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

Yutaka Sasaki and Kan Takeshita
Center for Analytical Chemistry and Science (CACs), Inc., Yokohama, Japan

Takayuki Shoda and Tetsuo Murayama
Mitsubishi Chemical Corporation, Science and Technology Research Center
Yokohama, Japan

Abstract

We applied highly sensitive time-resolved absorption spectroscopy to the study on the electronic structures and dynamics of ionic transient species in layered organic photoreceptors. Long-lived transient absorptions assignable to the cationic species of charge transport materials (CTMs) were observed in the visible, near- and mid-infrared wavelength regions. The bands in infrared region can be ascribed to the delocalized holes within some CTM molecules. We discuss the nature of ionic transients generated in photoreceptors.

Introduction

We reported the thermally stimulated current (TSC) study on the carrier generation process in layered photoreceptors comprised of azo pigments, as charge generation materials (CGMs), and charge transport materials (CTMs).[1] It was known that the sensitivity of this type of photoreceptors varied depending on the combination of CGMs and CTMs. Concerning the sensitivity, extrinsic carrier generation via the electron transfer from CTMs to CGM exciton was proposed. The result of our TSC study suggested that the formation yield of bound ion-pairs (CGM^-/CTM^+) contributed the sensitivity of the photoreceptors.

It was reported that the quenching efficiency of azo-CGM fluorescence by CTMs was well in accordance with the quantum efficiency of carrier generation.[2] We reported the result of time-resolved fluorescence study on primary process in photocarrier generation.[3] Efficiencies of CGM fluorescence quenching by CTMs could not be correlated with the sensitivities in all the combination of CGLs and CTLs. It was suggested that the exciplex-like interaction between CGM exciton and CTMs caused the fluorescence quenching and that the fluorescence quenching efficiency was not directly correlated with the ion-pair formation yield.

For further investigation on charge generation process the precise study of transient species generated from CGM exciton and CTM is required. 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 absorption technique is a very powerful tool for probing such transients as ionic species One of the difficulties in time-resolved absorption measurement is derived from a damage of the samples by intense laser excitation, and intense excitation often changes the dynamics of transients. Our highly sensitive measurement system makes it possible to acquire transient absorption data by very weak excitation.

This is the first observation of transient absorption spectra of organic photoreceptors in extremely wide range of wavelength. We discuss the nature of ionic transients generated in photoreceptors.

Experimental

Molecular structures of two azo pigments and three CTMs are shown in Fig. 1. The charge generation layer (CGL) contains 50wt% azo CGMs dispersed in poly(vinylbutyral). The charge transport layer (CTL) is a 50 wt% solid solution of CTMs in polycarbonate. CGL and CTL were successively coated on CaF_2 substrates. The sample thickness was typically 10 μm. Hereafter, CGL*n* and CTL*n* designate CGL including CGM*n* and CTL including CTM*n* respectively.

Time-resolved infrared absorption spectra were measured with a home-built spectrometer (Fig. 2). This system is similar to that reported previously and transient absorbance change as small as 10^{-6} can be detected by using this system.[4] In addition, we extended the spectral sensitivity to near-infrared and visible regions. $MoSi_2$ infrared light source or halogen lamp was used for probing. Frequency-mixed output (525 nm) of the OPG/OPA (1527 nm), pumped by an amplified Ti:sapphire laser (TiS), and a fundamental of TiS (800 nm) was used as an excitation source. Typical excitation power was below 1 μJ/pulse (32 μJ/cm^2). All the measurements were performed under no applied electric-field.

