A New Polymorph of Hydroxygallium Phthalocyanine and Its Application in a Photoreceptor

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In recent polymorphism studies of gallium phthalocyanines, a new crystal form of hydroxygallium phthalocyanine (Type V HOGaPc) was obtained. It shows an extremely high photosensitivity ($E_{1/2}$=1.3 mJ/m^2 at 780 nm) and excellent thermal stability. Furthermore, its photosensitivity is not affected by changing humidity. Hence, it is an useful charge generation material for an IR photoreceptor. From the TGA and Rietveld analysis of the Type V crystal, it is indicated that the highly photosensitive characteristic of this pigment does not depend on sensitization by water. The high sensitivity is attributed to the specific crystal structure and to the presence of the hydroxyl group, both of which are favorable for charge generation.

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Introduction

Today, highly photosensitive and stable charge generation materials in the near-IR region are needed for digital copiers and printers. Phthalocyanines are being studied extensively because of their stability and photosensitivity in the near-IR region. Metal-free phthalocyanine (H_2Pc) and titanyl phthalocyanine (TiOPc) are examples of pigments currently being used in commercial photoreceptors.[1, 2] It is known that the photosensitivity of phthalocyanine is enhanced by oxygen or other acceptors[3,4] and is influenced by its polymorphism.[5] Recently, the correlation between their polymorphism and photosensitivity has been a subject of considerable interest. In particular, the Y-form of TiOPc is well known as an outstanding charge generation material,[6] and it has been found that this form of TiOPc is sensitized by weakly adsorbed water.[7] Furthermore, its specific crystal structure has been shown by molecular modeling to have cavities of an appropriate size to adsorb water.[8] Therefore, it is possible that the photosensitivity of the Y-form is dependent on humidity because of the adsorption–desorption equilibrium of water.

To obtain highly stable photosensitive charge generation materials, we attempted to control the water adsorption; that is, our studies focused on the hydroxy metal phthalocyanines from three viewpoints: the increased possibility that water would be adsorbed, the sensitization by the presence of an OH group, and molecular stacking control by hydrogen bonding. Previous studies of the hydroxy metal phthalocyanines were limited; therefore, it was interesting to study the chemical and crystallographic behavior of these hydroxy metal phthalocyanines. We studied the polymorphism and electrical properties of the trivalent and tetravalent hydroxy metal phthalocyanines, with emphasis on the gallium phthalocyanines. As a result, we have found a new, highly stable, photosensitive pigment, Type V hydroxy gallium phthalocyanine (HOGaPc)[9] having a gallium atom as a central metal (Fig. 1). This article describes the new HOGaPc crystals and their specific xerographic properties in layered photoreceptors.

Experimental

Synthesis of HOGaPc. Chlorogallium phthalocyanine (ClGaPc) was synthesized by modifying a previous method,[10] in which phthalodinitrile (29.1 g) and gallium trichloride (10.0 g) were heated in 1-chloronaphthalene (100 mL) at 200°C for 24 h. The product pigment was filtered and purified by washing with N,N'-dimethylformamide (DMF) and methanol and then dried under reduced pressure to give 28.9 g of ClGaPc. The ClGaPc (2.0 g) was then dissolved in concentrated sulfuric acid (50.0 g), and Type I HOGaPc[11] was obtained after reprecipitation in water and neutralization by aqueous ammonia. The product was washed with distilled water and then dried under reduced pressure to give 1.8 g of HOGaPc.

Polymorphic Conversion and XRD Analysis. Using a ball mill, Type I HOGaPc (1.0 g) and an organic solvent (15 mL) were milled with glass beads in a vessel at room temperature for 24 h. Solvents used were dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), dimethyl acetamide (DMA), toluene, or xylene. The pigment was

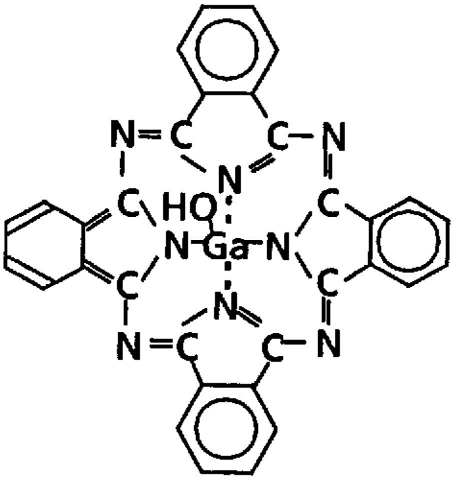

Figure 1. Structure of HOGaPc.

