# Gallium Phthalocyanines: Structure Analysis and Electroabsorption Study

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Electroabsorption has been measured with thin films of several (phthalocyaninato)galliums. It has been observed that the lowest energy absorption peak of most of the compounds studied is sensitive to the applied electric field. The shape of the electroabsorption spectrum is well reproduced by the second derivative of the corresponding absorption, indicating that the excited state has the character of a charge transfer state. It has been found that a clear correlation exists between the magnitude of the electromodulation and the sensitivity for the charge carrier generation. Crystal structure analysis of two compounds, hydroxygallium phthalocyanine type XI and chlorogallium phthalocyanine type II, made by Rietveld analysis, clarified that the molecules are stacked in pairs. The implication of the dimer structure is discussed.

#### Introduction

Phthalocyanines have been the subject of intensive study. They are extremely stable pigments and exhibit many interesting photochemical and photophysical properties. In addition to a wide variety of central metals, there are also many polymorphs. Some of them are efficient photocarrier generating pigments while others are not.<sup>1</sup> From an application point of view phthalocyanines are especially important since they belong to a few compounds which have a sensitivity in the deep red in the spectral region and can be excited with laser diodes. At the same time they pose an interesting challenge of how to rationalize the charge carrier generation with photons of such a low energy.

Unfortunately, many of the polymorphs of phthalocyanines are difficult to grow in large enough crystals for single crystal analysis. However, the structure of such a crystal could be obtained from powder X-ray diffraction data by employing Rietveld analysis<sup>2,3</sup> and Monte Carlo methods. The analyses produced plausible crystal structures for several kinds of phthalocyanine crystals.<sup>4–7</sup> Carrier generation by light absorption or, in other words, photoionization in a condensed phase is of fundamental importance in photophysics of solids, as well as of liquids, and has been the subject of intensive study for a considerable time. In a discussion of photocarrier generation, especially with low-energy excitation, an important issue is the possible involvement of a charge transfer (CT) state.

Generally, a CT state has a small absorption cross section and, as a result, is not easy to be observed directly. Very often a CT transition is mixed with absorption which has much larger absorption cross sections. The electromodulation technique provides a sensitive means for detecting such a transition.<sup>8,9</sup>

In the presence of an electric field  $\mathbf{F}$ , the energy of a molecule in its ground state  $\epsilon_G$  and that in the excited state  $\epsilon_E$  are shifted as

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$$\Delta \epsilon_{\rm G}(\mathbf{F}) = -\mathbf{m}_{\rm G} \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot \mathbf{p}_{\rm G} \mathbf{F}$$
(1)

$$\Delta \epsilon_{\rm E}(\mathbf{F}) = -\mathbf{m}_{\rm E} \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot \mathbf{p}_{\rm E} \mathbf{F}$$
(2)

where **m**'s are the dipole moments and **p**'s are the polarizabilities. Accordingly, the shift of the transition energy is given by

$$\Delta(\epsilon_{\rm E} - \epsilon_{\rm G}) = -\Delta \mathbf{m} \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot \Delta \mathbf{p} \mathbf{F}$$
(3)

This shift influences the absorbance at energy  $\epsilon = \epsilon_{\rm E} - \epsilon_{\rm G}$  as

$$\Delta A = \left(\frac{\partial A}{\partial \epsilon}\right) \Delta \epsilon + \frac{1}{2} \left(\frac{\partial^2 A}{\partial \epsilon^2}\right) (\Delta \epsilon)^2$$
  
=  $\frac{\partial A}{\partial \epsilon} \{-\Delta \mathbf{m} \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot \Delta \mathbf{p} \mathbf{F}\} + \frac{1}{2} \left(\frac{\partial^2 A}{\partial \epsilon^2}\right) \left\{-\Delta \mathbf{m} \cdot \mathbf{F} - \frac{1}{2} \mathbf{F} \cdot \Delta \mathbf{p} \mathbf{F}\right\}^2$ (4)