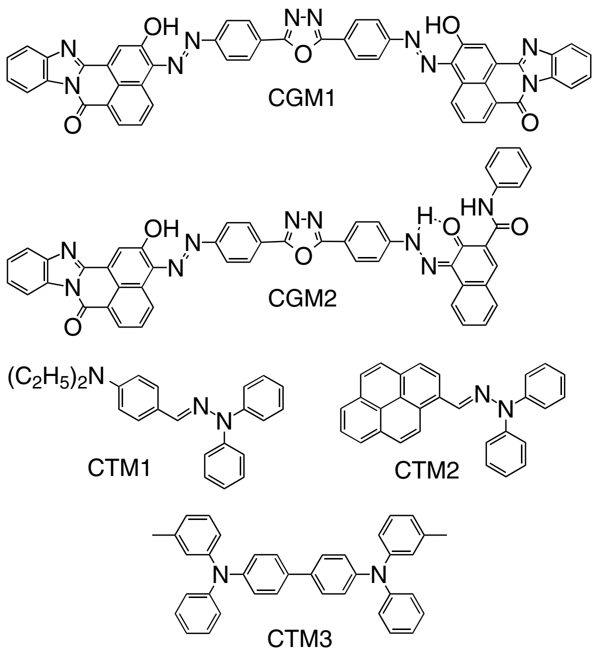

Figure 1. Molecular structures of two CGMs and three CTMs

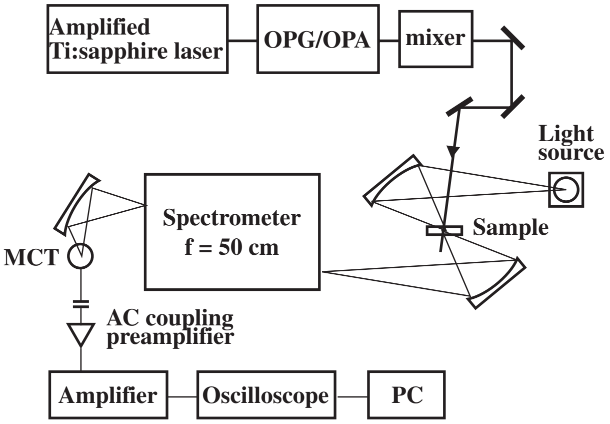

Figure 2. Time-resolved absorption apparatus

Results and Discussions

Figure 3 shows the transient absorption spectra of photoreceptors comprised of CGL1 and three CTLs. Absorption bands ranging from 1000 to 2500 nm are clearly seen in these spectra. Also in visible region shorter than 700 nm and mid-infrared region up to 10,000 nm, CTM-dependent transient absorption was obtained. In a single CGL sample, no absorption was observed in this spectral range. The decay dynamics of near-infrared transient absorption at 1100 nm in photoreceptors composed of CGLs and CTLs designated are compared in Fig. 4. The transients have lifetimes in μsec range and they vary depending on the combination of CGLs and CTLs.

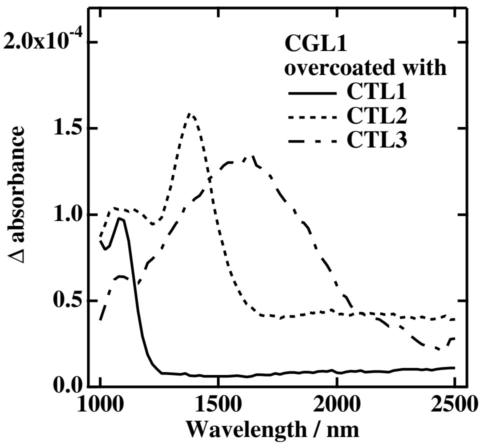

Figure 3. Transient near-infrared absorption spectra of CGL1 overcoated with CTL1, CTL2 and CTL3

