Time-resolved Spectroscopic Study on Photocarrier Generation Process in Layered Organic Photoconductors

Kan Takeshita, Yutaka Sasaki, and Tetsuo Murayama

Mitsubishi Chemical Group Science and Technology Research Center, Inc.,
1000, Kamoshida-cho, Aoba, Yokohama 227-8502, Japan

(Received 26 October 2004; Accepted 7 January 2005; Published 19 January 2005)

As a model for electron processes in organic thin films, carrier generation after photoexcitation of organic photoconductors was studied by the time-resolved infrared spectroscopy. A broad transient absorption was observed in the IR range after a photocarrier generation. We ascribed all these transients to the cationic species of a charge transport material (CTM) 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. Based on these observations, carrier generation mechanism in organic photoconductors is discussed. [DOI: 10.1380/ejssnt.2005.24]

Keywords: Laser methods; Infrared absorption spectroscopy; Electrical transport; Organic photoconductor

I. INTRODUCTION

Recently, considerable interest has been focused on optical and electronic properties of thin films of organic semiconductors, because they have a variety of applications such as organic photoreceptors, solar cells, light emitting devices, thin film transistors [1–4]. Among many processes that happen in organic semiconductors, carrier generation and transport play important roles to determine the performance of devices. Thus, understanding and controlling the carrier generation and transport behaviors are critical in designing all electronic and optoelectronic devices based on organic molecules.

Time-resolved absorption technique is a very powerful tool for investigating such processes, because it can directly observe carrier species in the time-resolved manner. However, the application of this technique to thin organic films 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.

The authors and other co-workers have developed a system which can detect transient absorbance change as small as $10^{-6}$ over a wide wavelength range (700-10000 nm) and also over a wide range of delay time (50 ns - 1 s) [5–7]. This sensitive system enabled us to detect carrier species with a weak excitation light. The greatest advantage of employing IR light for probing is that the absorption signal from carrier species is not obstructed by other sources. Carrier species also give transient absorption in the visible region, but the bleach signals of ground state molecules or emission from excited molecules falls on the target signal. For this reason, the IR region is more appropriate than the visible region for the present purpose.

In the present study, we applied our time-resolved infrared (TRIR) system to some organic photoconductors (OPC) and investigated the dynamics of photogenerated charge carriers. Organic photoconductors have been widely used in electrophotographic printers and copiers. Nowadays, over 99% of photoreceptor products are organic photoreceptors. The first organic photoreceptor was a single layered photoconductor based on poly-N-vinylcarbazole and 2,4,7-trinitrofluorenone (PVK/TNF) [8]. Then dual layered photoconductors were developed and produced. In these photoconductors, the function of photogeneration is separated from the charge carrier transport function [9, 10]. We can use a lot of combination of charge generation materials (CGM) and charge transport materials (CTM) to improve the performance of OPC. The typical structure of an OPC is shown in Fig. 1.

FIG. 1: Structure of a typical dual layered organic photoconductor. The abbreviations CGL and CTL stand for ‘charge generation layer’ and ‘charge transport layer’, respectively. A CGL is composed of charge generation materials and binder polymers and a CTL is composed of charge transport materials and binder polymers.
FIG. 2: Charge generation materials (CGMs) and the charge transport materials (CTMs) used in this study.

OPCs are good models for organic thin films to apply time-resolved absorption technique, because photocarrier generation step in an OPC consists of many complicated processes (exciton formation, migration, excited state electron transfer, charge generation, recombination, and trapping). Even more importantly, to elucidate these electronic processes in molecular level will be helpful for designing more efficient organic photo-electronic devices as well as OPCs.

Here we report our direct observation of transient species in OPCs after photo excitation. As far as we know, this is the first observation of transient absorption spectra of OPCs in extremely wide range of wavelength. We discuss the nature of ionic transient species generated in OPCs.

II. EXPERIMENTAL

A. Sample preparation

Figure 2 shows the molecular structures of CGMs and CTMs used in this study. Layered samples were prepared, as a CGM solution and a CTM solution were successively spin-coated on CaF$_2$ plate. The charge generation layer (CGL) contained 50 wt% of CGM particles dispersed in poly(vinylbutyral), and the charge transport layer (CTL) contained 3-50 wt% of a CTM dissolved in polycarbonate.

The concentration of CTM solutions was changed in order to examine concentration dependency. Both CGL and CTL had a thickness of roughly 1 µm.

