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X-Ray Crystal Structure Analysis of Silicon Phthalocyanines: Study of the Relationship between Intermolecular Interaction and Photochemical Sensitivity

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This paper reports on the crystal structures of the three silicon phthalocyanines: dichlorosilicon phthalocyanine [$\mathrm{SiCl_2Pc}$], dimethoxysilicon phthalocyanine [$\mathrm{Si(OMe)_2Pc}$] and bis(tetrahydrofurfuryloxy)silicon phthalocyanine [$\mathrm{Si(thff)_2Pc}$]. We found that although $\mathrm{Si(OMe)_2Pc}$ and $\mathrm{Si(thff)_2Pc}$ show sensitivity for an electrophotographic photoreceptor, $\mathrm{SiCl_2Pc}$ doesn't have photosensitivity. It is known that the difference in the photochemical property of phthalocyanines is related to the crystal structures. Although it is difficult for these materials to obtain single crystals with sufficient size for single crystal X-ray analysis, it is very important to determine the crystal structures in order to understand the mechanism concerning the performance of the electrophotographic photoreceptor. In this work we determined the crystal structures from very small (micrometer-sized) single crystals. The compounds crystallized in space group $P2_1/n$ for $\mathrm{SiCl_2Pc}$, $Z = 2$ with unit-cell parameters $a = 10.261(1)$ Å, $b = 14.618(2)$ Å, $c = 9.072(1)$ Å, $\beta = 98.51(1)°$; in space group $P\bar{1}$ for $\mathrm{Si(OMe)_2Pc}$, $Z = 1$ with unit-cell parameters $a = 11.606(4)$ Å, $b = 7.583(3)$ Å, $c = 8.304(3)$ Å, $\alpha = 96.46(3)°$, $\beta = 105.23(3)°$, $\gamma = 74.87(3)°$; and in space group $P\bar{1}$ for $\mathrm{Si(thff)_2Pc}$, $Z = 1$ with unit-cell parameters $a = 10.234(6)$ Å, $b = 10.266(7)$ Å, $c = 9.761(6)$ Å, $\alpha = 98.93(2)°$, $\beta = 117.94(2)°$, $\gamma = 68.83(2)°$. All molecules in the three crystals have a symmetry center on Si atom. In the crystal structure, although $\mathrm{SiCl_2Pc}$ has π-π stacking extended in only one direction (along c-axis), $\mathrm{Si(OMe)_2Pc}$ and $\mathrm{Si(thff)_2Pc}$ have intermolecular interactions extended in all directions in the crystals. $\mathrm{Si(OMe)_2Pc}$ includes water molecules in the crystal, which form hydrogen bonds. We discuss the relationship between the intermolecular interactions and the photochemical property of silicon phthalocyanines.

Phthalocyanines have been studied for electrophotographic photoreceptors of long-wavelength sensitivity. They are extremely stable pigments and exhibit many photochemical properties. In addition to a wide variety of central metals, there are also many polymorphs.[1] It is known that some of the polymorphs of oxotitanium phthalocyanine and a polymorph of hydroxogallium phthalocyanine exhibit high sensitivity for photocarrier generation.[2—5]

We previously found that dihydoxysilicon phthalocyanine [$\mathrm{Si(OH)_2Pc}$][6] has two polymorphs, and that one of them shows high photochemical activities. We believe that the photochemical properties depend on the crystal structures, and determined the crystal structure from powder X-ray diffraction data, since the two polymorphs of $\mathrm{Si(OH)_2Pc}$ have never grown in sufficiently large crystals for single crystal analysis, just like many other phthalocyanines polymorphs.[7] The structural results suggest that when intermolecular interactions extend in all directions in the crystals photochemical activity appears.