If the system under study is an ensemble of randomly oriented molecules (or crystallite)

$$\langle \mathbf{m} \cdot \mathbf{F} \rangle = 0$$

may be assumed, since the orientation of both  $\mathbf{m}_G$  and  $\mathbf{m}_E$  with respect to the field  $\mathbf{F}$  is random. The term proportional to  $\mathbf{F}^4$  can be neglected when  $\Delta \mathbf{m}$  is of a significant magnitude. In this case only terms proportional to  $\mathbf{F}^2$  remain. An isotropic average over the randomly oriented dipole moments gives

$$\Delta A = \frac{1}{2} \left( \frac{\partial A}{\partial \epsilon} \right) \Delta \mathbf{p} \mathbf{F}^2 + \frac{1}{6} \left( \frac{\partial^2 A}{\partial \epsilon^2} \right) (\Delta \mathbf{m})^2 \mathbf{F}^2$$
(5)

In this simplified model the molecular polarizability is assumed

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Figure 1. Synthesis and polymorphic conversion of gallium phthalocyanines.

to be isotropic. Equation 5 predicts that an electroabsorption spectrum should reproduce the first derivative of the absorption spectrum if the first term is dominant (i.e., the second-order Stark effect). If, on the other hand, the excited state has a large dipole moment, the second term becomes important, and accordingly the electroabsorption spectrum should give the second derivative of the absorption spectrum. This is expected to be the case when the final state of the transition is a CT state, which has a large dipole moment. There have been some reports on electroabsorption of phthalocyanine compounds.<sup>10–14</sup>

Here we report on electroabsorption of thin films of a few polymorphs of (phthalocyaninato)galliums (hereafter GaPc's). Crystal structure analysis of two compounds, hydroxygallium phthalocyanine type XI (HOGaPc-XI) and chlorogallium phthalocyanine type II (ClGaPc-II), made by Rietveld analysis, is presented. Daimon et al. reported that a polymorph of hydroxygallium phthalocyanine (HOGaPc) exhibits a high sensitivity for photocarrier generation.<sup>15</sup>

### **Experiments**

Synthesis of GaPc. Chlorogallium phthalocyanine (ClGaPc) was synthesized by a modification of the method described in ref 16 in which phthalodinitrile and gallium trichloride were heated in 1-chloronaphthalene at 200 °C for 24 h. The product pigments were filtered and purified by washing with N,Ndimethylformamide (DMF) and methanol and then dried under reduced pressure to give ClGaPc type I (ClGaPc-I). ClGaPc-II was obtained after grinding and milling ClGaPc-I with benzyl alcohol at room temperature for 24 h. HOGaPc type I (HOGaPc-I) was prepared in the following procedure:<sup>17</sup> Cl-GaPc-I was dissolved in concentrated sulfuric acid. HOGaPc-I precipitated when the solution was cast into water and neutralized with aqueous ammonia. HOGaPc type V (HOGaPc-V) was prepared by milling HOGaPc-I with DMF in a vessel with glass beads at room temperature for 24 h. HOGaPc-XI was obtained by changing the solvent on milling from DMF to xylene. The pigments were isolated by centrifugation and then dried under reduced pressure.

**Crystal Structure Analysis.** The powder crystals were pressed onto a standard glass holder and mounted on an X-ray diffractometer (Rigaku RU-200B). The sealed tube with a Cu target was operated at 40 kV and 30 mA. The Cu K $\alpha$  radiation ( $\lambda = 1.54$  Å) was monochromatized with a curved graphite crystal. Step-scan X-ray data up to  $2\theta = 40.0^{\circ}$  were collected with the speed of 0.5 s/step and the step length of 0.01° in  $2\theta$ . The densities of the pigments were measured at 25 °C using a density gradient tube.<sup>18</sup>