B. Transient IR Absorption

We used a similar system and procedure reported by Iwata et al. for transient IR absorption spectrum measurement [5]. Briefly, IR light emitted from a halogen lamp or a globe lamp was focused on the sample plate with ellipsoidal mirrors. (The halogen lamp and the MoSi$_2$ infrared source were used for 1000-2500 nm and 2500-10000 nm regions measurement, respectively.) The transmitted light was dispersed in a monochromator (JASCO, CT50TF) of 50 cm focal length. Gratings of 600, 300 and 150 grooves/mm were used for 700-1000, 1000-5000 and 5000-10000 nm measurements, respectively. The monochromatic output was detected by a low-noise photovoltaic MCT (mercury-cadmium-telluride) detector. The MCT 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 IR absorption spectra at different delay times. The time-resolution of the instruments was about 50 ns. Excitation pulse was frequency-mixed output (525 nm, 120 fs pulse) of the OPG/OPA pumped

http://www.sssj.org/ejssnt (J-Stage: http://ejssnt.jstage.jst.go.jp)
FIG. 3: (A) Transient absorption spectra of CGM1 (solid line) and CGM2 (dotted line) overcoated with CTM1. (B) Transient absorption spectrum of CGM1 overcoated with CTM1 (solid line), CTM2 (dotted line) or CTM3 (dashed line).

by an amplified Ti:sapphire laser. The pulse energy was varied in the range 0.1-2 µJ at the sample point (3-60 µJ/cm²). Transient absorbance change as low as 10⁻⁶ was detected by signal averaging at 1 KHz.

III. RESULTS AND DISCUSSIONS

A. The transient absorption spectra

When the OPC samples were excited by 525 nm laser pulse, a broad transient absorption was observed in the IR range (700-10000 nm). Figure 3A and 3B show the transient absorption spectra of various CGM/CTM combinations layered samples. A broad transient absorption was observed in the near-IR range (700 - 2500 nm). A weak and structureless absorption was also observed in mid-IR region (2500-10000 nm) like as in 1600-2500 nm region (data not shown). Since the CTM has no absorption at the excitation wavelength, the excitation pulse is absorbed only by the CGM. We also measured time-resolved IR spectrum of a CGM monolayer and no transient absorption was observed in this region. Consequently, the absorption in these figures is clearly attributed to the chemical species produced by the interaction between the CGM and the CTM.

B. The assignment of the IR absorption

When we measured the two CGMs overcoated with the same CTM (CTM1), almost the same spectra were observed (Fig. 3A). However, when we changed the CTMs and used the same CGM, fairly different spectra were observed (Fig. 3B). These observations mean the shapes of transient absorption spectra depend only on CTMs. Therefore, transient absorption is ascribed to some transient species originated from CTM. In the OPC sample, an initial ion-pair is formed between a CGM and a CTM (charge separation state), after the photon absorption by CGM molecules. And then the ion-pair separates into free carriers or disappears through recombination. From this point of view, this transient species could be assigned to cationic species of CTMs.

The absorption of the aggregate ion radicals of some aromatic compounds was reported previously [11, 12]. For example, the absorption maxima of characteristic bands of the unrelaxed dimer cations of naphthalene and pyrene are situated at about 2100 and 1600 nm, respectively [11]. Figure 4 shows the transition that corresponds to near-IR absorption. This transition is called a ‘charge resonance band’ (CR). At this moment, we ascribe the absorptions that reach the peaks at 1400 nm in CTM1, at 1100 nm in CTM2 and at 1600 nm in CTM3 to the CR band of the CTM dimer cations. The difference of absorption peaks was presumably originated from the difference of the interaction strength or intermolecular distance between CTM molecules.

C. The concentration dependence of the transient absorption spectra

The cationic species of CTMs observed by transient absorption are possibly CTM cations, CTM dimer cations, or larger aggregates including tetramer di-cations and trimer cations. To identify what species contribute to the observed spectra, we measured the dependence of transient absorption spectra on the concentration of CTMs in CTL. We can expect larger aggregations of CTM
molecules at higher concentration of CTMs.

Figure 5 shows the transient absorption spectrum of the CGM1 / CTM1 layer, where the concentration of CTM1 in CTL was changed from 3 wt% to 50 wt%. The absorption intensities are normalized, as the intensities at 1400 nm are the same in all the spectra. There were three distinctive transient absorptions in Fig. 5; a peak around 700 nm, a peak around 1400 nm and broad unstructured absorption around 2000 nm. The intensities of these three absorptions showed explicit concentration dependence. The relative intensity of the peak around 700 nm became smaller at higher concentration of CTMs. On the contrary, the broad absorption band around 2000 nm became larger at higher concentration of CTM. Since we can expect that larger aggregates of CTMs increase at higher concentration of CTMs, we now ascribe these three absorption bands 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.

The dimer cations peak observed around 1400 nm slightly spread to the longer wavelength at high CTM concentration. There are two possible reasons for this peak change.

( A ) The absorption of larger aggregate cations overlapped the dimer cations peak. Therefore, the peak seemingly spread to the long wavelength region particularly at high CTM concentration.

( B ) The CTM concentration affected the environment where CTM dimer cations existed. The absorption of dimer cations was dependent on that environment.

In either case, this slight peak change has little influence on the validity of our peak assignment.

The small peak observed around 900-1100 nm can not be precisely assigned to a specific cation at the present time. It is common that every CTM gave the peak in this region (Fig. 3B). One possible explanation is that larger aggregate cations, which are larger than dimer cations, have absorption in this region other than around 2000 nm, because the relative intensity of this peak became larger at high CTM concentration. However, we need further evidence for more accurate assignment.