In a previous study we could luckily determine the crystal structures of the phthalocyanine compound from only powder X-ray diffraction data. However, powder structure analysis is still far from routine, like the single crystal structure determination.[8,9] There are only a few known crystal structures of phthalocyanines to discuss the mechanism of the performance as a photoreceptor. In order to clarify the relationship between intermolecular interactions and the photochemical property, it is very important to obtain many crystal structures of phthalocyanines. Recently, we also found away to measure the intensity of a small single crystal (10—100 μm) by high sensitive area detector, synchrotron radiation and their combination, and determined the crystal structures.[10] It is possible to select the best analytical method to obtain the crystal structures quickly. Powder structure analysis should be applied to the crystalline powder of which a grain has never grown to even a micrometer-sized single crystal, just like the two polymorphs of $\mathrm{Si(OH)_2Pc}$.

In this work we report on micrometer-sized single crystal analyses of three silicon phthalocyanine compounds. The results show the relationship between the intermolecular interactions and the photochemical activity in the silicon phthalocyanines series.

Experimental

Synthesis. Details of the synthetic procedures of the $\mathrm{SiCl_2Pc}$ and $\mathrm{Si(OMe)_2Pc}$ have been reported elsewhere.[7]

$\mathrm{Si(thff)_2Pc}$. After 10 g of dimethoxysilicon phthalocyanine was added to 150 ml of tetrahydrofurfurylalcohol and reacted under reflux for 2 h, the reaction product was thermally filtrated and washed with N-methyl-2-pyrrolidone and methanol in that order. The crystalline powder was separated by filtration and dried to obtain 8.1 g of bis(tetrahydrofurfuryloxy)silicon phthalocyanine.

The color of the crystalline powder was dark purple and the size of a grain was 0.05×0.03×0.005 mm.

Measurement of Electric Properties. The photochemical sensitivity of the obtained photoreceptor ($SiCl_2Pc$, $Si(OMe)_2Pc$, and $Si(thff)_2Pc$) was evaluated using an electrostatic copy paper testing machine (Model EPA-8100 of Kawaguchi Denki Seisakusho Co.). The photoreceptor was negatively charged by corona discharge for 2.4 s at an application voltage which was set to ensure that the corona current would be 22 μA in the dark (the surface potential at this point was taken as charge potential). The negatively charged photoreceptor was then exposed to 1.0 $\mu W/cm^2$ monochromatic light having a wavelength of 780 nm for 10 s continuously to measure the attenuation of the surface potential (the surface potential after 10 s of exposure was taken as residual potential). The reducing potential one second after charging was taken as dark decay, and the amount of exposure ($E1/2$) required to reduce the surface potential from −450 V to −225 V was taken as half-decay exposure sensitivity (= sensitivity). The results are given in Table 1.

Crystal Structure Analysis. Dark purple crystals of $SiCl_2Pc$ and $Si(OMe)_2Pc$ were grown by slow evaporation from chloroform solution at room temperature. The sizes of the crystals were 0.1×0.08×0.03 mm for $SiCl_2Pc$ and 0.1×0.05×0.02 mm for $Si(OMe)_2Pc$. A grain of the synthesized $Si(OMe)_2Pc$ powder was also used for the X-ray diffraction measurement using synchrotron radiation. The size of a grain was 0.05×0.01×0.003 mm. Because $Si(thff)_2Pc$ crystals from recrystallization have never grown larger than a grain of the crystalline powder from the synthesis, the grain was used.

The X-ray diffraction data of recrystallized $SiCl_2Pc$ and $Si(OMe)_2Pc$ were collected at room temperature using ENRAF-Nonius CAD4 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation (λ = 1.5418 Å) by ω scan in the range $1° < 2\theta < 141°$. The intensity of the standard reflections continuously decayed to about 85% for $Si(OMe)_2Pc$. The intensities were corrected based on the standard reflections. The X-ray diffraction data of a grain of the synthesized $Si(OMe)_2Pc$ powder were also collected using synchrotron radiation, because the single crystal analysis for the recrystallized $Si(OMe)_2Pc$ showed that water molecules were included in the single crystal. The measurement was carried out at room temperature at 6A beam line (λ = 1.0 Å) of synchrotron light source, KEK, with an imaging plate detector. The data collection was taken 30 s per frame, and 20 frames of 10° φ-oscillation range were used. Figure 1 shows an example of diffraction spots on the imaging plate. The data were processed and scaled with DENZO and SCALEPACK from the HKL suite of programs.[11] The X-ray data of $Si(thff)_2Pc$ were measured at room temperature using Bruker SMART 3-circle diffractometer equipped with a 1 K CCD area detector with graphite-monochromatized Mo $K\alpha$ radiation (λ = 0.71073 Å) by ω scan (in steps of 0.3° ω each), nominally covering over a hemisphere of reciprocal space, and integrated using SAINT software.[12] For $Si(thff)_2Pc$, a semi-empirical absorption correction (using SADABS program[13]) was applied.