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isolated by centrifugation, washed with *n*-butyl acetate, and then dried under reduced pressure. The x-ray diffraction (XRD) spectrum of the pigment obtained was measured by a Rigaku x-ray diffractometer, using a $\mathrm{CuK}\alpha$ source. Crystal forms were distinguished by the XRD Spectra. Structures were also characterized by their IR spectra (Perkin Elmer, 1600 series FTIR), mass spectra (JEOL, DX 303), and NMR spectra (Varian, Unity 300).

Stability Test of Crystal Form in Solvent. Pigment (0.4 g) was dispersed and stirred in a solvent (15 mL) at room temperature for 6 days. XRD spectra of the pigment were compared before and after this solvent treatment.

Preparation of Reference Sample. Type II ClGaPc,[12] Y-form,[8] and Phase II[8] of TiOPc were prepared as described in the references indicated.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was performed on a Shimazu DT-40 instrument in a nitrogen atmosphere at the rate of 10°C/min. The weight change was recorded between room temperature and 400°C.

Optical Absorption Spectra. The optical absorption spectra of pigments in a binder resin film were measured by a Hitachi U-4000 spectrophotometer. The film composition was the same as that of the charge generation layer (CGL) described under photoreceptor device configuration.

Karl Fischer Titration. Karl Fischer titration was performed on a Mitsubishi KF-05 instrument. First the pigment was dried at 150°C for 10 min. Then the pigment was heated at 400°C for 20 min, and the water produced was titrated.

Photoreceptor Device and Xerographic Characteristic Measurements. The device configuration is shown in Fig. 2. The undercoat layer (UCL) consists of an organic silicon and zirconium compound on an aluminum substrate. The CGL is 0.2 *µ*m thick and consists of 60% by volume of pigment in a polyvinyl butyral resin. The charge transporting layer (CTL) is 25 *µ*m thick and consists of 40% by weight of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) in a polycarbonate matrix [PC(Z)].

Photosensitivity and dark decay were measured on a universal scanner. The photoreceptors were charged negatively to about –800 V. Dark decay potential was measured as the difference between the initial surface potential and that after 0.53 s. Photoinduced discharge curves (PIDCs) were measured in terms of surface potential versus exposure at 780 nm in an environmental chamber at 20°C and 40% relative humidity (RH). The initial slope of the PIDC (dV/dE) and the required exposure for reducing the surface potential from –800 to –400 V($E_{1/2}$) were calculated.

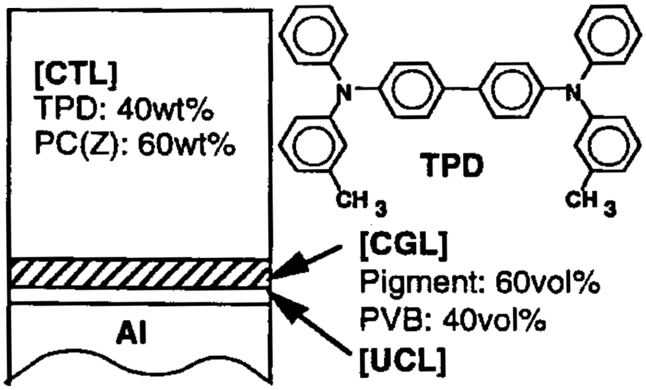

Figure 2. Photoreceptor configuration.