The refinement procedure for the Rietveld analysis has been reported in previous papers.<sup>5,7</sup> We used the Lorentz function

for the peak profile description and March function for the correction of preferred orientation.<sup>19</sup> The error function, which is defined as the square of the difference between observed XRD intensities and the calculated ones, was minimized by the Monte Carlo method. Optimized were unit cell parameters, coordinates of the center of mass of the molecules with respect to the crystal axes, and Euler angles which determine the orientation of the molecules. The molecules were considered to be rigid. Other adjustable parameters were the half-width  $\omega$  of the Lorentz function for the peak profile and the preferred orientation parameter *r* of the March function. The isotropic temperature factors were fixed in our calculations because their influences on XRD patterns were small. At the end of the minimization cycle, the *R* factor

$$R = \frac{\sum_{i} |F_{obs}(\theta_{i}) - F_{calc}(\theta_{i})|}{\sum_{i} |F_{obs}(\theta_{i})|}$$

was evaluated to assess the accuracy of the fit, where  $F(\theta_i)$  is the square root of the intensity at equidistant  $2\theta$  values between 5° and 35°.

**Electroabsorption Measurement.** Electroabsorption measurements were carried out on a thin film of GaPc particles dispersed in a copolymer of vinyl chloride and vinyl acetate (VMCH from Union Carbide Co.). Two different types of cell structures were employed. The structure used for measuring electroabsorption spectrum was composed of a dispersed layer of GaPc (50 wt %) on top of a *N*-(methoxymethyl)nylon (LM5003 from DIC Co.) layer formed on a NESA glass plate. The thickness of the GaPc layer was about 0.2  $\mu$ m, and that of the *N*-(methoxymethyl)nylon layer was about 5  $\mu$ m. A field dependence of the modulation was measured with a cell of single layer structure, in which the concentration of GaPc was reduced to 5 wt %. The GaPc pigments studied were ClGaPc-II, HOGaPc-V, HOGaPc-XI,  $\mu$ -oxogallium phthalocyanine ((GaPc)<sub>2</sub>O), and methoxygallium phthalocyanine (CH<sub>3</sub>OGaPc).

We have constructed an extrastable unit for absorption measurements with single-beam arrangement. Light transmission was measured with and without an applied dc electric field. The light from a tungsten halogen lamp was monochromatized with a 25 cm monochromator (Nikon P250). The intensity of the light transmitted through a sample was detected with a lownoise Si photodiode (Hamamatsu S1137-16BQ), amplified with a low noise preamplifier (NF, LI-76) and measured with a  $6^{1/2}$ digit multimeter. The monochromator was set to a wavelength, a square pulse of a voltage was applied for 250 ms, and light transmission was measured. The transmission at 0 V was then measured during the next 250 ms. This was repeated 100 times in 25 s, and the results were averaged on a PC. The monochromator was then advanced to the next wavelength. This averaging procedure, combined with a stable mechanical construction careful selection of a light source and a low noise photodiode, enabled us to attain a resolution in absorbance ( $\Delta A$ ) ranging from  $2 \times 10^{-5}$  to  $1 \times 10^{-4}$ , depending on the wavelength region. All measurements were performed in ambient atmosphere and at room temperature.

### Results

The structure parameters and final R factors of HOGaPc-V, HOGaPc-XI, and ClGaPc-II are shown in Table 1. The result of the structure analysis for HOGaPc-V has been published in ref 4. The atomic coordinates for HOGaPc-XI and ClGaPc-II are shown in Tables 2 and 3. The observed XRD patterns, the

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 TABLE 1:
 Crystallographic Data of HOGaPc-V,