The structures were solved by direct method with SHELXS-86[14] and refined by full-matrix least squares against F^2 of the observed reflections with SHELXL-93.[15] For $Si(OMe)_2Pc$, the structures of the recrystallized crystal and a grain of the synthesized powder were determined respectively; the results showed that the two crystal structures were the same. Because the number of the observed reflections for the recrystallized crystal (1215 reflections) was larger than that of the grain (786 reflections), the refinement was carried out using the reflection data for the recrystallized crystal. All non-hydrogen atoms were refined anisotropically, except for the disordered C atom of the methoxy group and O atom of the water molecule in $Si(OMe)_2Pc$. Hydrogen atoms were located at ideal positions and refined in isotropic approximation. Crystal data and the X-ray experimental details are given in Table 2. The complete data for the three crystals are deposited as Document No. 73061 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free charge, by quoting the publication citation and the deposition numbers CCDC 148330—148332.

Table 1. The Results of the Initial Electric Properties for $SiCl_2Pc$, $Si(OMe)_2Pc$ and $Si(thff)_2Pc$

	Charge potential /−V	Dark decay /−V	Sensitivity /$\mu J\,cm^{-2}$	Residual potential /−V
$SiCl_2Pc$	135	—	—	—
$Si(OMe)_2Pc$	724	14	0.56	15
$Si(thff)_2Pc$	729	10	0.31	15

Fig. 1. X-ray diffraction spots of a grain of $Si(OMe)_2Pc$ on imaging plate using synchrotron radiation.

Table 2. Crystal Data and the X-ray Experimental Details

Formula	$SiCl_2Pc$ $C_{32}H_{16}N_8Cl_2Si$	$Si(OMe)_2Pc$ $C_{34}H_{22}N_8O_2Si$ $\cdot 0.48H_2O$	$Si(thff)_2Pc$ $C_{42}H_{34}N_8O_4Si$
M.W.	611.52	611.31	742.91
a/Å	10.261(1)	11.606(4)	10.234(6)
b/Å	14.618(2)	7.583(3)	10.266(7)
c/Å	9.072(1)	8.304(3)	9.761(6)
α/°	90.0	96.46(3)	98.93(2)
β/°	98.51(1)	105.23(3)	117.94(2)
γ/°	90.0°	74.87(3)	68.83(2)
V/Å^3	1345.8(3)	680.0(4)	845(2)
Z	2	1	1
D_x/g cm^{-3}	1.509	1.493	1.460
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
R	0.0697	0.0902	0.0846
R_{wp}	0.1094	0.1260	0.1215
Crystal size/mm	0.1 × 0.08 × 0.03	0.1 × 0.05 × 0.02	0.05 × 0.03 × 0.005
No. of measured reflections	2017	2173	5334
No. of independent reflections	1864	2073	2348
No. of observed reflections [$I > 2\sigma(I)$]	954	1215	1158
S	0.866	1.056	0.958
No. of parameter	204	226	258

X-Ray Powder Diffraction. The X-ray diffraction analysis was conducted on a Philips PW1700 X-ray diffractometer with monochromatic Cu $K\alpha$ radiation (λ = 1.5418 Å).

Thermal Analysis. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of $Si(OMe)_2Pc$ powder were carried out using a RIGAKU TAS-300 at a heating rate of 10 °C min^{-1} from r.t. up to 550 °C under a helium atmosphere.

Results and Discussion

The results concerning the photochemical sensitivity of the three silicon phthalocyanines are given in Table 1. Although $Si(OMe)_2Pc$ and $Si(thff)_2Pc$ have photosensitivity, $SiCl_2Pc$ is almost inferior in charge acceptance, and cannot actually be used.

