# Time-Resolved Absorption Study on the Photocarrier Generation Process in Layered Organic Photoreceptors: A Role of Delocalized Holes in Photocarrier Generation

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## Abstract

We have applied time-resolved absorption spectroscopy to the study on the photocarrier generation process in layered organic photoreceptors. The photoreceptors are comprised of azo-pigments as charge generation materials (CGMs) and charge transport materials (CTMs). Two or three distinct transient absorptions ranging from visible to mid-infrared wavelength region (600 – 2500 nm) were observed after photoexcitation in these photoreceptors. We ascribed all these transients to the cationic species of CTMs from the results of the measurements in various conditions. The transient absorption spectrum showed remarkable dependence on the CTM concentration. From this observation, we concluded that the cationic species of CTMs were monomer, dimer and larger aggregate cations. The latter two cationic species are regarded as the holes delocalized within some CTM molecules. The role of delocalized holes in photocarrier generation is discussed from the decay dynamics.

## Introduction

Photocarrier generation in an organic photoreceptor consists of many complicated processes (exciton formation, migration, excited state electron transfer, recombination, and trapping), and each step can contribute to the total sensitivity as a photoreceptor. Among these fundamental processes, some may have large contribution to the sensitivity and the other not. Therefore it is very important to observe each process directly and clarify how much each process contributes to the sensitivity. However, these matters are not completely understood in spite of a lot of studies.

So far, we have investigated these processes in the carrier generation mechanism by thermally stimulated current (TSC)[1] and time-resolved fluorescence[2-4] techniques. When we used the photoreceptors comprised of azo pigments for charge generation materials, TSC study showed the formation yield of bound ion-pairs between charge generation materials (CGMs) and charge transport materials (CTMs) influenced the sensitivity of the photoreceptor. In time-resolved fluorescence measurement, we observed that the CTM considerably shortened the lifetime of CGM excitons.[4] We ascribed this quenching phenomenon to the exciplex-like interaction between CGM excitons and CTMs. We also found that this fluorescence quenching efficiency could be qualitatively correlated with the photosensitivity. These two studies strongly suggest 'CTM-assisted' charge generation.[1,4]

Even though these techniques have revealed the photo carrier generation process to a certain extent, they were not direct observation of carrier species. Photocurrent analysis including TSC measurement does not provide the molecular nature of a charge carrier (geminate ion-pair, free and trapped carriers *etc*.). Time-resolved fluorescence study can provide the molecular nature, however, the monitored species are CGM excitons, which are precursors of charge transfer reaction between a CGM and a CTM. Therefore, for further investigation of charge generation and transport processes, we need the precise and direct study of transient species generated from CGM excitons and CTMs.

Time-resolved absorption technique is a very powerful tool for probing such ionic transient species.[5,6] However, the application of this technique to the photoreceptor systems has not been easy. One of the difficulties is derived from a damage of the samples by intense laser excitation. Furthermore, intense laser excitation often changes the dynamics of transients.

At the last conference (NIP 18), we reported the application of our highly sensitive time-resolved absorption system to the observation of charge generation.[7] We observed the transient absorption in near-IR range after pulse excitation and assigned this absorption to delocalized holes in CTM molecules.

In the present work, we expanded probe light window from the near-IR region (1000 - 2500 nm) to visible region (600 – 1000 nm) to examine the transient species more precisely. We also examined the difference in the decay of the transient absorption for different combination of CGMs and CTMs in order to investigate the role of this transient species in carrier generation processes.

## Experimental

### Sample Preparation

Figure 1 shows the molecular structures of CGMs[8] and CTMs used in this study. Layered samples were prepared on $CaF_2$ plates by spin-coating method. The charge generation layer (CGL) contained 50wt% CGM dispersed in poly(vinylbutyral), and the charge transport layer (CTL) contained 3-50wt% CTM dispersed in polycarbonate. The CTM concentrations were changed in order to examine concentration dependency.