 HOGaPc-XI, and ClGaPc-II
 ClGaPc-II

	HOGaPc-V <sup>4</sup>	HOGaPc-XI	ClGaPc-II
crystal system	triclinic	monoclinic	triclinic
space group	$P\overline{1}$	$P2_{1}/c$	$P\overline{1}$
Z	2	4	2
<i>a</i> (nm)	1.152	1.663	1.293
b (nm)	1.275	2.632	1.273
c (nm)	0.889	0.716	0.773
α (deg)	95.87	90.00	107.05
$\beta$ (deg)	96.00	129.93	102.48
$\gamma$ (deg)	69.45	90.00	91.72
density (g/cm <sup>3</sup> )	1.64	1.66	1.77
(measured)	(1.61)	(1.66)	(1.67)
R factor	0.195	0.279	0.216

 
 TABLE 2: Positional Parameters of HOGaPc-XI with Respect to the Triclinic Axes

	а	b	С		а	b	с
Ga	0.136	0.026	0.647	С	-0.119	-0.155	0.697
0	0.143	-0.001	0.420	С	-0.132	-0.108	0.582
Ν	0.267	0.009	0.957	С	-0.041	-0.082	0.659
Ν	0.077	-0.025	0.713	С	0.126	-0.065	0.868
Ν	0.003	0.059	0.467	С	-0.025	-0.037	0.587
Ν	0.193	0.094	0.711	С	-0.132	0.115	0.215
Ν	0.228	-0.071	1.031	С	-0.175	0.070	0.215
Ν	-0.105	-0.009	0.412	С	-0.285	0.065	0.075
Ν	0.041	0.142	0.411	С	-0.350	0.107	-0.067
Ν	0.375	0.079	1.027	С	-0.305	0.152	-0.067
С	0.615	-0.021	1.640	С	-0.195	0.157	0.075
С	0.571	-0.067	1.641	С	-0.025	0.106	0.370
С	0.462	-0.076	1.461	С	-0.091	0.038	0.370
С	0.400	-0.038	1.282	С	0.386	0.240	0.877
С	0.443	0.006	1.281	С	0.399	0.189	0.953
С	0.552	0.016	1.459	С	0.310	0.159	0.837
С	0.294	-0.035	1.083	С	0.211	0.177	0.655
С	0.360	0.034	1.082	С	0.195	0.228	0.576
С	0.057	-0.101	0.842	С	0.284	0.260	0.690
С	0.072	-0.147	0.961	С	0.295	0.108	0.865
С	-0.017	-0.174	0.886	С	0.143	0.137	0.585

 
 TABLE 3: Positional Parameters of ClGaPc-II with Respect to the Triclinic Crystal Axes

	а	b	с		а	b	с
Ga	0.228	0.002	0.853	С	0.650	0.354	1.378
Cl	0.274	-0.066	0.614	С	0.679	0.265	1.440
Ν	0.169	0.147	0.837	С	0.617	0.165	1.379
Ν	0.357	0.104	1.044	С	0.521	0.158	1.248
Ν	0.256	-0.100	1.017	С	0.435	0.066	1.160
Ν	0.069	-0.055	0.812	С	0.354	-0.104	1.137
Ν	0.330	0.277	0.981	С	0.352	-0.201	1.188
Ν	0.436	-0.025	1.200	С	0.427	-0.242	1.304
Ν	0.090	-0.221	0.902	С	0.403	-0.340	1.328
Ν	-0.018	0.083	0.688	С	0.302	-0.403	1.234
С	0.067	0.160	0.748	С	0.255	-0.360	1.122
С	0.062	0.269	0.727	С	0.251	-0.262	1.099
С	-0.018	0.322	0.645	С	0.194	-0.193	0.995
С	0.004	0.427	0.650	С	0.038	-0.155	0.824
С	0.105	0.488	0.750	С	-0.077	-0.180	0.730
С	0.183	0.433	0.827	С	-0.149	-0.274	0.700
С	0.165	0.326	0.818	С	-0.253	-0.274	0.594
С	0.226	0.249	0.882	С	-0.282	-0.188	0.530
С	0.384	0.208	1.055	С	-0.213	-0.094	0.561
С	0.492	0.244	1.182	С	-0.109	-0.092	0.666
С	0.552	0.345	1.243	С	-0.015	-0.012	0.721

calculated ones, and their differences are shown in Figures 2 and 3. The R factor for HOGaPc-XI is relatively large as compared with that of HOGaPc-V and ClGaPc-II. This is caused by inadequate peak profile function. While diffraction peaks observed are asymmetric in shape, the Lorentz function used for peak profile description is symmetric. The R factor is very sensitive to peak profile, although the calculated peak