For the three crystals, the observed reflections were not collected sufficiently, since the crystal size was very small (Table 2). Especially, $Si(thff)_2Pc$ was used as a grain of synthesized powder for single crystal X-ray analysis; the crystal size [50×30×5μm] was too small compared with an ideal 0.3 mm spherical crystal. Figure 2 shows the crystal structures of the three silicon phthalocyanines. All of compounds take a tetragonal structure, and the symmetry center is on Si atom, just like in dihydroxysilicon phthalocyanine.[7] The bond lengths and angles of the phthalocyanine planes in the three crystals are similar.

Although we never used water for recrystallization as a solvent, $Si(OMe)_2Pc$ included water molecules in the crystal. TG-MAS results of the synthesized $Si(OMe)_2Pc$ powder are given in Table 3. H_2O gas at 89.0 °C resulted from a water solvent in the crystalline powder. MeOH gas at 347.4 °C resulted from decomposition of the methoxy ligands, and benzenedicarbonitrile ($C_8H_4N_2$) gas at 473.7 °C resulted from the decomposition of the phthalocyanine fragments. It could be estimated from the results of TG-MAS that the water molecules and $Si(OMe)_2Pc$ molecules in the powder existed in a mole ratio of about 1 to 3. TG-MAS results showed the crystalline powder that before recrystallization included water molecules.

Table 3. The Results of TG-MAS Measurement

Temperature/°C	Amount of Loss/%	Gas	Mass Number
89.0	0.94	H_2O	18, 17
347.4	8.70	CH_3OH	31, 29
473.7	—*	$C_8H_4N_2$	128

*The reaction was continued at 550 °C.

Before considering the relation between the crystal structures and the electric property, we confirmed that the crystal structures determined by the single crystal analysis were identical to the crystal structures of the synthesized powder that was used to measure the photochemical sensitivity. This is because it is known that some phthalocyanines have many polymorphs and that the photochemical properties depend on the crystal structures.[2] A grain of the synthesized powder of $Si(thff)_2Pc$ was used for the single crystal analysis. It is thus expected for $Si(thff)_2Pc$ that the crystal structures of the grain and the powder are the same. The single crystal analyses for $Si(OMe)_2Pc$ show that the crystal structure of the recrystallized single crystal obtained from a chloroform solution was identical with that of a grain of the synthesized powder. It is thus expected for $Si(OMe)_2Pc$ that the crystal structures of the recrystallized single crystal and the synthesized powder