D. The decay profile of the IR absorption

The decay measurement and analysis of the transient absorption are helpful to investigate kinetics of photogenerated carriers. Figure 6 depicts the decay of near-infrared transient absorption in some combinations of CGMs and CTMs. The signals rose quickly after the excitation and decayed non-exponentially in microsecond range. The
TABLE I: The parameters used for the fitting of the decay curves at three different excitation energies.

| Laser energy (μJ/pulse) | A₀    | n₀γ/s⁻¹ | k/s⁻¹  |
|------------------------|-------|---------|--------|
| 0.19                   | 1.14×10⁻⁴ | 1.28×10⁵ | 8.02×10³ |
| 0.99                   | 4.38×10⁻⁴ | 1.94×10⁵ | 7.98×10³ |
| 2.13                   | 7.14×10⁻⁴ | 2.49×10⁵ | 7.68×10³ |

FIG. 7: Transient absorption decay at 1400 nm of a CGM1/CTM1 film under the different excitation energies: (a) 2.13 μJ/pulse, (b) 0.99 μJ/pulse, and (C) 0.19 μJ/pulse. Break lines show the measured signals and the solid lines show the fittings.

The decay curve of transient absorption contained two components; a fast (some microsecond) and a slow (tens of microsecond) component. When we varied the excitation light energy, this profile changed as shown in Fig. 7. Because the fast decay rate appears to have excitation intensity dependence, it is considered to represent a bimolecular process such as exciton-exciton annihilation. The slower decay is rather independent of excitation intensity and is attributed to a monomolecular decay without interaction between excitons.

If we assume a constant decay rate via bimolecular annihilation processes (we denote it as γ) and a constant decay rate without interaction between excitons (we denote it as k), the exciton density n(t) at the time t after delta function pulse excitation is

\[ n(t) = \frac{n₀ \exp(-kt)}{1 + (n₀γ/k)(1-\exp(-kt))}, \]

where \( n₀ \) is the initial exciton density at time zero. In the present case, monomolecular decay probably implies geminate recombination between a CGM anion and a CTM cation, and bimolecular decay implies non-geminate recombination. Because the intensity of the transient absorption \( A(t) \) is proportional to the exciton density, \( A(t) \) is expressed as

\[ A(t) = \frac{A₀ \exp(-kt)}{1 + (n₀γ/k)(1-\exp(-kt))}, \]

where \( A₀ \) is a proportional constant. We can fit all the range of data in Fig. 7 with this equation. The fitting parameters are listed in Table 1.

E. Discussion on charge generation mechanism

The carrier generation mechanism in OPCs has been also investigated by other photo-electronic methods, such as a thermally stimulated current (TSC) technique [13] and transient photocurrent (TRC) measurements with delayed collection field (DCF) [14]. Here we consider the relationship between the cationic species of CTMs detected by transient absorption and the current transients detected by other methods.

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. For these reasons, we tentatively assume that cationic species of CTMs observed by the spectroscopic method are precursors of the current transients detected by TRC, which are not optically detectable. From the results of this work and the former works, we presume that carrier generation in layered organic photoreceptor based on azo-pigment CGM takes 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.

IV. CONCLUSIONS

In conclusion, photocarrier generation processes of organic photoconductors were investigated by the time-resolved spectroscopy. A broad transient absorption was...
observed in the IR range after a photoexcitation. We ascribed this transient species to the cationic species of a charge transport material (CTM), namely the delocalized holes within 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. We also assumed that these cationic species were precursors of the current transients detected by TRC measurements.

[1] C. W. Tang, S. A. Van Slyke, Appl. Phys. Lett. 51, 913 (1987).
[2] J. H. Burroughs, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. B. Holmes, Nature 347, 539 (1990).
[3] S. R. Forrest, IEEE J. Sel. Top. Quantum Electron. 6, 1072 (2000).
[4] D. Schlettwein, Supramolecular Photosensitive and Electroactive Materials, pp. 211-338, (Academic Press, San Diego, 2001).
[5] K. Iwata, H. Hamaguchi, Appl. Spectrosc. 44, 1431 (1990).
[6] A. Yamakata, T. Ishibashi, H. Onishi, J. Phys. Chem. B 105, 7258 (2001).
[7] K. Takeshita, Y. Sasaki, M. Kobashi, Y. Tanaka, S. Maeda, A. Yamakata, T. Ishibashi, H. Onishi, J. Phys. Chem. B 107, 4156 (2003).
[8] R. M. Shaffert, IBM J. Res. Develop. 15, 75 (1971).
[9] D. M. Pai, B. E. Springett, Reviews of Modern Physics, 65, 163 (1993).
[10] P. M. Borsenberger, D. S. Weiss, Organic Photoelectroreceptors for Xerography, (Merel Dekker, New York, 1998).
[11] A. Kira, M. Imamura, T. Shida, J. Phys. Chem. 80, 1445 (1976).
[12] Y. Tsujii, A. Tsuchida, Y. Onogi, M. Yamamoto, Macromol. 23, 4019 (1990).
[13] T. Shoda, S. Aramaki, T. Murayama, Proceedings for 13th International Conference on Digital Printing Technology, pp. 220-223 (The Society for Imaging Science and Technology, 1997).
[14] S. Aramaki, T. Shoda, T. Murayama, Jpn. J. Appl. Phys. 43, 659 (2004).