The humidity dependence of the photosensitivity was measured as follows. Exposure was initially set such that the surface potential could be decreased from –800 to –200 V in an environment of 20°C and 40% RH. The RH level was then varied, and the final surface potential was measured at the different controlled levels of humidity. Cyclic stability of the photoreceptor was measured in an environmental chamber at 28°C and 85% RH. The photoreceptor was charged negatively to about –700 V and was exposed with 660-nm light (10 mJ/m^2). Dark development potential (V_{DDP}) was measured as surface potential at 0.12 s after charging. Residual potential (V_{RP}) was measured as surface potential at 0.12 s after 660-nm light exposure. Total process speed was 0.48 s/cycle. V_{DDP} and V_{RP} were measured while the testing was performed for 500,000 cycles. In this experiment, the photoreceptor rested for 6 h every 125,000 cycles.

Results and Discussion

Chemistry and Polymorphism of HOGaPcs. Several new polymorphs of interest were obtained, using solvent treatments. The results of these studies are summarized in Fig. 3, and the XRD patterns are shown in Fig. 4. Acid pasting of ClGaPc into aqueous media gave the Type VIII crystal form, which we think is a protonated form of HOGaPc. It is only after the pigment is neutralized that the Type I HOGaPc is formed. We attempted many kinds of solvent treatment. Milling of Type I HOGaPc with a dipolar aprotic solvent, such as DMF, gave the Type V form. Several other solvents, such as xylene, gave Type XI HOGaPc. When Type I HOGaPc was treated in the presence of methanol, however, a conversion to methoxygallium phthalocyanine (MeOGaPc) occurred. Both HOGaPc and MeOGaPc were further converted to µ-oxogallium phthalocyanine (PcGaOGaPc) by heating at 400°C. A repeat of the acid pasting process on the PcGaOGaPc converted it back to the original HOGaPc. FD mass of MeOGaPc showed a peak corresponding to M^+ (m/z of 512) and PcGaOGaPc showed a peak corresponding to M^+ (m/z of 1180). Absorption peaks corresponding to the hydroxyl group disappeared in the IR spectra of both compounds. The methyl group on the MeOGaPc was also characterized by NMR spectra. In summary, only two new crystal forms, Type V and Type XI, were obtained as stable polymorphs of HOGaPcs.

These results are characteristic of hydroxy metal phthalocyanines; the reactive hydroxyl group plays a strong role in determining and stabilizing the final crystal structure of the pigment.

Optical Absorption Spectra. The optical absorption spectra for gallium phthalocyanines (GaPcs) are shown in Fig. 5. The absorption maxima of Type V (840 nm) and Type XI (895 nm) GaPcs pigments are red-shifted relative to those of other GaPcs. It is proposed that a strong interaction between phthalocyanine molecules results from the specific molecular stacking, which may be similar to that of a J-aggregate, and is regulated by the hydroxyl group.

Xerographic Properties of HOGaPcs. Photosensitivity and dark decay of the product hydroxygallium phthalocyanines, as compared with other highly photosensitive phthalocyanines, are summarized in Table I. Type V HOGaPc showed high photosensitivity ($E_{1/2}$=1.3 mJ/m^2), which is superior to that of phase II TiOPc and Type II ClGaPc and is approaching that of Y-form TiOPc. These reference phthalocyanines are known as highly photosensitive pigments. However, Type XI HOGaPc did not show such high photosensitivity. Kinoshita et al.[6] reported that J-type aggregated crystals tend to show high photosensitivity in the TiOPc polymorphism. From the viewpoint of the optical absorption spectrum, because the Type XI

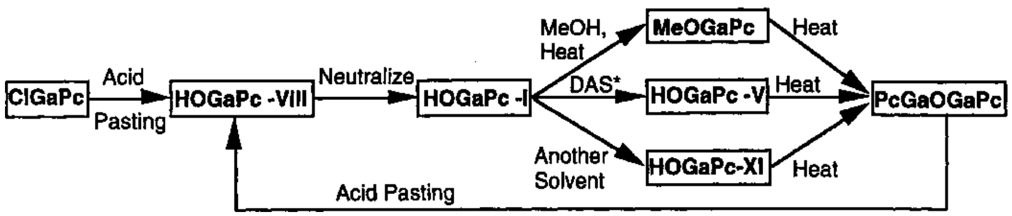

Figure 3. Chemistry and polymorphism of HOGaPc. (*DAS; Dipolar Aprotic Solvent)