### Transient Absorption

We used the similar systems and procedures reported by Iwata et al.[5] and Yamakata et al.[6] for transient absorption spectrum measurement. The detail experiment setups and procedures are described elsewhere.[5-7] Briefly, the light emitted from a halogen lamp was focused on the sample plate with ellipsoidal mirrors. The transmitted light was dispersed in a monochromator (JASCO, CT50TF) of 50cm focal length. The monochromatic output was detected by a low-noise photovoltaic MCT detector (Kolmer; for 1000 – 2500 nm measurement) or Si-PIN photodiode (S-5971 Hamamatsu; for 600 - 1000 nm measurement). The signal output was amplified in AC-coupled amplifiers and accumulated in a digital sampling oscilloscope (Lecroy, LT342L) as a function of delay time at a fixed wavelength. The temporal profiles were reconstructed to transient absorption spectra at different delay times. The time-resolution of the instruments was about 50 ns. Excitation pulse was frequency-mixed output (525nm, 120fs pulse) of the OPG/OPA pumped by an amplified Ti:Sapphire laser. The pulse energy was varied in the range 0.1-2 μJ at the sample point (3 - 60 $\mu J/cm^2$). Transient absorbance change as low as $10^{-6}$ was detected by signal averaging at 1KHz. All the measurements in this study were conducted without external electric field.

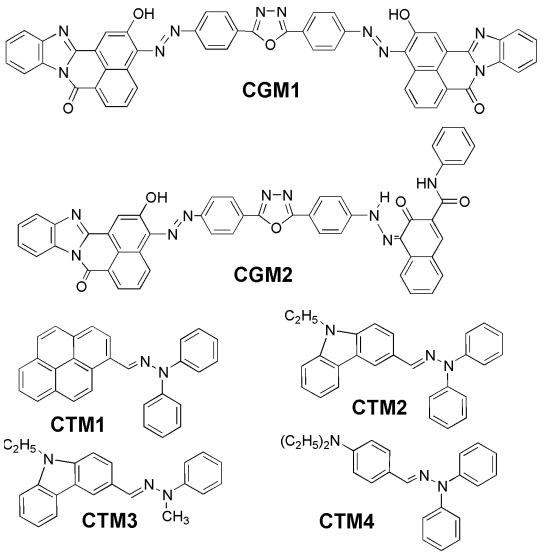


*Figure 1. Charge generation materials (CGM) and the charge transport materials (CTM) used in this study.*

## Results and Discussion

Figure 2 shows the transient absorption spectra of CGM1/CTMx (x = 1, 2, 3) layered samples after the photo irradiation of 525 nm laser pulse. A broad transient absorption was observed in the near-IR range (1000 - 2500 nm). It has been reported that aggregate cations of many aromatic compounds give transient absorption in near-IR region due to charge resonance band.[9] Therefore, we attributed this transient absorption to the cationic species of CTMs.[7] We have already reported the transient absorption for CGM1/CTM4 layer.[7] The transient absorption was similar to those of CTM2 and CTM3. However, the differential absorbance was far smaller than those of CTM2 and CTM3, and the data was difficult to use for further discussion. Therefore, we eliminate the data for CTM4 in this paper.

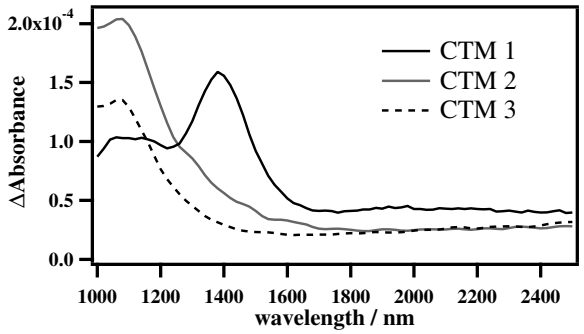


*Figure 2. Transient absorption spectra of CGL1/CTLx layers*

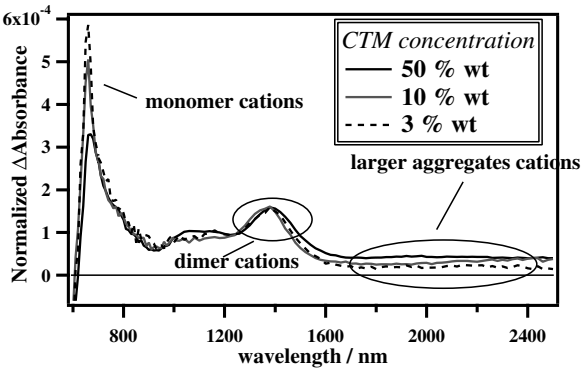


*Figure 3. Transient absorption spectrum of the CGM1/CTM1 layer in the VIS ~ near-IR range at various CTM concentrations.*

