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Crystal Structure of Magnesiumphthalocyanine and Its Polarized Reflection Spectra

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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, $\beta = 119.890(9)$. The MgPc molecule is not flat, but the Mg atom is projected upward, 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 resulting polarized reflection spectra look quite unique.

1. Introduction

Magnesiumphthalocyanine (MgPc) is a blue pigment whose X-phase exhibits an intense near-IR absorption as shown in Figure 1. Because of this, MgPc has recently attracted attention as a material useful for laser printers[1,2] as well as for optical disks[3] based on GaAsAl laser diodes. 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)$_2$ (NMP: *N*-methyl pyrrolidone) is found to exhibit an intense near-IR absorption. In addition, thermogravimetric analysis (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 crystals of MgPc from the vapor phase in order to clarify its crystal and electronic structures.

2. Results and Discussion

2-1. Crystal Structure of MgPc. The single crystals of MgPc were grown from the vapor phase, using a two-zone furnace.[6] During the data collection for the structure analysis, special care was taken to the atmosphere of the single crystal, because the single crystal of MgPc is known to rapidly polycrystallize due to moisture in the air.[4,5] For this reason, the reflection data were collected under dry N_2 at 273 K.

The crystallographic parameters are listed in Table 1. The structure of MgPc is found to be isomorphous with the β phase of various phthalocyanines.[7] The molecular conformation is shown in Figure 2. To our surprise, the Mg atom is projected upward, 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.

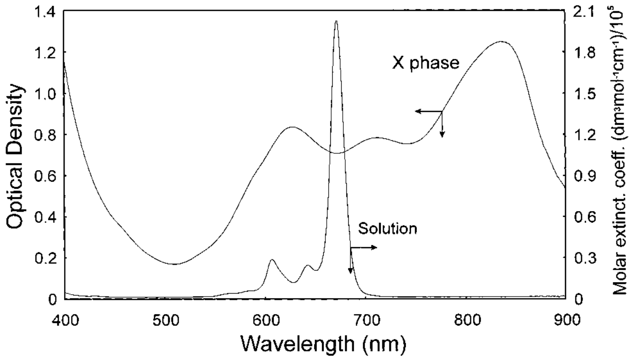

Figure 1. Solution spectrum MgPc and solid-state spectrum of evaporated MgPc of the X-phase.

TABLE 1: Crystallographic Parameters of MgPc

formula	$C_{32}H_{16}N_8Mg$
formula weight	536.84
crystal system	monoclinic
space group	$P2_1/a$
Z	2
a (Å)	18.971(2)
b (Å)	4.916(2)
c (Å)	14.401(2)
β (°)	119.890(9)
V (Å^3)	1164.3(6)
D_x	1.530
D_m	1.527

As shown in Figure 3, the molecules are stacked in a herringbone fashion along the *b*-axis where two kinds of columns are formed: one is with the Mg atom facing upward and the other is facing down. The interplanar spacing along the *b*-axis is 3.19 Å and is considerably smaller as compared with that of the ordinary phthalocyanines.[7] In addition, the distance between the Mg atom and the nitrogen atom in the upper layer (Figure 3) is quite small and amounts to 2.70 Å. This suggests that the Mg atom is in a position to accept an electron lone pair of the nitrogen atom to form a five-coordinate complex in the solid state.

2-2. Molecular Distortion and Its Influence on the Direction of the Transition Dipole and the Optical Absorption. As is well-known, the excited state of the metal phthalocyanines

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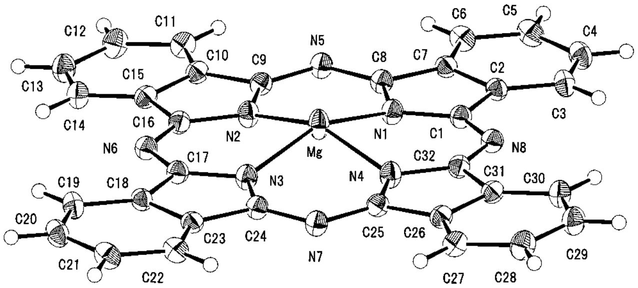


Figure 2. Molecular conformation of MgPc.

TABLE 2: Molecular Distortion of the MgPc Skeleton

plane 1	plane 2	opt. geo. (solution)	crystal
N1, N2, N3, N4	phenyl C2···C7	0.0°	−3.50°
N1, N2, N3, N4	phenyl C10···C15	0.0°	−4.78°
N1, N2, N3, N4	phenyl C18···C23	0.0°	+3.50°
N1, N2, N3, N4	phenyl C26···C31	0.0°	+4.78°
symmetry		D_{4h}	C_1

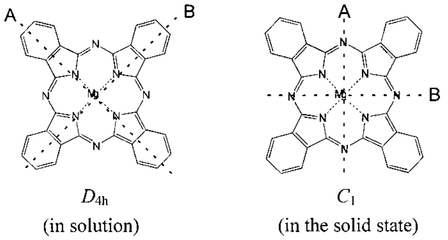
is doubly degenerate. so the molecular distortion upon crystallization (lowering of the molecular symmetry, for example, from D_{4h} to C_1) can remove the degeneracy to cause the band splitting to occur as observed in titanylphthalocyanines[8] (TiOPc). For this reason, the extent of molecular deformation was evaluated by measuring the angles between the plane of the four central nitrogen atoms (plane 1: N1, N2, N3, and N4 in Figure 2) 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 as characterized by C_1 while the optimized geometry is completely planar and has a molecular symmetry of D_{4h}.