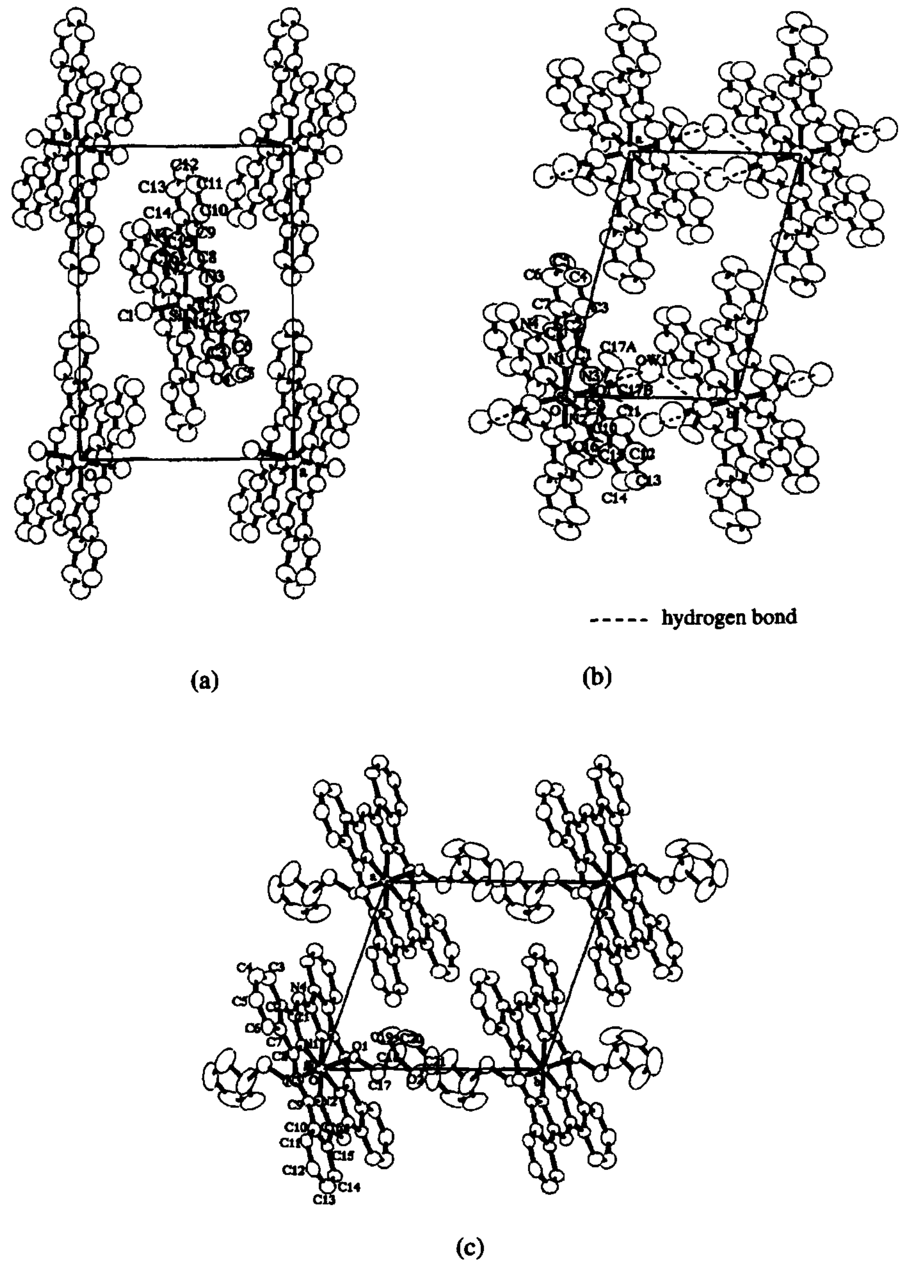
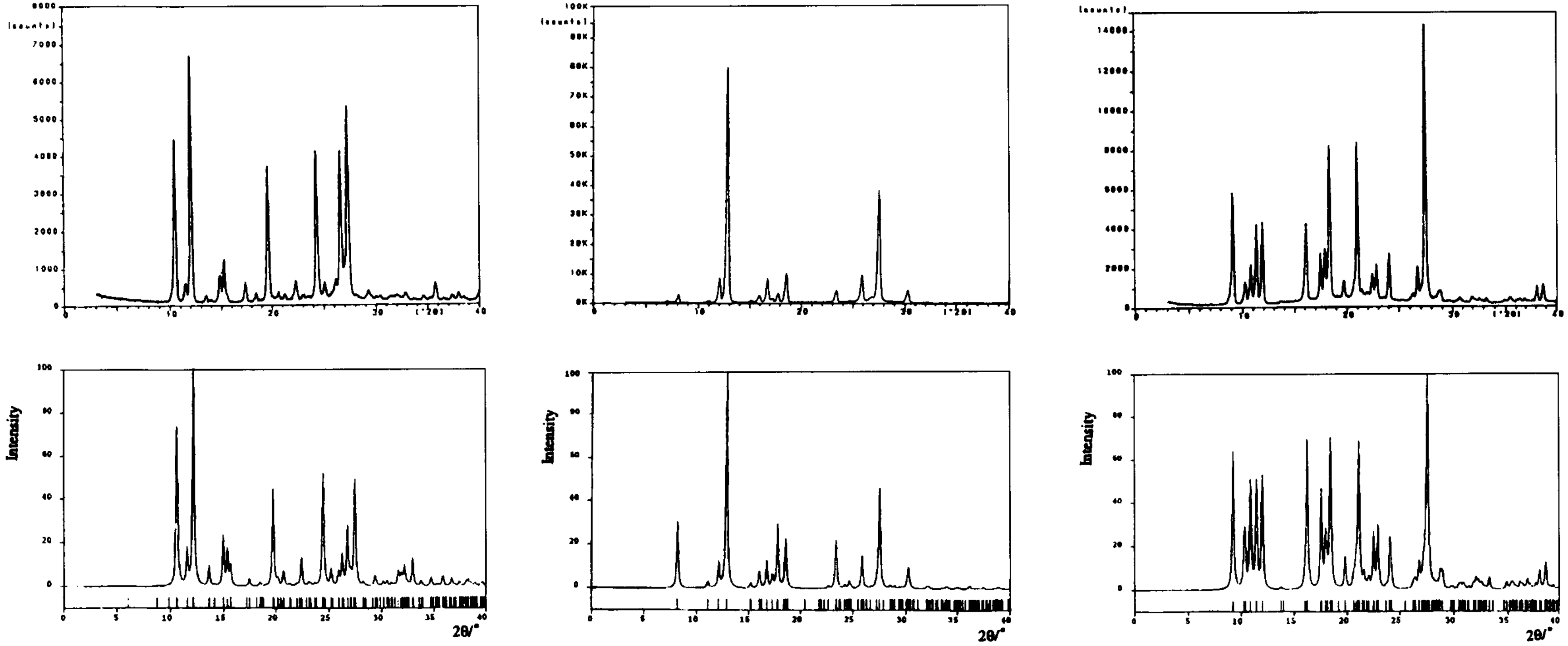