To examine the transient species more precisely, we expanded probe light window to visible region (600 – 1000 nm) for the CGM1/CTM1 sample. Figure 3 shows the transient absorption spectrum of the CGM1/CTM1 layer in the VIS ~ near-IR range (600 - 2500 nm). The dependence of the spectrum on the CTM concentration is also shown. There are three distinctive transient absorption in the figure 3; a peak around 700 nm, a peak around 1400 nm and broad unstructured absorption around 2000 nm. The intensities of these three absorption show explicit concentration dependence. If we normalize the spectrum at 1400 nm, the relative intensity of the peak around 700 nm becomes smaller at higher concentration of CTM. On the contrary, the broad absorption around 2000 nm becomes larger at the higher concentration of CTM. Since we can expect larger aggregates of CTM molecules at higher concentration of CTM, we now ascribe these three absorption to monomer (for the peak around 700 nm), dimer (for the peak around 1400 nm) and larger aggregate (for broad absorption around 2000 nm) cations, respectively.

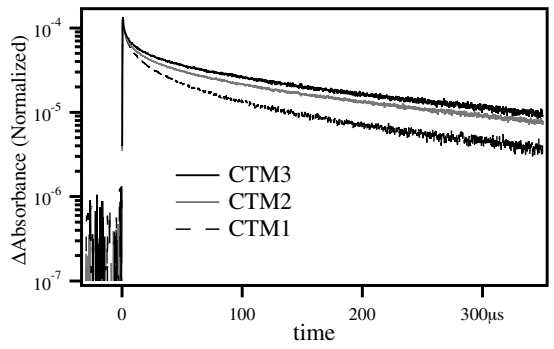


*Figure 4. Comparison of the transient absorption decay of CGM1 /CTMx (x = 1, 2, 3) at 1200 nm.*

Figure 4 shows the transient absorption decay of CGM1/CTMx (x = 1, 2, 3) at 1200 nm. All the signals were approximately fitted by a sum of two exponential functions. The signal decay considerably depended on CTM species. We found that the decay speed (signal lifetime) had strong relation to the drift mobility of CTM (Table 1). First of all, the signal of a CTM that has larger drift mobility decayed faster. In addition, the lifetime of the second exponential function was more dependent on the drift mobility than that of the first exponential function. From these observations, we presume that the decay processes, especially the second exponential component, are governed by the migration of holes in the CTL or the CTL/CGL interface.

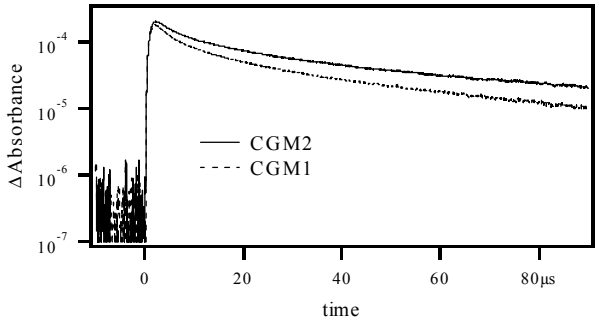


*Figure 5. Comparison of the transient absorption decay of CGMx/CTM (x = 1, 2) at 1400 nm.*

**Table 1. Preexponential parameters and lifetimes determined from the fitting ($A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$) with drift mobility.**

| | CGM1/CTM1 | CGM1/CTM2 | CGM1/CTM3 |
|---|---|---|---|
| $A_1$ [a] | 0.41 | 0.45 | 0.36 |
| $A_2$ | 0.59 | 0.55 | 0.64 |
| $\tau_1$/μs | 6.1 | 6.7 | 7.1 |
| $\tau_2$/μs | 69 | 97 | 110 |
| Drift mobility [b] ($10^{-6}$ $cm^2$/Vs) | 8.5 | 3.8 | 0.66 |

a. The values are normalized, as the sum of $A_1$ and $A_2$ becomes unity.
b. The drift mobility values are taken from ref. 10