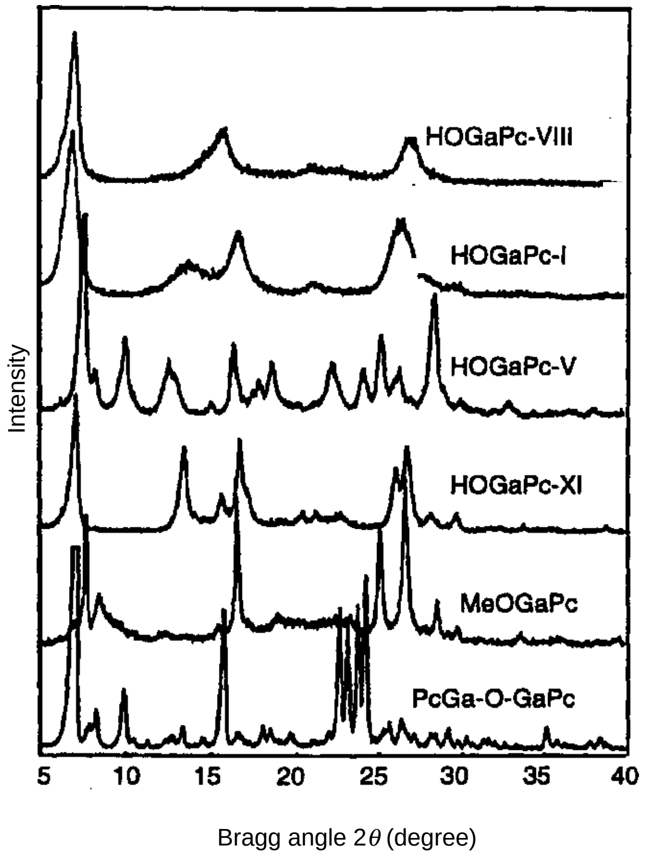

Figure 4. XRD spectra of gallium phthalocyanines.

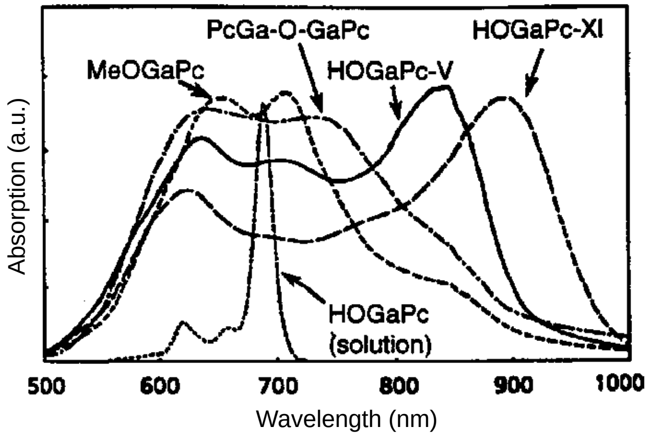

Figure 5. Absorption spectra of gallium phthalocyanines.

TABLE I. Xerographic Properties of HOGaPcs as Compared with Other Phthalocyanines

	Dark decay (V)	Photosensitivity dV/dE (kV•m^2/J)	 $E_{1/2}$(mJ/m^2)
HOGaPc-V	27	314	1.3
HOGaPc-XI	115	75	5.3
ClGaPc-II	28	206	2.0
TiOPc-II	17	192	2.1
Y-TiOPc	18	400	1.0

absorption maximum extended to 895 nm, one would expect a much higher photosensitivity, but this was not the case. This result indicates that factors other than J-aggregate-like molecular stacking should be considered in this HOGaPc polymorphism.