The influence of the molecular distortion on the optical absorption was evaluated by spectroscopic calculations on one single molecule using the X-ray *x*, *y*, *z* coordinate sets using the INDO/S Hamiltonian.[9] 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 in solution (D_{4h}) and for the deformed molecule in the crystal lattice (C_1). 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 experiment for the solution spectrum shown in Figure 1. On the other hand, the reduction in molecular symmetry on crystallization ($D_{4h} \rightharpoonup C_i$) lifts the degeneracy to give two absorption bands. However, the present band splitting is too small to observe two distinguishable absorption bands in experiments.

TABLE 3: Calculated Absorption Bands for MgPc and Their Direction of the Transition Dipoles

	optimized geometry		crystal	
abs. bands	A	B	A	B
$\lambda_{\max}$ (nm)	711.6	711.3	712.9	699.5
f^a	0.906	0.907	0.921	0.868
	$\lambda = 0.3$ (7 cm^{-1})		$\Delta\lambda = 13.4$ (269 cm^{-1})	

[a] Oscillator strength.



In contrast to the optical effect described above, the reduction of the molecular symmetry from D_{4h} to C_1 brings about a drastic change in the direction of the transition dipoles as designated by dotted lines in the inset of Table 3. This is quite unusual, because the direction of the transition dipoles remains usually unchanged upon crystallization in ordinary phthalocyanine compounds, although the molecule is sometimes deformed: MgPc/(2-methoyethanol)$_2$[5] and MgPc/(H$_2$O)$_2$(NMP)$_2$,[5] TiOPc,[7] and metal-free phthalocyanine[10] (MfPc). Therefore, the present change can exert a significant influence on the optical absorption in the solid state as described below, because the excitonic interactions greatly depend on the geometrical arrangement of the transition dipoles.

2-3. Polarized Reflection Spectra. Figure 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

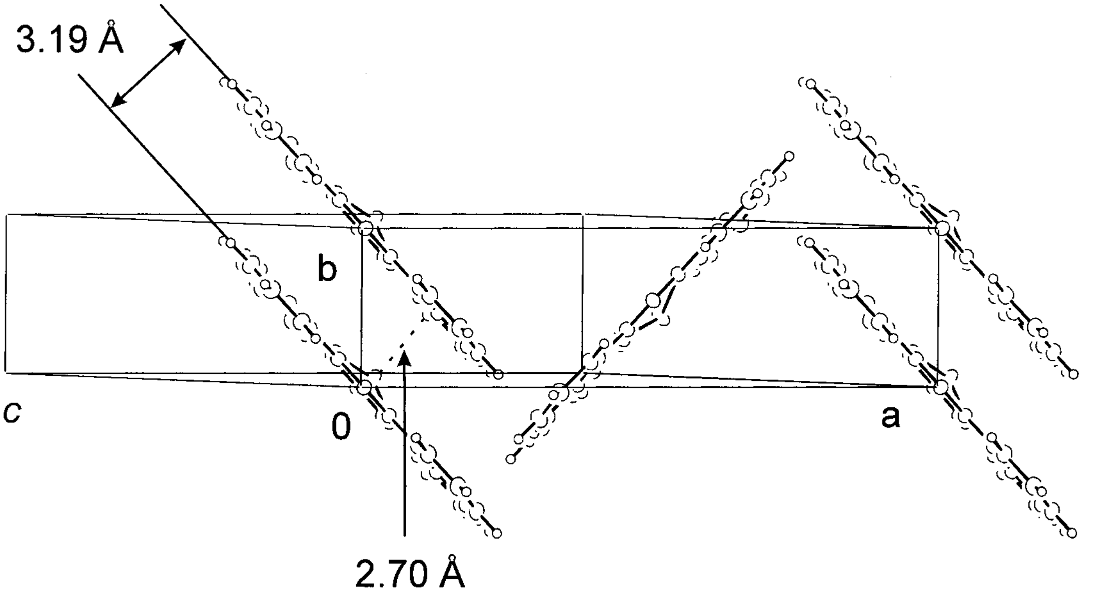


Figure 3. Molecular arrangement of MgPc.

