Crystal Structure of Magnesiumphthalocyanine and its Polarized Spectra

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Abstract

The electronic structure of magnesiumphthalocyanine (MgPc) has been investigated on single crystals grown from the vapor phase. MgPc is found to crystallize in the space group of $P2_1/a$ (monoclinic): Z=2, a=18.971(2), b=4.916(2), c=14.401(2) Å, β=119.890(9). The MgPc molecule is not flat, but the Mg atom is projected out of the plane of the four central nitrogen atoms by about 0.45 Å, forming a pyramidal structure (C_1 symmetry). The present molecular deformation has, however, no significant influence on the optical absorption according to the MO spectroscopic calculations. On the other hand, the molecular distortion induces a drastic change in the direction of the transition dipoles, so that the interactions between transition dipoles in the solid state are strikingly different from those of ordinary phthalocyanines and the polarized reflection spectra look therefore quite unique.

Introduction

Magnesiumphthalocyanine (MgPc) is a blue pigment whose X-phase exhibits an intense near IR-absorption as shown in Fig.1. Because of this, MgPc has recently attracted attention as a material useful for laser printers[1,2] as well as for optical discs based on GaAsAl laser diodes.[3] We have so far investigated the mechanism of the near-IR absorption of the X-phase as well as solvated single crystals of MgPc.[4,5] The MgPc complex based on MgPc/$(H_2O)_2$(NMP)$_2$ is found to exhibit an intense near-IR absorption. In addition, TGA revealed that the X-phase also includes two water molecules in the form of MgPc/$(H_2O)_2$. On the basis of these observations, we have concluded that the near-IR absorption of the MgPc complexes arises from exciton coupling effects (i.e. interactions between transition dipoles) based on the molecular arrangement of MgPc/$(H_2O)_2$.[5]

In the present investigation, an attempt was made to grow single crystal of MgPc from the vapor phase in order to clarify its crystal and electronic structures.

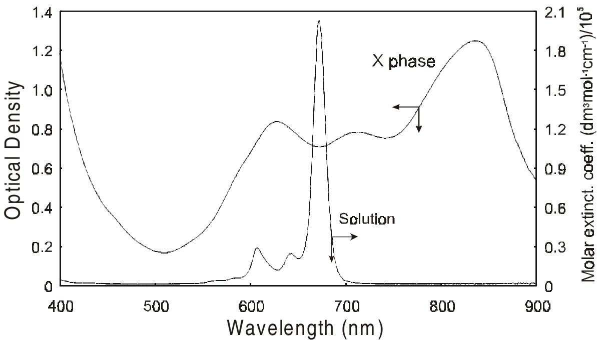


Figure 1 Solution spectrum MgPc and solid-state spectrum of evaporated MgPc of the X-phase.

Results and Discussion

1. Crystal Structure of MgPc

The single crystals of MgPc were grown from the vapor phase. During the data collection for the structure analysis, special care was taken to the atmosphere of the single crystal, because the single crystal is known to rapidly polycrystallize due to moisture in the air.[4] For this reason, the reflection data were collected under dry N_2 at 273 K.

Table 1 Crystallographic parameters

Formula	MgPc
Formula weight	536.84
Crystal system	monoclinic
Space group	$P2_1/a$
Z	2
a (A)	18.971(2)
b (A)	4.916(2)
c (A)	14.401(2)
β (°)	119.890(9)
V (A^3)	1164.3(6)
D_x	1.530
D_m	1.527

The crystallographic parameters are listed in Table 1. The structure of MgPc is found to be isomorphous with the β phase of various phthalocyanines.[6] The molecular conformation is shown in Fig. 2. To our surprise, the Mg atom is projected out of the plane of the four central nitrogen atoms by about 0.45 Å, forming a pyramidal structure. The molecular symmetry is C_1 in contrast to D_{4h} assumed usually for MgPc in the free space.

As shown in Fig. 3, the molecules are stacked in a herringbone fashion along the *b*-axis. The interplanar spacing along the *b*-axis is 3.19 Å and is considerably smaller as compared with that of the ordinary phthalocyanines.[6)] In addition, the distance between the Mg atom and the nitrogen atom in the upper layer (Fig.3) is quite small and amounts to 2.70 Å. This suggests that the Mg atom is in the position to accept an electron lone pair of the nitrogen atom in the solid state to form five-coordinate complex.