The humidity dependence of the photosensitivity of Type V HOGaPc and Y-form TiOPc is shown in Fig. 6. The surface potential of Y-form TiOPc changed about 80 V as the RH changed from 10 to 80%. On the other hand, no change in photosensitivity was observed for Type V HOGaPc over this range. The TGA curves of Type V HOGaPc and Y-form TiOPc are shown in Fig. 7. Weight loss corresponding to the desorption of water was observed close to room temperature in the Y-form TiOPc; however, a weight loss was not observed until 200°C in Type V HOGaPc. These TGA results show that there is no weakly adsorbed water in the Type V HOGaPc, which explains its excellent stability under various humidity environments.

Xerographic cycling data of Type V HOGaPc are shown in Fig. 8. The dark development potential, V_{DDP}, decreased

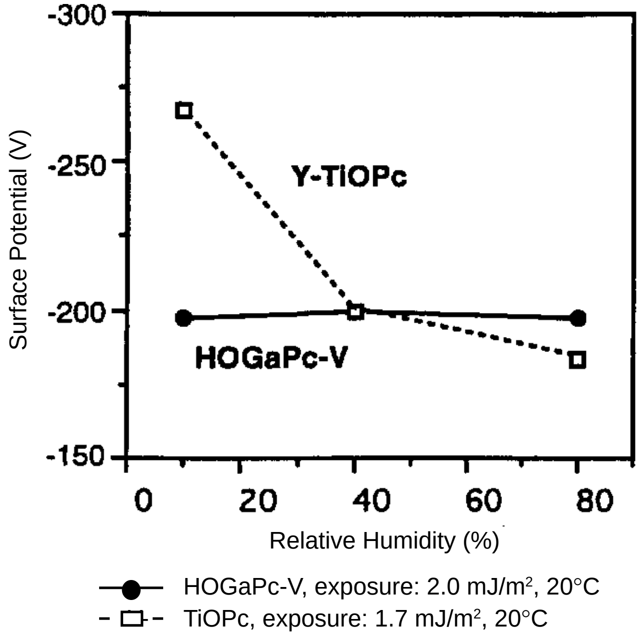

Figure 6. Humidity dependence of the photosensitivity.

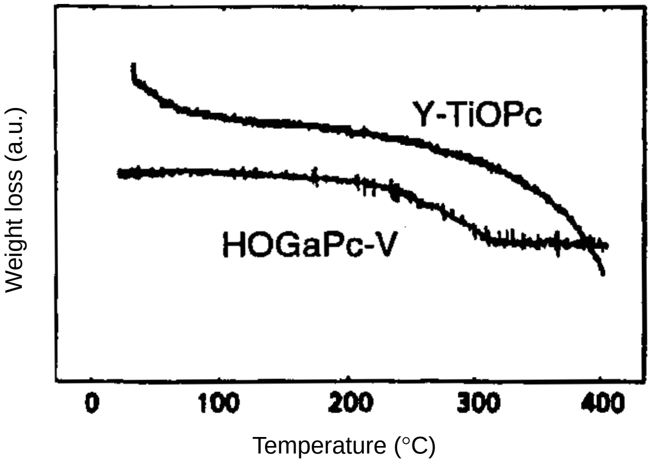

Figure 7. TGA curves of Type V HOGaPc and Y-form TiOPc.

by about 30 V, and the residual potential, V_{RP}, increased by about 65 V over 500,000 cycles. These changes were very small in a stress test of over 500,000 cycles. These data also indicate excellent stability of Type V HOGaPc even over the long term and demonstrate the feasibility of using this pigment as a charge generation material (CGM) in a photoreceptor.

Stability Against Temperature and Solvent. The XRD spectrum of Type V HOGaPc remained unchanged after the pigment had been heated to 200°C. From this observation and the TGA result showing that the weight loss curve is flat up to 200°C, it is obvious that the Type V crystal would be thermally stable under the typical conditions in which it would be used as a CGM in a photoreceptor.

Furthermore, the XRD spectrum change in solvent over 6 days was examined, as summarized in Table II. No change in XRD was observed in many kinds of solvents, except for methanol. Therefore, the Type V crystal is also chemically stable in the various solvents used to coat the CGL in a photoreceptor.