Fig. 2. ORTEP drawing of crystal structures of $SiCl_2Pc$ (a), $Si(OMe)_2Pc$ (b), and $Si(thff)_2Pc$ (c) showing 50% thermal ellipsoids and the numbering of atoms.

are also the same. However, the single crystal analysis for $SiCl_2Pc$ was carried out using only a recrystallized crystal obtained from a chloroform solution; thus a confirmation of the crystal forms of the recrystallized single crystal and the synthesized powder is essential for this study. The raw XRD data of the synthesized powder [$SiCl_2Pc$, $Si(OMe)_2Pc$, $Si(thff)_2Pc$] and the simulated powder diffraction pattern from the single crystal structures are shown in Fig. 3. For the three phthalocyanines, the peak positions of XRD data were equal to those of the simulated data, but the peak intensity was slightly different, because of the preferred orientation of XRD data of powder samples. The results show for the three compounds that the crystal forms of which the structures were determined by the single crystal analysis are identical to the crystal forms of the synthesized powder that was used to measure the photochemical sensitivity, respectively.

$SiCl_2Pc$ crystal has π-π stacking interaction along *c*-axis (Fig. 4). The distance between the phthalocyanine planes is 3.48(4) Å. Along *a*-, and *b*-axis in the $SiCl_2Pc$ crystal there is no particular intermolecular interaction. It is known that the crystal structures of dichlorochromium phthalocyanine [$CrCl_2Pc$], dichloroiron phthalocyanine [$FeCl_2Pc$] and dichlorocobalt phthalocyanine [$CoCl_2Pc$] are isostructural.[16] In this analysis we found that $SiCl_2Pc$ crystal was also isomorph with $CrCl_2Pc$, $FeCl_2Pc$ and $CoCl_2Pc$.

In the $Si(OMe)_2Pc$ crystal, O atom of the water molrcules forms O···H–O hydrogen bonds (O1···OW1: 2.87(2) Å and OW1···O1$^{\#}$1: 2.85(2) Å, symmetry operation for $^{\#}$1:



(a)

(b)

(c)

Fig. 3. Raw XRD data of the synthesized powder (upper) and the simulated powder diffraction pattern from the single crystal structures with peak markers (lower) for $SiCl_2Pc$ (a), $Si(OMe)_2Pc$ (b), and $Si(thff)_2Pc$ (c), (λ = 1.5418 Å).