2. Molecular distortion and its influence on the direction of the transition dipole and the optical absorption

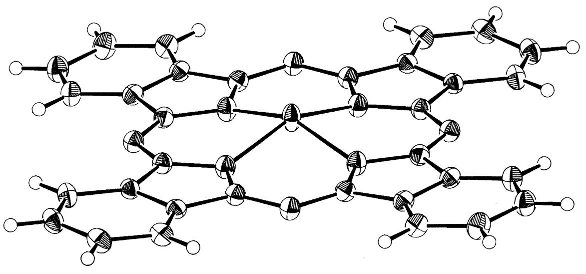


Figure 2 Molecular conformation of MgPc

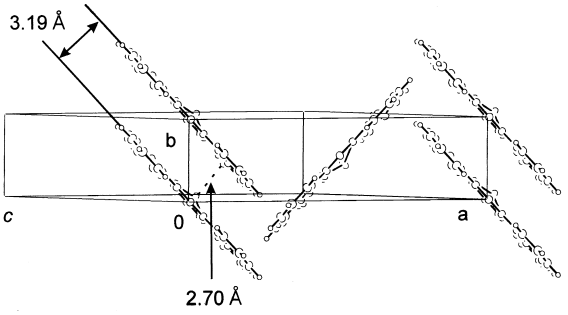


Figure 3 Molecular arrangement of MgPc

The extent of molecular distortion was evaluated by measuring the angles between the plane of the four central nitrogen atoms (plane 1) and the plane of each phenyl ring (plane 2). If these angles are equal, this is taken as C_4 symmetry. The angles are listed in Table 2 together with those of the optimized geometry which corresponds to the conformation in solution.

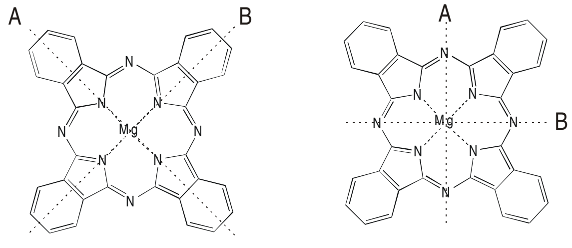
It is apparent that the molecule in the lattice is deformed (C_1) while the optimized geometry is characterized by D_{4h}.

Table 2 Molecular distortion of the MgPc skeleton

Plane 1	Plane 2	opt .geo (solution)	Crystal
N1,N2,N3,N4	phenyl C2…C7	0.0º	-3.50º
N1,N2,N3,N4	phenyl C10…C15	0.0º	-4.78º
N1,N2,N3,N4	phenyl C18…C23	0.0º	+3.50º
N1,N2,N3,N4	phenyl C26…C31	0.0º	+4.78º
Symmetry		D_{4h}	C_1

Table 3 Calculated absorption bands for MgPc

		Optimized geometry		Crystal	
		A	B	A	B
MgPc	λ_{max}(nm)	711.6	711.3	712.9	699.5
	f	0.9058	0.9068	0.9212	0.8676
		$\Delta\lambda$= 0.3	(7.0 cm^{-1})	$\Delta\lambda$= 13.4 (268.9 cm^{-1})	



(A) (B)

The influence of the molecular distortion on the optical absorption was evaluated by spectroscopic calculations using the X-ray x, y, z coordinate sets using the INDO/S Hamiltonian.[7)] The calculated bands and their oscillator strengths are shown in Table 3 together with the direction of transition dipoles A and B for the optimized geometry (conformation (A)) and for the deformed molecule in the crystal lattice (conformation (B)). It should be noted that the reduction of the molecular symmetry from D_{4h} to C_1 induces a drastic change in the direction of the transition dipoles as indicated by dotted lines in the inset of Table 3. The present change plays an important role in the assignment of the reflection bands of MgPc single crystals.

In the present calculation, no significant distortion effect on the optical absorption is noticed. The optimized geometry (D_{4h}) gives a single absorption band since the excited state of MgPc is doubly degenerate. This agrees with the experiment for the solution spectrum shown in Fig.1. On the other hand, the reduction in molecular symmetry on crystallization ($D_{4h} \rightarrow C_i$) lifts the degeneracy to give two absorption bands. However, the present band splitting is too small to observe two distinguishable absorption bands in experiments.

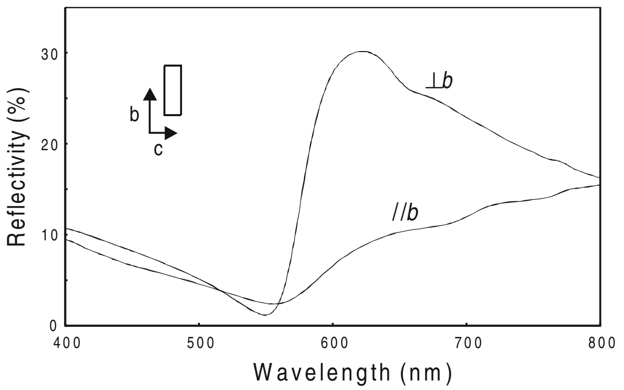


Figure 4 Polarized reflection spectra measured on the (100) plane.

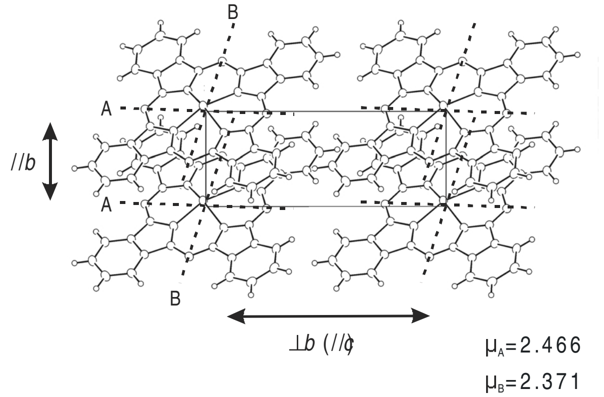


Figure 5 Projection of the crystal structure onto the (b,c) plane.