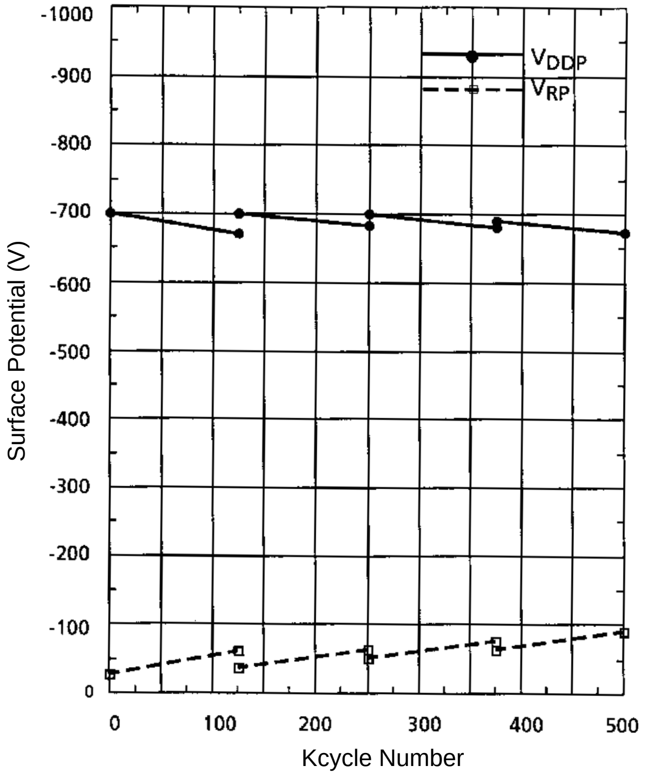

Figure 8. Xerographic cycling property of Type V HOGaPc.

TABLE II. XRD Change of the Type V HOGaPc in Various Solvents

Solvent	after 1 day	after 6 days
n-Butyl acetate	unchanged	unchanged
Cyclohexanone	unchanged	unchanged
Methyl Alcohol	MeOGaPc	MeOGaPc
Chlorobenzene	unchanged	unchanged
Dichloromethane	unchanged	unchanged
Tetrahydrofuran	unchanged	unchanged

Photosensitive Property and Crystal Structure. At the beginning of this study, we thought that water would adsorb strongly in the hydroxy metal phthalocyanine crystal and improve the photogeneration efficiency by a sensitization similar to that of Y-form TiOPc. From the result of TGA, the weight loss over 200°C in Type V HOGaPc is attributed to dehydration by the dimerization reaction of HOGaPc, as previously described. A weight loss of 1.5 wt% water, as measured by Karl Fischer titration, corresponds to the theoretical amount lost by this dimerization reaction. These results indicate that there is no adsorbed water in the Type V crystal and that its high photosensitivity is not dependent on sensitization by adsorbed water.

XRD spectra for Phase II TiOPc and Type II ClGaPc are shown in Fig. 9. It is interesting that the XRD spectrum of Type V HOGaPc resembles the spectra of these crystals and that all of them show high photosensitivity. The crystal structures of Type V HOGaPc and Type II ClGaPc were calculated[13] by Rietveld analysis with the Monte Carlo method, and both were very similar to Phase II TiOPc.[14] The common molecular overlap of the two types of Type V HOGaPc neighbors are shown in Figs. 10 and 11.

Oka and Okada[15] suggest that the molecular overlapping shown in Fig. 10 is important for charge generation and that the highly charge generative characteristics are explained by using the exciton trap model in which J-aggregate-like molecular stacking is favorable for fast exciton migration. Type V HOGaPc also has a molecular overlapping like that of other highly photosensitive phthalocyanines, and this result reinforces their suggestion.

