

Photocarrier generation in metal-free phthalocyanines: Effect of the stacking habit of molecules on the photogeneration efficiency

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The photocarrier generation mechanism in metal-free phthalocyanines (H_2Pc) was studied by time-of-flight photoconductivity measurements. The quantum efficiencies of photogeneration of holes depend on the crystal structure of H_2Pc . The photogeneration efficiencies in X - and τ - H_2Pc are high compared with those of α - and β - H_2Pc . The lifetimes of the precursor state of free carriers in X - and τ - H_2Pc are between those of α - H_2Pc and β - H_2Pc . Moreover, infrared absorption and Raman spectra show that X - and τ - H_2Pc are intermediate states between α - H_2Pc and β - H_2Pc . It is pointed out that the photogeneration dynamics of H_2Pc is controlled by the intermolecular overlap of the π -electron wavefunctions and the stacking habit of molecules.

Recently, numerous organic photoconductive materials having high quantum efficiencies of photocarrier generation have been developed in order to produce high photosensitive photoconductor devices. These are phthalocyanines, squaraines, polyazo materials, polycyclic aromatics, and other compounds.^{1,2} However, the basic photogeneration mechanism in these photoconductors is poorly understood. The understanding of the photogeneration process would reveal a guiding principle for developing new photoconductive materials.

A typical class of high-photosensitive materials, phthalocyanines, has received considerable attention as charge generating materials in electrophotographic receptors and solar cells. Many features of the photogeneration of free charge carriers are explained by the geminate recombination theory of Onsager.^{3,4} The parameters used in the fitting are Y_0 and r_0 , the initial yield and spatial separation of thermalized electron-hole pairs, respectively. However, the relationship between two parameters and intramolecular and intermolecular properties is not yet clear.⁵ For example, the observed electric field dependence of the photogeneration efficiency shows very large thermalization lengths of the geminate pairs ($r_0 = 2$ -3 nm),^{2,6} although the charge transfer (CT) state due to the nearest-neighbor electron transfer is a plausible precursor of free charge carriers.⁷⁻⁹ The evolution process from an initial nearest-neighbor separation to the much larger thermalized-pair separation and the photogeneration efficiency depend on the intermolecular spacing and the stacking habit of molecules.

In this work, we used metal-free phthalocyanine (H_2Pc) as a prototypical organic photoconductor and studied the photocarrier generation in four polymorphic forms of H_2Pc in order to clarify effects of stacking of molecules on the photogeneration efficiency. It is pointed out that the structure of the nearest-neighbor molecules and the intermolecular overlap of the π -electron wavefunction determine the photocarrier generation in H_2Pc .

Metal-free phthalocyanine (H_2Pc) has been prepared in several polymorphic forms:² α (tetragonal), β (face centered monoclinic), X (hexagonal) and recently τ . α -, β -,

X -, and τ - H_2Pc characterized by x-ray diffraction were dispersed in a polyester matrix (Vylon 200, Toyobo) purified by repeated reprecipitation. These were coated on an aluminumized Mylar sheet to 0.2 μm (50 wt % H_2Pc :polymer) or 5 μm (20 wt % H_2Pc :polymer) thickness. Furthermore, a 0.2 μm α - H_2Pc film was deposited onto the Al Mylar sheet by vacuum evaporation. All 0.2 μm films were overcoated with a 10- μm charge transport layer (CTL) in order to amplify the transient photocurrent in the time-of-flight experiment. The CTL film was a solid solution of 50% *p*-diethylaminobenzaldehyde-diphenyl hydrazone in polycarbonate. In two-layer samples, a semitransparent gold electrode was finally deposited by vacuum evaporation.

The quantum efficiency of photogeneration of holes, $Y(E)$, is obtained by the potential discharge technique.⁶ In this method, the CTL surface was initially charged by corona, and then discharged by a 0.5- μs , 0.6- μm light pulse of 0.2 $\mu\text{J}/\text{cm}^2$. The temporal change in surface voltage was monitored by using an electrostatic voltmeter and a storage oscilloscope. The quantum efficiency $Y(E)$ is given by, $Y(E) = C\delta V/eN$, where C is the capacitance of the film, N is the absorbed photon number, e is the electric charge, and δV is the light-induced voltage drop.

