalization of the excited state).¹ In particular, the periodicity along the stacking axis is found to be determinant because the excitonic interaction along the molecular stack causes mainly the near-IR absorption to appear.¹ The spectral change of the X-phase due to heat treatment at 100°C is very little as shown in Fig. 3 since the water molecules are still present in evaporated films and coordinated to the Mg atom. Further heat treatment at 200 and 300°C brings about some reduction in the near-IR absorption, however no drastic change in the absorption spectrum is observed. This indicates that the molecular arrangement along the stacking axis is not greatly influenced by desorption of water molecules. Unfortunately, we cannot see the present short-periodicity around $2\theta = 26.5^\circ$ on the X-ray diffraction diagram shown in Fig. 4 because the evaporated film is highly oriented.

Conclusions

The conclusions from the present investigation can be summarized as follows:

1. The desorption of water molecules over 150°C causes the formation of vacancies of water molecules. These vacancies immediately collapse, leading to the rearrangement of MgPc molecules.
2. The collapsed vacancies are assumed to scatter charge carriers in dark as well as under illumination, resulting in the significant reduction of dark conductivity and photoconductivity. Especially, the photoconductivity is very sensitive to subtle structural changes due to thermal motion of water molecules.
3. It is crucial to keep the water molecule firmly coordinated to the central metal for the stable operation of MgPc-photoreceptors.

References

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Biography

Jin Mizuguchi obtained his B. Sc. in chemistry from Sophia University in 1970, Dr. of Sc. from the University of Tokyo in 1982 and Venia Docendi ("Habilitation") from the University of Bern in 1994. He worked at Sony Corporation Research Center from 1970 to 1985 and at Ciba-Geigy AG (Switzerland) from 1985 to 1995. During this time, he was mainly involved in research and development of photoconductors for laser printers as well as optical recording materials using organic pigments. He also gave a lecture on electronic devices and their materials at the University of Bern from 1994 to 1995. Since 1995, Prof. Mizuguchi has been at Yokohama National University as professor of materials science. His current interest is centered on the electronic characterization of organic pigments as viewed from exciton coupling effects as well as on the electronic applications of organic pigments.