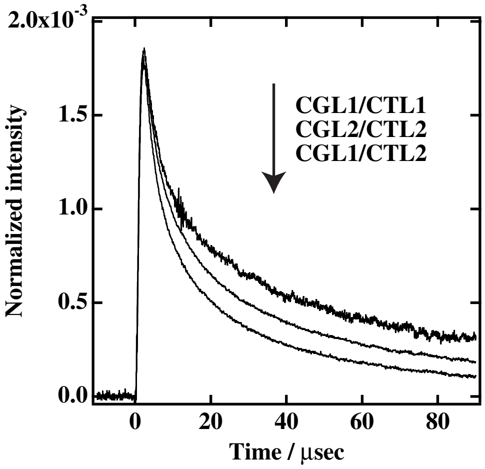

Figure 4. Temporal profiles of near-infrared absorption

It has already been reported that the cations of some hole transport molecules possess the visible absorption.[5] Transient absorptions in near-infrared regions have been reported for the excimer and exciplex (CT-band)[6,7] and the aggregate cation (charge resonance band).[8] Figure 5 shows the CGM dependence of the spectra. The spectral feature (peak position, band shape *etc.*) considerably varies with combined CTLs (Fig. 3). On the other hand, CGM dependence of the feature is negligible (Fig. 5). We performed the electric-field modulated absorption measurement of a single CTL2 and the spectral feature was nearly identical with those obtained by photoexcitation of CGL/CTL2. Therefore these transient absorption might be assignable to the cationic species of CTMs generated after the electron transfer from CTMs to CGM exciton. It was reported that the dimer and tetramer cations of many aromatic molecules possess the near- and mid-infrared absorption which is called "charge resonance band".[8] Figure 6 shows the transition which gives a charge resonance band

(CR). At this stage, we ascribe the bands at 1100 nm in CTL1, at 1400 nm in CTL2 and at 1600 nm in CTL3 to the dimer cations of CTMs. The difference of absorption peaks was presumably originated from the difference of the interaction strength or intermolecular distance between CTM molecules.

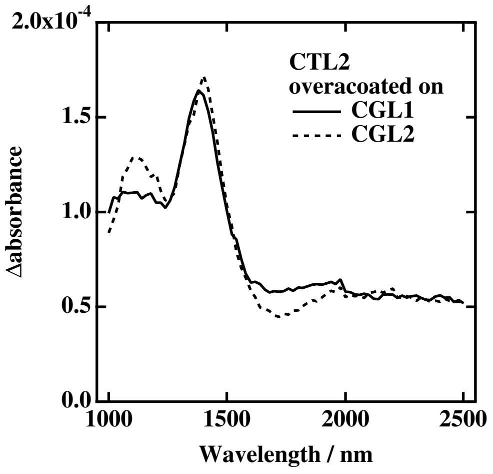

Figure 5. Transient near-infrared absorption spectra of CGL1 and CGL2 overcoated with CTL2

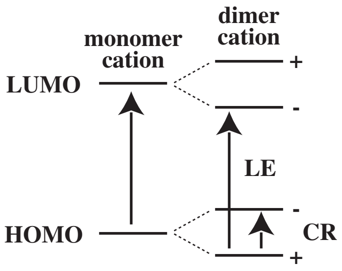

Figure 6. Charge resonance band

These spectral features depend on the concentration of CTM in CTL as shown in Fig. 7. Absorption intensities are normalized, as the intensity at 1400 nm is same in all the spectra. The relative intensities of the small absorption around 1100 nm and very broad absorption longer than 1600 nm are larger in CTLs with more concentrated CTMs. These bands are assignable to the absorptions of aggregate cations larger than the dimer, which is a tetramer at this stage.

Here we analyze the dynamics of the transient infrared absorption. Supposed decay mechanism is the recombination of CGM$^-$ and cationic species of CTMs. We can fit the observed decay curves to the model function in Eq. 1,

$$\frac{n}{n_0} = \frac{exp[-kt]}{1 + (n_0\gamma/k)(1 - exp[-kt])} \qquad (1)$$

where k is monomolecular decay constant, γ is bimolecular decay constant. All the decay data were successfully fitted by this function. This model function is obtained from supposing the decay mechanism as the combination of monomolecular (geminate) and bimolecular (non-geminate) recombination. Figure 8 shows the excitation power dependence of the decay dynamics in CGL1/CTL2. Decay curves under different excitation power are well fitted by the function in Eq. 1, where same k values were used. Broken lines and solid lines designate the measured and fitted curves respectively.