**Figure 2.** Powder XRD pattern observed  $y_{obs}(\theta_i)$  of HOGaPc-XI, calculated pattern  $y_{calc}(\theta_i)$ , and their difference.



**Figure 3.** Powder XRD pattern observed  $y_{obs}(\theta_i)$  of ClGaPc-II, calculated pattern  $y_{calc}(\theta_i)$ , and their difference.



Figure 4. Molecular stacking in HOGaPc-V crystal. Two molecules encircled are most adjacent to each other and constitute a pair.

positions and intensities which are used in determining the crystal structure are in good agreement with the observed ones.

The molecular stacking in the crystals is shown in Figure 4 for HOGaPc-V, in Figure 5 for HOGaPc-XI, and in Figure 6 for ClGaPc-II. In all these crystals the molecules are arranged



Figure 5. Molecular stacking in HOGaPc-XI crystal. Two molecules encircled are most adjacent and form a pair.



Figure 6. Molecular stacking in CIGaPc-II crystal. Two molecules encircled are the most adjacent molecules which constitute a pair.

in pairs. Figure 7 shows the molecular overlap within the pairs, projected onto the average molecular plane. It could be argued that molecules with their Ga-O (or Ga-Cl) bonds sticking to each other may also be regarded as a pair. Actually, when viewed down along the Ga-O (or Ga-Cl) bonds, these molecules overlap much less, compared to a pair shown in Figure 7.<sup>4</sup>

Figure 8 shows an ordinary absorption spectrum and an electroabsorption spectrum for ClGaPc-II, HOGaPc-V, HOGaPc-XI, (GaPc)<sub>2</sub>O, and CH<sub>3</sub>OGaPc. The ordinary absorption spectrum of ClGaPc-II has two peaks, one at 12 700 cm<sup>-1</sup> and the other at 14 800 cm<sup>-1</sup>. It can be decomposed into two overlapping Gaussians (A, which is centered at 12 700 cm<sup>-1</sup>, and B, centered at 14 800 cm<sup>-1</sup>). The electroabsorption spectrum of ClGaPc-II exhibits two negative peaks, one around 12 700 cm<sup>-1</sup> (790 nm) and the other around 14 800 cm<sup>-1</sup> (680 nm). The spectrum can be decomposed into a superposition of the second derivatives of A and B. This seems to indicate that the final states of these transitions are of a CT character. The amplitude of the modulation is larger at the lower energy peak at 12 700 cm<sup>-1</sup> than at the higher energy peak at 14 800 cm<sup>-1</sup>, although in the absorption spectrum the lower energy peak has a smaller absorption coefficient. This indicates that the dipole moment associated with the final state of the transition A is larger than that of the transition B (see eq 5).

In HOGaPc-V, the ordinary absorption spectrum has two absorption bands, one around 11 780 cm<sup>-1</sup> (849 nm) and the other around 15 630  $\text{cm}^{-1}$  (640 nm). The small peak which is seen at 14 500  $\text{cm}^{-1}$  (690 nm) gains its intensity relative to other peaks on dilution and is considered to be due to the monomer dissolved in the matrix polymer. The peak at 690 nm is observed also with HOGaPc-XI, CH<sub>3</sub>OGaPc, and (GaPc)<sub>2</sub>O samples. The electroabsorption spectrum of HOGaPc-V exhibits two negative peaks, one around 12 200 cm<sup>-1</sup> (820 nm) and the other around  $14\ 300\ \text{cm}^{-1}$  (700 nm). The electromodulation at 14 300 cm<sup>-1</sup> may not be associated with the monomer peak at 14 500 cm<sup>-1</sup> (690 nm), since modulation is observed around 14 500 cm<sup>-1</sup> with other samples which have an absorption peak at this energy. The electroabsorption spectrum is reproduced by the second derivative of two Gaussians centered at 12 200 and 14 300 cm<sup>-1</sup>.