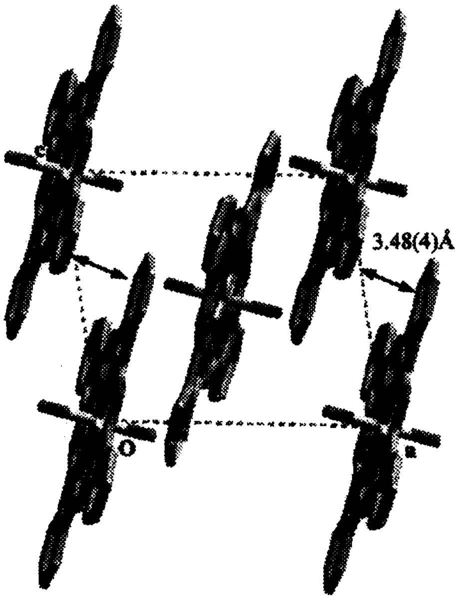


Fig. 4. Crystal structure of $SiCl_2Pc$ (Projection of (010) face) shows π-π stacking of the phthalocyanine planes along *c*-axis.

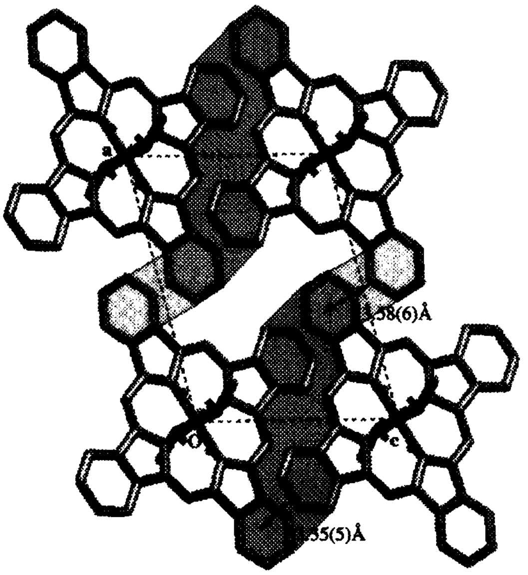


Fig. 5. Crystal structure of $Si(OMe)_2Pc$ (Projection of (010) face) shows π-π stacking of the phthalocyanine planes extends in *ac* plane. The stacking areas are drawn by shadow.

−x, −y + 1.0, −z) along *b*-axis. (Fig. 2) The occupancy factor of O atom of the water molecule was 0.24(4). This result showed that the water molecule and $Si(OMe)_2Pc$ in the single crystal existed in a mole ratio of about 1 to 2. The proportion of water molecules in the single crystal was larger than that of the powder shown by TG-MAS. It is expected that $Si(OMe)_2Pc$ crystal is stabilized by forming hydrogen bonds with water molecules. The crystal structure maintains a cavity of suitable size for water molecules; also, the water molecules dissolved in the solvent are taken into the crystal during synthesis and recrystallization. The methyl groups that exist near to the water molecules in the crystal are disordered. The occupancy factors were 0.71(4) for C17A and 0.29(4) for C17B; the minor part of the methyl group and the water molecule were too close (C17B···OW1: 1.57(3) Å). The results show that there is large space around the methyl group, because the occupancy factor of the water is small (0.24(4)) and the methyl group is disordered.

Along *a*-, and *c*-axes in the $Si(OMe)_2Pc$ crystal there is π-π stacking interaction between the phthalocyanine planes. The distances between the phthalocyanine planes are 3.58(6) Å for the direction of *a*-axis and 3.35(5) Å for the direction of *c*-axis. Figure 5 shows that the intermolecular interactions extend in *ac* plane by π-π stacking of the phthalocyanine planes. In the $Si(OMe)_2Pc$ crystal, intermolecular interactions consisting of hydrogen bonds along *b*-axis and π-π stacking interactions along *a*- and *c*-axes extend in all directions.