In the delayed-collection-field (DCF) experiment, the two-layer structure films were illuminated through the gold electrode by a 0.6- μm , 0.5- μs flash pulse. The light pulse excited in the H_2Pc layer only in zero field and a high field of 3.5×10^5 V/cm was applied after a variable time delay t_d . This method can be used to study the time evolution of photogeneration.¹⁰

Figure 1 shows the quantum efficiency of photogeneration of holes $Y(E)$ in 5 μm H_2Pc single-layer films and two-layer films. The efficiency depends on the crystal structure: The efficiencies $Y(E)$ in X - and τ - H_2Pc are high compared with those in α - and β - H_2Pc . According to the Onsager theory, the parameters Y_0 and r_0 in X - and τ - H_2Pc are much larger than those of α - and β - H_2Pc . However, although α - H_2Pc exhibits a large carrier mobility,¹¹ the photogeneration efficiency in α - H_2Pc is low compared with other polymorphic forms. In Fig. 2, the collected charge

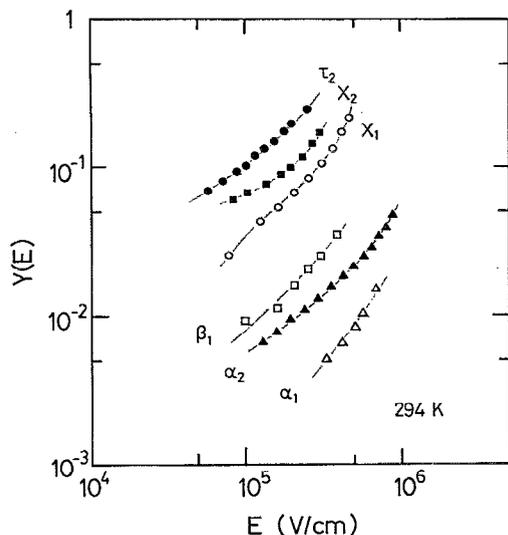


FIG. 1. Quantum efficiency of photogeneration of holes in metal-free phthalocyanines vs applied electric field. Greek letters show the crystal structure of phthalocyanines. The subscript numbers mean the sample structure: The subscript 1 denotes the single-layer structure and the subscript 2 denotes the two-layer structures.

signal Q obtained from the DCF experiment is plotted as a function of delay time t_d . No significant decrease in Q in β -H₂Pc was observed within 100 ms time delay. The lifetime of a precursor state of free-charge carriers in α -H₂Pc is shorter than other polymorphic forms. Here, we ascribe the precursor state to the CT state due to the nearest-neighbor electron transfer. It is regarded as the geminate charge pair separated by the nearest-neighbor intermolecular distance.^{8,9} The lifetime and structure of the initial CT state as well as the short-range carrier mobility play an important role in determining parameters of the Onsager theory, Y_0 and r_0 .

The infrared (ir) absorption spectra of α -, β -, X -, and τ -H₂Pc dispersed in KBr were measured using an ir spectrometer in order to study the structural difference among the four H₂Pc types. The N—H stretching absorp-

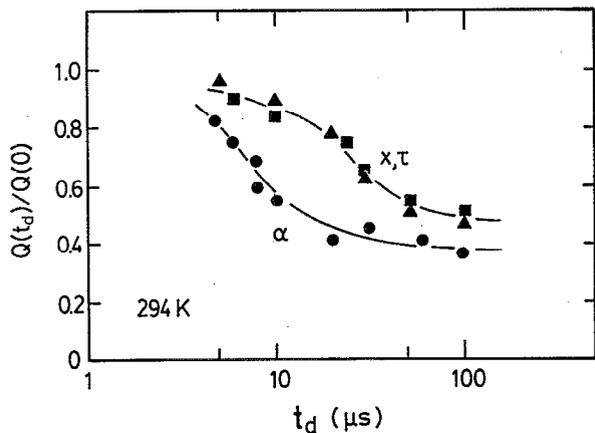


FIG. 2. Collected charge signals Q in α -, X -, and τ -H₂Pc vs delay time t_d .

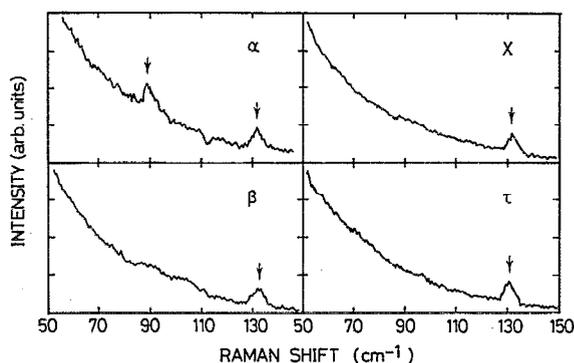


FIG. 3. Raman spectra of α -, β -, X -, and τ -H₂Pc in a low wavenumber region. Note that α -H₂Pc has an additional Raman peak at 89 cm⁻¹.