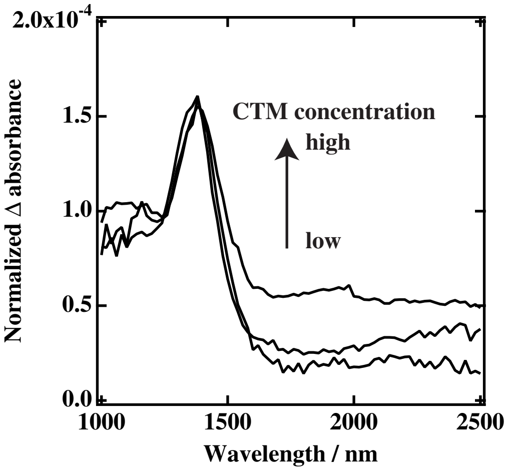

Figure 7. CTM concentration dependence of transient absorption spectra of (CGL1 / CTL2).

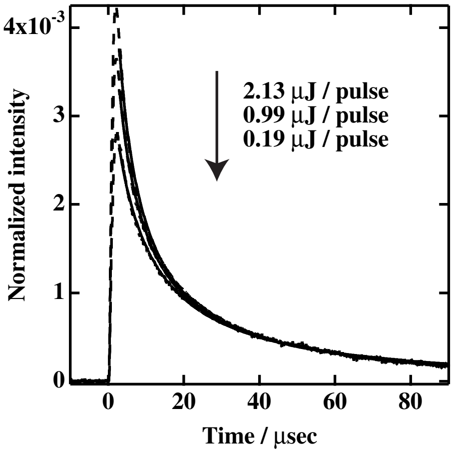

Figure 8. Excitation power dependence of decay dynamics

In this way, transient absorption observed in infrared region could be assigned to charge resonance band of CTMs cations. Observation of charge resonance band indicates that part of the photogenerated holes delocalize within some CTM molecules. The energy level of the delocalized holes is considered to be lower than that of localized oneas shown in Fig. 6. This state might work as a trap state of a hole in carrier generation and transport process. Now we are proceeding the experiment for clarifying the relation between the transients bringing about infrared absorption and the charge carrier.

Summary

We reported the transient absorption in layered organic photoreceptors for the first time. Photogenerated holes possess the absorption bands in the visible, near- and mid-infrared wavelength region according to the extent of charge delocalization.

Acknowledgement

The authors acknowledge Dr. A. Yamakata, Dr. T. Ishibashi and Prof. H. Onishi (Surface Chemistry Labora-tory, Kanagawa Academy of Science and technology) for their advice and support in constructing the time-resolved absorption spectrometer.

References

1. T. Shoda, S. Aramaki and T. Murayama, *Proc. NIP14*. pg. 508 (1999).
2. T. Niimi and M. Umeda, *J. Appl. Phys.,* **74**, 465 (1993).
3. Y. Sasaki, S. Yamaguchi, T. Shoda, S. Aramaki and T. Murayama, *Proc. ICIS*, pg. 302. (2002).
4. A. Yamakata, T. Ishibashi and H. Onishi, *Chem. Phys. Lett.*, **333**, 271 (2001).
5. M. Redecker, H. Bässler and H. H. Hörhold, *J. Phys. Chem. B*, **101**, 7398 (1997).
6. R. Katoh, S. Shinha, S. Murata and M. Tachiya, *J. Photochem. Photobiol. A*, **145**, 23 (2001).
7. R. Katoh, S. Murata and M. Tachiya, *Chem. Phys. Lett.,* **352**, 234 (2002).
8. A. Kira and M. Imamura, *J. Phys. Chem.*, **83**, 2267 (1979).

Biography

Yutaka Sasaki received his M. E. degree in Applied Chemistry from Waseda University in 1986 and joined the Yokohama Research Center of Mitsubishi Chemical Corporation (MCC). Analytical Science Division came to a subsidiary of MCC in 2000 (CACs). His work has focused on the application of laser spectroscopy, including time-resolved spectroscopy, to industrially important materials.