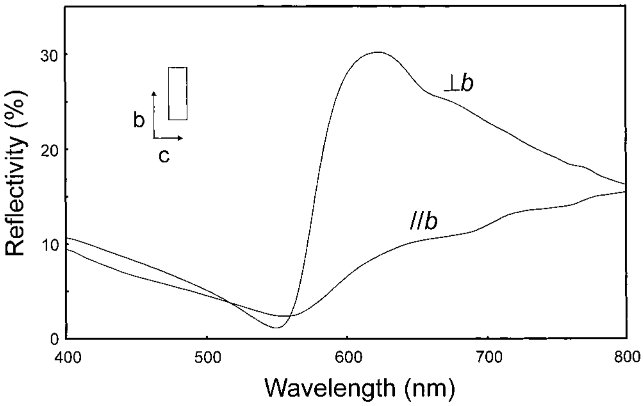


Figure 4. Polarized reflection spectra measured on the (100) plane.

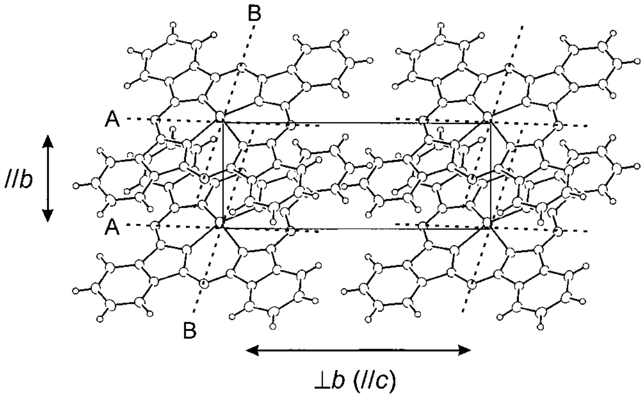


Figure 5. Projection of the crystal structure onto the (*b*,*c*) plane.

hand, only a monotonic increase in reflectivity is observed here for polarization parallel to the *b*-axis. In phthalocyanines, the visible absorption spectrum is usually composed of two absorption bands. However, there observed only one single reflection maximum around 625 nm and the present band is located at shorter wavelengths than that in solution (670 nm in Figure 1). Furthermore, no reflection maximum is present in the spectral region from 400 nm to the measurable limit of 800 nm for polarization parallel to the *b*-axis. The present spectroscopic behavior is quite unique and not explicable in terms of the ordinary direction of the transition dipoles shown in Table 3 (D_{4h} in solution).

Let us discuss the excitonic interaction on the basis of the direction of the transition dipoles shown in Table 3 (C_1 in the solid state) as well as of the molecular arrangement on the (*b*,*c*) plane as shown in Figure 5. Polarization perpendicular to the *b*-axis induces interactions between transition dipole A of the upper 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 causes a bathochromic displacement to occur. In fact, the band around 625 nm can be interpreted to correspond to the hypsochromically displaced band, since the present band is located at shorter wavelengths by about 45 nm (ca. 1074 cm^{-1}) as compared with that in solution (670 nm). On the other hand, no bathochromically shifted band maximum is observed for polarization parallel to the *b*-axis, although there is a marked tendency for the reflection maximum to appear above 800 nm. To estimate the probable reflection maximum, the spectral displacement energies have been calculated on the basis of the exciton coupling effects as presented below.

TABLE 4: Six Neighboring Molecules around the Molecule at (000) and Their Displacement Energies

transition dipoles	molecular site	no. of eq. molecules	*r* (Å)	θ (°)	ΔE
AA	(010)	2	4.9	88.1	5912
(⊥*b*)	(001)	2	14.4	51.6	−37
	(011)	2	17.2	21.7	−221
	(010)	2	4.9	39.4	−4326
(//*b*)	(001)	2	14.4	59.2	46
	(011)	2	17.2	77.8	111

2-4. Spectral Displacement Due to Exciton Coupling Effects. The spectral shifts have been calculated by the dipole−dipole equation:[11] $\Delta E_{\mathrm{exciton}} = |\mu|^2 (1 - 3\cos^2\theta)/r^3$, where μ denotes the transition dipole, and *r* and θ the distance and angle, rspectively, between two transition dipoles.

The exciton displacement energies are computed for the six translationally equivalent, 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.

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 also include the energy contribution from the translationally inequivalent molecules, amount to about 7933 and −9627 cm^{-1}, respectively. This means that one band is displaced toward shorter wavelengths while the other leads to the bathochromic shift. If we assume that the hypsochromically displaced band corresponds to the band around 625 nm in Figure 4, the bathochromically shifted band is supposed to appear around 829 nm according to the present calculations.

3. 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:

i. The MgPc molecule in the solid state is not flat, but the Mg atom is projected upward, out of the plane by about 0.45 Å, thus forming a pyramidal structure (C_1 symmetry).

ii. 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.

iii. The molecular distortion brings about 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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