**Table 2. Initial intensities and lifetimes determined from the fitting ($A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$) with photoconductive sensitivity.**

| | CGM1/CTM1 | CGM2/CTM1 |
|---|---|---|
| $\tau_1$/μs | 6.1 | 6.6 |
| $\tau_2$/μs | 69 | 81 |
| Initial intensity [a] ($A_1$+$A_2$) | 1.00 | 1.18 |
| Photoconductive Sensitivity [b] ($cm^2$/μJ) | 4.0 | 4.8 |

a. Relative intensity
b. Reciprocal half-decay exposure from 700V, by monochromated light (525nm)

Figure 5 shows the transient absorption probed at 1400 nm of CGM1/CTM1 and CGM2/CTM1 obtained under the same experimental condition. We found that the initial intensity and the decay rate of the transient absorption correlated with the photoconductive sensitivity (Table 2). The initial intensity reflects the amount of cationic species of CTM right after photoexcitation. Therefore it is quite understandable that it correlates with photoconductive sensitivity. Furthermore, decay rates also correlate with photoconductive sensitivity. If the decay processes were governed only by the migration of holes in the CTL, the decay would not depend on CGM. However, this is not the case. The CGM also affects the decay rate. This suggests that the decay processes could be governed also by charge recombination between a CTM cation and a CGM anion under zero electric field. Slow charge recombination seems to one of the important factors that contribute to high sensitivity. From the discussion above, we can say the total photoconductive sensitivity could be determined by amounts of the CTM cationic species formation and the charge recombination rate.

Here we consider the relationship between the cationic species of CTMs detected by transient absorption and the current transients detected by transient photocurrent (TRC) measurements with delayed collection field (DCF) technique.[1] TRC measurements showed that the carrier (collected by applied electric field) had several seconds lifetime under no external field. On the contrary, the transient absorption disappeared within one millisecond over the all wavelength measured. Meanwhile, we can assume that the majority of an excitation pulse was consumed for the formation of the cationic species of CTMs because a weak excitation pulse gave such a large transient absorption. For these reasons, we tentatively assume that cationic species of CTMs are precursors of the current transients detected by TRC, which are not optically detectable.

From the results of this work and our former works, we suggest that carrier generation in layered organic photoreceptor take place through the following processes.

(i) Formation of cationic species of CTM and anionic species of CGM by electron transfer between CTM molecules and excited CGM molecules. These cationic species of CTM give the transient absorption.
(ii) The cationic species of CTM recombine with the anionic species of CGM or change into the stable cations. This process takes place within one millisecond.
(iii) The stable cations play a role of free carriers when external electric field is applied.
(iv) These stable cations have lifetime of several seconds without external electric field and do not have transient absorption.

Now we are conducting the transient absorption measurement under applied electric field in order to support our model.

## Summary

Photocarrier generation processes of organic photoconductors were investigated by the time-resolved spectroscopy. A broad transient absorption was observed in the visible ~ near-IR range (600 - 2500 nm) after a photoexcitation. We ascribed this transient species to the cationic species of a charge transport material (CTM), namely the delocalized holes among some CTM molecules. From the dependence of transient absorption spectra on the concentration, it was suggested that the cationic species of CTM contain monomer cations, dimer cations and larger aggregate cations.

From the decay dynamics, we presumed that these cationic species decayed through both the migrations of holes in the CTL and charge recombination between a CTM cation and a CGM anion. We also assumed that these cationic species were precursors of the current transients detected by TRC measurements.

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## Biography

**Kan Takeshita** received his M.S. degree in physical chemistry from Kyoto University in 2001. Subsequently, he joined CACs Inc., the analytical subsidiary of Mitsubishi Chemical Corporation. He is also working as a visiting researcher at Kanagawa Academy of Science and Technology since 2002. He has worked on physical chemistry, especially photo and electric properties, of organic and inorganic molecules including important industrial materials by use of various techniques of laser spectroscopy.