Direct Observation of Photogenerated Carriers in Organic Photoreceptors by Time-Resolved Spectroscopic Techniques

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Abstract

Time-Resolved spectroscopy is a powerful tool for investigation of photogeneration and photoconduction mechanism in layered organic photoreceptors because it can directly detect transient species in each step. So far, we have measured the transient absorption spectra of layered organic photoreceptors using azo pigments as charge generation materials (CGMs). As an extension work of our previous study, we applied this technique to photoreceptors using titanyl phthalocyanines (TiOPcs) as CGMs. For photoreceptors containing TiOPcs and CTMs, we obtained almost the same transient absorption spectrum as we observed in azo-CGM/CTM layers. However, TiOPcs gave weak transient absorption even without CTMs, whereas azo CGMs did not. We also found that the response to external electric field largely depended on the crystalline phase of TiOPc. It is interesting that these results strongly correlate with the photocarrier generation mechanism and the sensitivity of photoreceptors. These experimental results are discussed in connection with photocarrier generation mechanism.

Introduction

In xerographic printing using organic photoreceptors, photocarrier generation and transport processes play important roles to determine the performance. In the microscopic view, photocarrier generation and transport processes consist of many complicated processes (exciton formation, migration, excited state electron transfer, recombination, and trapping), and each step contributes to the sensitivity of photoreceptors. In order to design materials and formulations for better photoreceptor, it is very helpful to connect the performance with these elementally processes. However, these processes have not been fully understood in spite of a lot of studies.

Recently, we have reported that transient absorption method in near-IR region is a powerful tool to investigate photocarrier generation process in layered organic photoreceptors.[1] In this method, we detected the transient absorption of cationic species of CTMs with our highly sensitive time-resolved absorption system. 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. The photoreceptors studied in the previous work were layered ones using azo pigments as CGMs and hydrozone compounds as CTMs. In an azo-hydrazone photoreceptor, carrier generation is largely dependent on the CTM combined and occurs even under no electric field.[1,2] However, in some organic photoreceptors, carrier generation is affected also by external electric field and presence of impurities such as oxygen. It is known that these effects become prominent when we use phthalocyanines as CGMs. These facts indicate that carrier generation mechanism is partially different between phthalocyanine-based and azo-based CGMs. In this paper, we apply the transient absorption method to photoreceptors using titanyl phthalocyanines (TiOPcs) as CGMs to compare the carrier generation process with that of azo-hydrazone photoreceptors.

The photocarrier generation yield of TiOPc depends on the crystal structure. Indeed, many studies have tried to reveal the relationship between the polymorphism and photoconductivity.[3-6] From xerographic measurements and X-ray powder diffraction patterns, Fujimaki and co-workers showed that TiOPc(IV), often referred to as TiOPc-Y, is more sensitive than TiOPc(I).[3] Popovic and co-workers have intensively studied the carrier generation mechanism in the different crystalline forms of TiOPc using electric field induced fluorescence spectroscopy and time-resolved electric field induced fluorescence spectroscopy.[4,5] They concluded that one distinguishing characteristic of TiOPc(IV) is the contribution to photocarrier generation from the trapped state, when compared with TiOPc(I). Although their measurements have clearly showed the difference in the behavior of the excited state of each crystalline form, they were not direct observation of carrier species. In time-resolved fluorescence study, the monitored species are CGM excitons, which are not carrier species , but just precursors of charge transfer reaction between a CGM and a CTM.

One of the advantages of transient absorption method over time-resolved fluorescence is that it can detect transient species that does not emit fluorescence, such as ionic species of CTM. As mentioned above, we can detect the transient absorption of cationic species of CTM very sensitively after pulse excitation. Here we report our transient absorption study for photoreceptors using TiOPcs as CGMs. We present the difference in carrier generation by different crystalline forms, also with the effect of external field.

Experimental

Sample Preparation

We show in figure 1 the molecular structures of CGMs and CTMs used in this study. CGMs were phase I TiOPc, phase IV TiOPc, and azo-CGM1 as a reference. CTMs were hydrozone type one (CTM1) and arylamine type one (CTM2). The CGMs were dispersed in a poly(vinylbutyral) matrix (50%wt) and the CTMs were dissolved into this solution. The weight ratio of CTM to CGM was 1:1. This solution was spin-coated on a CaF_2 plate. We used a plate coated with ITO electrodes shown in figure 2 to measure the signal under electric field.

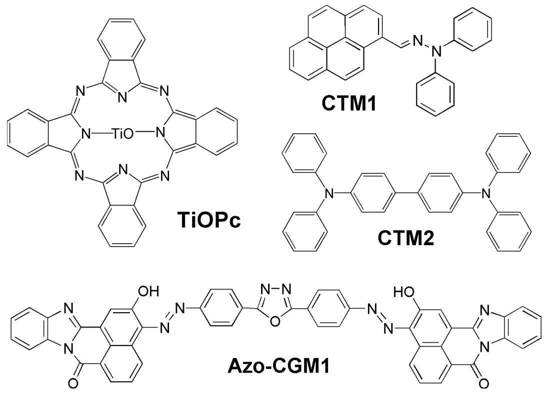

Figure 1. Charge generation materials (CGM) and the charge transport materials (CTM) used in this study.