$Si(thff)_2Pc$ crystal has π-π stacking interactions along *a*-, *b*-, and *c*-axes. The distances between the phthalocyanine planes are 3.40(5) Å for the direction of *a*-axis, 2.90(5) Å for the direction of *b*-axis and 3.45(3) Å for the direction of *c*-axis. Although the distance between the phthalocyanine planes along *b*-axis is very short (2.90(5) Å), the strength of the π-π stacking interaction would not be large, because the size of the stacking of the phthalocyanine planes along *b*-axis is very small (0.3 when the size of a benzene ring = 1). Figure 6 shows that π-π stacking of the phthalocyanine planes extends in all directions in $Si(thff)_2Pc$ crystal.

The results of the three crystal structures show the relationship between intermolecular interactions and the photochemical activity in the silicon phthalocyanines. $SiCl_2Pc$ has intermolecular interactions that extend in only one direction (along *c*-axis) and photochemical activity does not

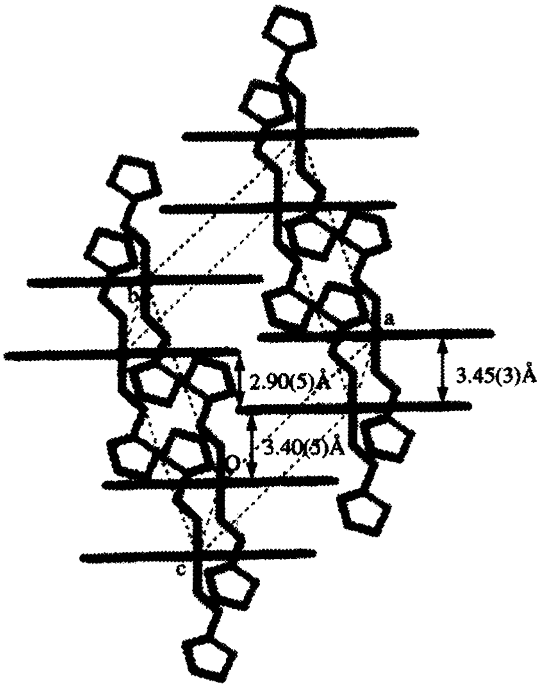


Fig. 6. View of π-π stacking with the distances between the phthalocyanine planes in $Si(thff)_2Pc$ crystal.

appear. On the other hand, $Si(OMe)_2Pc$ and $Si(thff)_2Pc$ have intermolecular interactions that extend in all directions in the crystals, and both compounds have photosensitivity.

In the case of dihydroxysilicon phthalocyanine, there are two polymorphs (Phase I & Phase II); only Phase II shows photochemical activity. In Phase I the intermolecular interactions consisting of π-π stacking, and hydrogen bonds extend in *bc* plane, and in Phase II the intermolecular interactions consisting of π-π stacking interactions, hydrogen bonds and T-interactions (C-H···π interaction) extend in all directions.[7]

From the results of the silicon phthalocyanine series we can state the simple rule that when the intermolecular interactions extend in all directions in the crystal, photochemical activity appears. This simple rule suggests that the intermolecular interactions cause the flow of electrons upon the irradiation of light, and that it is important for photochemical activity of a charge generation material that electrons flow in all directions in the crystal. In the crystals of silicon phthalocyanines we found various kinds of intermolecular interactions (π-π stacking interaction, hydrogen bonds and T-interaction); all of them were effective for photosensitivity. In those intermolecular interactions, π-π stacking interactions between the phthalocyanine planes were included in all of the silicon phthalocyanine crystals. We believe that for the appearance of photochemical activity in addition to π-π stacking interaction extended in at least one direction, some intermolecular interaction network extended in all directions is essential.

It is interesting that the water molecules in $Si(OMe)_2Pc$ crystal form hydrogen bonds with $Si(OMe)_2Pc$, and would play an important role for the photochemical activity of a charge generation material. To clarify the role of water molecules in phthalocyanines for photosensitivity, more quantitative analyses of electronic behavior and more crystal structure analyses for phthalocyanine compounds including water molecules are necessary.

To develop crystalline materials, the structural information from a very small crystal or powder is very important, since not only the molecular structure, but also the crystal structure determines the property of the material. Many crystal structures of crystalline materials will be determined by the combination of micrometer-sized single crystal analysis and *ab-initio* powder structure analysis in the near future. The new analytical methods of crystallography offer many tremendous possibilities for the progress of material science.

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