3. Polarized reflection spectra

Fig. 4 shows the polarized reflection spectra measured on the (100) plane of MgPc single crystals. An intense reflection band appears around 625 nm for polarization perpendicular to the *b*-axis. On the other hand, only a monotonous increase in reflectivity is observed for polarization parallel to the *b*-axis. In phthalocyanines, in general, the visible absorption band is composed of two absorption maxima. However, only a single reflection maximum is recognized around 625 nm and is positioned at shorter wavelengths than the band in solution (670 nm in Fig.1). In addition, no reflection maximum is present for polarization parallel to the *b*-axis; instead, a monotonous increase in reflection. The present spectroscopic behavior is quite unique and not explicable in terms of the direction of the transition dipoles shown in conformation (A) of Table 3.

Fig. 5 shows the projection of the crystal structure onto the (*b,c*) plane. Let us discuss the excitonic interaction on the basis of the direction of the transition dipoles shown in conformation (B) of Table 3. Polarization perpendicular to the *b*-axis induces interactions between transition dipole A of the uuper layer and transition dipole A of the lower layer in a fashion nearly “parallel”. This leads to the hypsochromic shift. Similarly, polarization parallel to the *b*-axis causes interactions between transition dipole B of the upper layer and transition dipole A of the lower in a fashion nearly “head-to-tail”. This induces a bathochromic displacement. In fact, the band around 625 nm corresponds to the hypsochromically-displaced band, since the present band is located at shorter wavelengths by about 45 nm (1074 cm^{-1}) as compared with the one in solution (670 nm). On the other hand, no bathochromically-shifted band is observed for polarization parallel to the *b*-axis, although there is a tendency for the reflection maximum to appear above 800 nm.

As stated above, the reflection spectra can mostly be interpreted on the basis of the interactions between transition dipoles ("exciton coupling effects"). To confirm this, the spectral displacement energies are calculated as shown below.

4. Spectral displacement due to exciton coupling effects

The spectral shifts are calculated by the following dipole-dipole equation[8)]: $\Delta E_{exciton} = |\mu|^2 (1-3\cos^2\theta) / r^3$, where μ denotes the transition dipole, r and θ the distance and angle between two transition dipoles.

The exciton displacement energies are computed for the six nearest-neighbor molecules in the lattice on the basis of the crystal structure. The results are shown in Table 4. The AA or BB denotes the coupling of transition dipole A (or B) of one MgPc molecule with that (or B) of the neighboring one. The molecular sites are designated in fractional coordinates. The minus or plus sign of ΔE denotes the bathochromic or hypsochromic displacement, respectively.

Table 4 Six neighboring molecules around the molecule at (000) and their displacement energies

Transition dipoles	Site	No.of eq. molecules	r (A)	θ (°)	ΔE (cm^{-1})
AA	(010)	2	4.916	88.07	5912
(per. *b*)	(001)	2	14.401	51.64	-37
	(011)	2	17.175	21.76	-221
BB	(010)	2	4.916	39.37	-4326
(para. *b*)	(001)	2	14.401	59.19	46
	(011)	2	17.175	77.83	111

Among three pairs in AA interactions, the stack pair makes the largest contribution (due to the *quasi* “parallel” arrangement) to the hypsochromic displacement energy: about 5912 cm^{-1}. Similarly, the BB interaction gives the largest bathochromic shift of about -4326 cm^{-1} because of the *quasi* “head-to-tail” arrangement. The total energies for the hypsochromic and bathochromic shifts which includes the energy contribution from the translationally-inequivalent molecules amount to about 7933 and –9627 cm^{-1}, respectively. This means that one band is displaced towards shorter wavelengths while the other leads to the bathochromic shift. The hypsochromically-displaced band corresponds to the band around 625 nm in Fig.4 while the bathochromically-shifted band is expected to appear around 829 nm according to the present calculations.

Conclusions

The electronic structure of MgPc has been investigated from the standpoint of molecular distortion and exciton coupling effects. The conclusions drawn from the present investigation can be summarized as follows:

1. The MgPc molecule in the solid state is not flat, but the Mg atom is projected out of the plane by about 0.45 Å, thus forming a pyramidal structure (C_1 symmetry).
2. The molecular deformation upon crystallization lifts the degeneracy of the excited state to induce a band splitting. However, the band splitting is too small to observe an appreciable optical effect.
3. The molecular distortion induces a drastic charge in the direction of the transition dipoles. Thus, the excitonic interactions in the solid state are strikingly different from those of ordinary phthalocyanines.

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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 from the University of Bern in 1994. He worked in the field of organic semiconductors at Sony Corporation Research Center from 1970 to 1985 and at Ciba-Geigy AG (Switzerland) from 1985 to 1995. Since 1995, Prof. Mizuguchi has been at Yokohama National University as professor of materials science.