However, Type V HOGaPc shows much higher photosensitivity than that of Phase II TiOPc and Type II ClGaPc. The difference in the photosensitivity of these pigments cannot be explained by this molecular stacking alone. It has been proposed that the hydroxyl group might possibly interact with the nitrogen atom of the

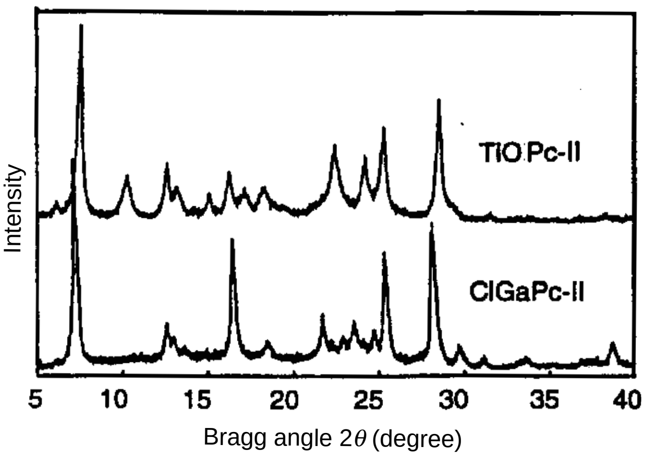

Figure 9. XRD spectra of Phase II TiOPc and Type II ClGaPc.

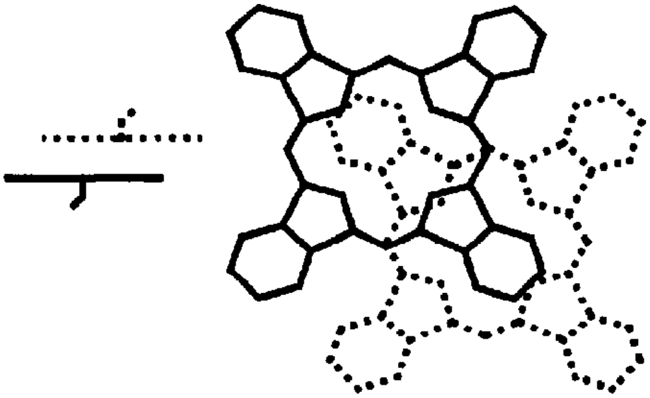

Figure 10. Molecular overlap of Type V HOGaPc (HO group on GaPc facing outside).

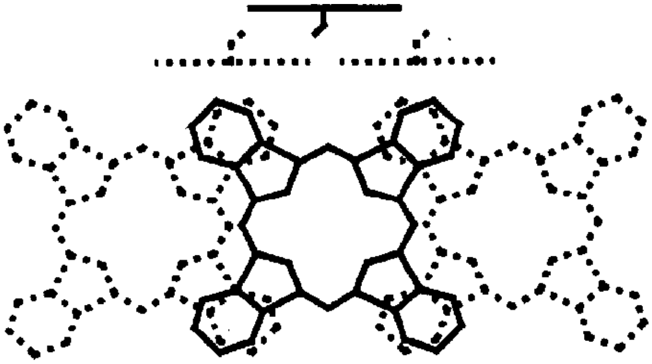

Figure 11. Molecular overlap of Type V HOGaPc (HO group on GaPc facing inside).

adjacent molecules by hydrogen bonding O-H···N.[13] The hydrogen bonding would help to produce a strong interaction between the two facing molecules. Also it is plausible that the OH group may sensitize the photogeneration of HOGaPc as does H_2O sensitization of Y-form TiOPc. Hor and Popovic[16] also suggested that Type V HOGaPc might have a special molecular packing that produces a high carrier generation efficiency even at zero electric field. These workers used electric-field-induced fluorescence quenching techniques. From these results, the role of the hydrogen bonding is assumed to create a strong intermolecular interaction that favors charge generation. However, further investigation is needed to explain the charge generation mechanism in Type V HOGaPc.

Conclusions

In our study of hydroxy metal phthalocyanines, a new crystal form of hydroxygallium phthalocyanine (Type V HOGaPc) having a gallium atom as a central metal component was obtained, and the specific behavior of the hydroxyl group was observed. This crystal shows an extremely high photosensitivity and is thermally stable. Because the photosensitivity is stable under various humidity conditions, this material is a useful charge generation material for an IR photoreceptor.

The highly photosensitive characteristic of Type V HOGaPc is not caused by water sensitization. It is probably due to the specific molecular stacking and the presence of the hydroxyl group, which facilitates charge generation.

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