HOGaPc-XI and  $(GaPc)_2O$  exhibit an electroabsorption spectrum having a peak at about 11 100 cm<sup>-1</sup> (900 nm) and another at 13 900 cm<sup>-1</sup> (720 nm). It is the compound which has absorption in the longest wavelength region among this group of compounds. CH<sub>3</sub>OGaPc shows only a small electroabsorption signal. Figure 9 summarizes the electric field dependence of the magnitude of the electromodulation. It clearly shows that the modulations are proportional to the square of the applied field, the expected behavior of a CT state described in eq 5.

### Discussion

Most of GaPc's studied exhibit two absorption peaks, while the solution spectrum has only one prominent peak at 14 500  $cm^{-1}$  (690 nm). This splitting must reflect the strength of the intermolecular interaction. [Mizuguchi et al. accounted for the solid state spectrum of titanyl phthalocyanine type II in forms of molecular distortion without considering any intermolecular interaction.<sup>14</sup> However, as they pointed out, it is quite probable that the distortion in the crystal lattice is the result of intermolecular interaction and that this is automatically included in their calculation.] An easy comparison of the intermolecular interaction is difficult, since the molecules are not planar. However, if we compare the distances between the centers of gravity of the molecules in a pair, they seem to be correlated with the magnitude of the spectral splitting: they are 4.51 Å in HOGaPc-XI (which exhibits the largest splitting of  $4500 \text{ cm}^{-1}$ ), 4.62 Å in HOGaPc-V (3700 cm<sup>-1</sup>), and 5.42 Å in ClGaPc-II  $(2300 \text{ cm}^{-1})$ . Unfortunately, the crystal structures of CH<sub>3</sub>-OGaPc and (GaPc)<sub>2</sub>O are not known so far.



Figure 7. Molecular arrangement in a pair in (a) HOGaPc-V, (b) HOGaPc-XI, and (c) ClGaPc-II projected down to the average molecular plane of phthalocyanine.





**Figure 8.** Ordinary absorption spectrum (drawn out line) and electroabsorption spectrum (dotted line) of (a) ClGaPc-II, (b) HOGaPc-V, (c) HOGaPc-XI, (d) CH<sub>3</sub>OGaPc, and (e) (GaPc)<sub>2</sub>O dispersive films. The applied electric field is about  $5.0 \times 10^5$  V/cm. In (a) thin dotted line represents the second derivative of the two Gaussian peaks which fit the ordinary absorption spectrum.

A common feature in the molecular arrangement found in the three structures analyzed here is that molecules are stacked in pairs with their centers staggered along the diagonal direction of the molecules (Figure 10). This type of staggered overlap is also common in all highly photosensitive phthalocyanine pigments whose crystal structures have been determined: Titanyl phthalocyanine phase I (TiOPc-I) and phase II (TiOPc-II),<sup>20</sup> Y-type TiOPc (Y-TiOPc),<sup>7</sup> vanadyl phthalocyanine phase II (VOPc-II),<sup>21</sup> and x-form metal-free phthalocyanine (x-H<sub>2</sub>- Pc).<sup>5</sup> The sensitivity of HOGaPc-V is close to that of Y-TiOPc, which is known as an extremely photosensitive crystal. ClGaPc-II and HOGaPc-XI also have a photosensitivity comparable to TiOPc-II. The structural findings support the proposal<sup>22</sup> that the specific molecular arrangement (as in Figure 10) within the pair, or in a one-dimensional stack (as in x-H<sub>2</sub>Pc), is essential in realizing a high photosensitivity of phthalocyanine crystals.