tion region near 3300 cm⁻¹ and the 700-800 cm⁻¹ region¹² were particularly sensitive for observing differences among the four crystal structures. The ir spectra of X - and τ -H₂Pc were similar to those of α -H₂Pc near 3300 cm⁻¹, but similar to that of β -H₂Pc in the 700-800 cm⁻¹ region: X - and τ -H₂Pc are intermediate states between α - and β -H₂Pc. Furthermore, Fig. 3 shows Raman spectra of α -, β -, X -, and τ -H₂Pc in a low wavenumber region. The intermolecular interaction and the stacking habit of molecules are considered to affect low-wavenumber Raman spectra. The sample powders were excited by a significantly attenuated 514.5 nm Ar laser (~ 1 W/cm²)¹³ in a vacuum under a quasibackscattering configuration. In α -H₂Pc, two peaks were observed at 89 and 132 cm⁻¹. On the other hand, in β -, X -, and τ -H₂Pc, only the peak at 132 cm⁻¹ was observed. At present, we cannot assign these peaks to characteristic vibrational modes. Raman spectra of α -H₂Pc significantly differ from those of other polymorphic forms. Furthermore, the time-resolved ir absorption experiment¹⁴ shows that the lifetime of triplet excitons in α -H₂Pc (10 μ s) is shorter than those in β - and τ -H₂Pc (100 μ s). It is therefore concluded that the stacking of molecules and electronic structure of X - and τ -H₂Pc bear some resemblance to those of β -H₂Pc rather than α -H₂Pc.

Let us now consider the relationship between the stacking habit of H₂Pc molecules and the photocarrier generation process. Normal projection of two parallel molecules is illustrated in Fig. 4. The electronic properties are related to the overlap between molecules. α -H₂Pc has a large intermolecular π wavefunction overlap resulting in a large carrier mobility. In β -H₂Pc, on the other hand, the intermolecular hydrogen (N—H) bonding is formed and the intermolecular π wavefunction overlap is small.¹⁵ Consequently, β -H₂Pc exhibits a low carrier mobility. As mentioned above, the stacking of molecules in X - and τ -H₂Pc is between that of α - and β -H₂Pc, and the structure of X - and τ -H₂Pc bears some resemblance to that of β -H₂Pc. However, the photogeneration efficiencies in X - and τ -H₂Pc are an order of magnitude higher than those in β -H₂Pc. These results imply that the photogeneration process in H₂Pc is very sensitive to the degree of the intermolecular overlap of π electron wavefunctions. Moreover, Sharp and Lardon¹²

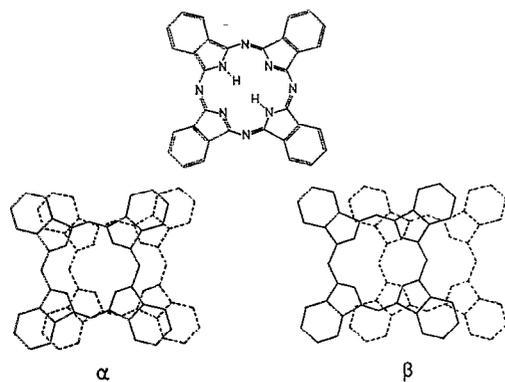


FIG. 4. Normal projection of two parallel molecules in α - and β - H_2Pc . Solid and dotted lines outline the upper and the underlying molecules, respectively.

proposed that $X-H_2Pc$ has a dimer structure. The initial charge separation due to the nearest-neighbor electron transfer is enhanced and the precursor CT state of free carriers is stable in the dimer structure of $X-H_2Pc$. Therefore, the initial yield Y_0 is very high. Since there is no significant difference in photoelectronic properties between X - and τ - H_2Pc , τ - H_2Pc may have a dimer structure like $X-H_2Pc$. We point out that the overlap of the intermolecular wavefunction and the structure of the nearest-neighbor separation charge pairs control the photocarrier generation in H_2Pc .

In conclusion, we have shown that the quantum effi-

ciency of photocarrier generation in metal-free phthalocyanines is very sensitive to the stacking habit of metal-free phthalocyanine molecules. It is pointed out that the intermolecular overlap of the π electron wavefunctions and the stacking habit of molecules control the photoconduction dynamics of H_2Pc . Organic photoconductors having a stable initial CT state due to the nearest-neighbor electron transfer are expected to exhibit high photogeneration efficiencies.

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