Figure 11 shows the relationship between the magnitude of the modulation at the peak position normalized to the peak



**Figure 9.** Amplitude of the electroabsorption signal at wavelengths indicated versus the square of the electric field applied to the thin films of several GaPc's.



**Figure 10.** Molecular overlapping characteristic of (a) highly photosensitive pigments and (b) low-photosensitivity pigments.



**Figure 11.** Relationship between the quantum yield of the photocarrier generation and the magnitude of the modulation  $\Delta A$  normalized to the absorbance *A* at the peak position.

absorbance and the quantum yield of the photocarrier generation, obtained through xerographic gain measurements.<sup>1</sup> The two quantities show a linear correlation: The larger the modulation is, the higher is the sensitivity. Saito et al. studied electroabsorption of titanyl phthalocyanines<sup>12</sup> and also concluded that there is a correlation between the magnitude of electromodulation and the photocarrier generation efficiency.

We consider the excited states of a molecular pair to be described by a mixture of a locally excited state  $|mm^*\rangle$  and a CT state  $|CT\rangle$ . The mixed states are represented by

$$|-\rangle = \alpha |\mathrm{mm}^*\rangle - \beta |\mathrm{CT}\rangle \tag{6a}$$

$$|+\rangle = \beta |\mathrm{mm}^*\rangle + \alpha |\mathrm{CT}\rangle$$
 (6b)

where  $\alpha^2 + \beta^2 = 1$ . The dipole moments of the mixed states are expressed by the following formulas:

$$\Delta m_{-} = \langle -|\mathbf{m}| - \rangle \approx \beta^2 m_{\rm CT} \tag{7a}$$

$$\Delta m_{+} = \langle +|m| + \rangle \approx \alpha^{2} m_{\rm CT} \tag{7b}$$

where  $m_{\rm CT}$  is the dipole moment of the CT state. The absorption, which can be modulated, is assumed to have a Gaussian shape with a width  $\Gamma$ . Substituting eqs 7 and 8 for eq 5, we obtain eq 9

$$A(\epsilon) = A(\epsilon_0) \exp\left\{-\left(\frac{\epsilon - \epsilon_0}{\Gamma}\right)^2\right\}$$
(8)

$$\left(\frac{\Delta A}{A}\right)_{\epsilon_0} = \frac{(\Delta \mathbf{m})^2 \mathbf{F}^2}{\Gamma^2} = \frac{(\beta^2 \mathbf{m}_{\rm CT})^2 \mathbf{F}^2}{\Gamma^2}$$
(9)

when the second term of eq 5 is dominant. Structure analysis with X-rays shows that the molecules are arranged in dimer structures and that intermolecular distances are approximately the same in the crystals studied. Hence, it may be reasonable to assume that CT states in all GaPc's studied have dipole moments of comparable magnitude,  $m_{\rm CT}$ . The width  $\Gamma$  appears to be the same in different Pc's, judging from the observed widths of the longest wavelength absorption peaks of GaPc's which are approximately the same. Hence, from eq 9 the magnitude of electromodulation should be proportional to  $(\beta^2)^2$ . The results shown in Figure 11 seem to indicate that the efficiency of the photocarrier generation is indeed closely related to the amount of the CT character admixed in the excited state. The magnitude of  $\beta$  should be determined by the energy difference of a CT state and of the lowest excited state.<sup>10</sup> In this context it is interacting to note that HOGaPc-XI, which seems to have the largest intermolecular interaction in the pair, exhibits a lower efficiency of carrier generation compared to HOGaPc-V and ClGaPc-II. A CT state may be located close to the lowest excited state in HOGaPc-V (and to a lesser extent in ClGaPc-II), whereas the strong intermolecular interaction pushes down the lowest excited state so that it is situated much lower than the CT state and, as a result, the mixing is small.

It is customary to model the carrier generation as a two-step process,<sup>23</sup> as shown in Figure 12a. In the first step the system is brought, by absorption of light, to the lowest singlet excited state which undergoes nonradiative transition to a CT state which ionizes by the applied electric field. Popovic studied the effect of an applied electric field upon the fluorescence of Pc's.<sup>24</sup> He observed that the fluorescence was indeed quenched by applying an electric field which he interpreted in terms of two competing channels, i.e., the fluorescence and the field-assisted transformation into a CT state. A high field favors the formation of a CT state, or the dissociation of it, but since these are secondary processes occurring after an optical transition, this should not influence the absorption. With the present method, however, one directly observes the influence of the external field upon the state which itself is the final state of an optical transition. Hence, we propose that a CT state, directly produced by light absorption, is the intermediate for carrier generation: a model shown in Figure 12b.

Generation of a CT state itself does not necessarily mean the generation of charge carriers. A CT state is a pair of charged molecules bound with Coulombic force. The charges are not free. An additional energy is needed in order for the charges





Figure 12. Schematic representation of charge carrier generation in which (a) a CT state is produced indirectly following the photoexcitation to singlet Frenkel exciton state (S\*) and (b) the photoexcitation populates directly a CT state, which dissociates into charge carriers. The energy shift of the CT state due to external electric field is reflected in the electroabsorption while in (a) the absorption should be essentially insensitive to the electric field.

to separate. A classical discussion based on that first proposed by Lyons relates the energy of the charge carries with ionization energy and electron affinity of the material as well as with electrostatic polarization energy associated with the presence of a pair of charges in a condensed phase:

$$E = I - A - P - C \tag{10}$$

where I is the ionization potential, A is the electron affinity, Pis the polarization energy, and C is the Coulombic energy.<sup>25</sup> It has been known that in many organic materials P has a magnitude on the order of 1.5 eV.26

At this point it is interesting to note that there is a certain similarity between the dimeric structure found in highly photosensitive Pc's and systems which are known to undergo spontaneous ionization on photoexcitation.

In solution photochemistry photoinduced electron transfer is known to occur when, for example, bianthryl is photoexcited in a sufficiently polar solvent.<sup>27</sup> This compound is composed of a pair of identical (anthracene) molecules connected together with a covalent bond. It shows absorption spectrum similar to that of anthracene monomer. The neutral excited state which is generated by photoabsorption, however, rapidly relaxes into a charge-separated state, in which one anthracene moiety is positively charged while the other is negatively charged. This is only possible when the stabilization provided by polarization induced in the solvent environment is sufficiently large, so that the condition

$$I - A - P - C < 0 \tag{11}$$

is fulfilled.

This type of spontaneous ionization could also be involved in the primary step in photosynthesis. It has been known since the elucidation of the crystal structure of photosynthetic unit in rhodobacterium by Deisenhofer et al.<sup>28</sup> that the first act of charge separation occurs in the special pair which lies in the center of the photosynthetic unit. It is a pair of (seemingly identical) bacteriochlorophyll molecules, and recombination of charges which should be very fast, is efficiently suppressed by an arrangement of molecules which conduct electrons and holes to both ends of the protein structure which is embedded in the membrane. It is conceivable that in Pc's, as well as in those molecules mentioned above, the molecular environment provides with a large enough polarization energy which favors an ion pair state against a neutral (excited) dimer.

In conclusion we have studied structural and spectral features of some photoconductive GaPc's. Rietveld analysis has revealed that in ClGaPc-II and HOGaPc-XI Pc molecules are arranged in dimeric units with a specific molecular overlap which we believe is characteristic of most highly photosensitive Pc's. In all GaPc crystals studied, except for CH<sub>3</sub>OGaPc, which dose not belong to highly sensitive pigments, the longest wavelength absorption peak can be modulated by external electric field which indicates the CT nature of the final state of the transition. The amount of the CT character has been shown to correlate with the efficiency of photocarrier generation.

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#### **References and Notes**

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