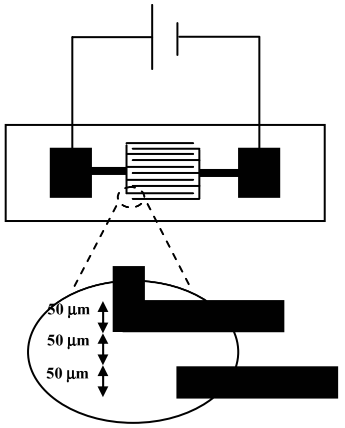

Figure 2. ITO electrode coated CaF_2 plate used for the measurement under electric field.

The layers prepared in this study were not dual layers but single layers, in which CGMs and CTMs were dispersed together. However, these are appropriate systems for investigation of initial charge generation, because photocarriers are generated at the interface between the CGL and the CTL in dual layer systems, where electron transfer is occurred between a CGM and a CTM.[7]

Transient Absorption

The detail of the experimental setup for time-resolved infrared absorption is shown elsewhere.[8,9] For an excitation pulse, we used frequency-mixed output (wavelength tunable, 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 µJ / cm^2). A probe light (emitted from the $MoSi_2$ source) was focused on the sample plate with an ellipsoidal mirror. The transmitted light was dispersed in a monochromator of 50 cm focal length and the monochromatic output was detected by an 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 was about 50 ns, which was determined by the response of the detector. Transient absorbance change as low as 10^{-6} was detected by signal averaging at 1KHz. Transient absorption measurements were conducted under desired applied voltage. All experiments were carried out under air.

Results and Discussion

When we excited CGM/CTM combined layers by the laser pulse that only CGM can absorb (800 nm pulse for TiOPc, 525 nm pulse for azo-CGM1), a broad transient absorption spectrum was observed in the near-IR range. Figure 3 shows the transient absorption spectra of TiOPc (IV)/CTM1 or CTM2 layers. The transient absorption spectra of azo-CGM1/CTM1 or CTM2 layers are also shown as a reference.

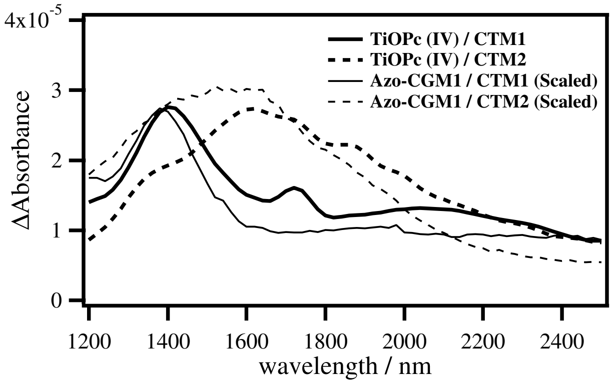

Figure 3. Transient absorption spectra of TiOPc(IV) /CTM1, 2 and azo-CGM1/CTM1, 2 layers at 1 µs after a pulse excitation.

In this measurement, we applied constant voltage when TiOPc(IV) was used as CGM, whereas no voltage was applied for azo-CGM1. In the previous paper, we ascribed this transient absorption to the cationic species of CTMs for azo-CGM1/CTM1 or CTM2 layers. The cationic species of CTM give various transient absorption depending on the degree of aggregation.[1] This transient absorption arises from charge resonance band.[10]

In figure 3, the shape of spectra for TiOPc/CTMx and azo-CGM/CTMx (x=1 or 2) were roughly the same. This fact means that observed transient absorption can be assigned to cationic species of CTMs also for TiOPc/CTMx layers. The small variation in spectra between TiOPc and azo-CGM1 implies that the influence of a CGM anion on a CTM cation spectrum is different between these two CGMs.

To investigate how polymorphs affect the charge generation, we measured the transient absorptions of TiOPc (I)/CTM1 and TiOPc(IV)/CTM1 layers under the same experimental condition. The spectra are depicted in figure 4A and 4B. The shapes of the spectra were almost the same because monitored species was derived only from CTM1 (cationic species of CTM1). However, the intensities of the spectra were considerably different. The transient absorption spectra shown here were measured applying 400V to the sample plate. Under this condition, the transient absorption spectrum of TiOPc(IV)/CTM1 was more than twice as large as that of TiOPc(I)/CTM1. This fact means that more than twice cationic species of CTM, that is delocalized holes in CTM, emerge at that time (1 μs after pulse excitation) in TiOPc(IV)/CTM1 compared with TiOPc(I)/CTM1.

Another interesting observation in figure 4 is that TiOPc gave transient absorption even without CTMs. (For a reference, we have carrier out the transient absorption experiment of an azo-CGM1 alone layer. Azo-CGM1 gave no transient absorption without CTMs.) Although this transient absorption appeared broadly in the near-IR region, the shape was fairly different from cationic species of CTM1. One of the most probable species that give this transient absorption is a TiOPc cation. It is known that charge generation occurs in TiOPc without the assistance of CTM. In that case, impurities such as adsorbed oxygen are considered to work as an electron acceptor. Based on these facts, it is not strange that considerable TiOPc cations remain at 1 μs after pulse excitation. On the other hand, if CTMs co-exist in the layer, TiOPc cations (or holes on TiOPc) may undergo rapid charge transfer. (< 50ns, not detectable in the present experiment) Consequently, when we measure transient absorption spectrum of a TiOPc/CTM layer, there is no or relatively small contribution from TiOPc cations, so that cationic species of CTMs are mainly detected.

Figure 5A and 5B show the decay of the transient absorption at 1400 nm for TiOPc(I)/CTM1 and TiOPc (IV)/CTM1. The dependence of signals on voltage is also shown. Surprisingly, the signal was almost independent of the voltage applied (electric field) in TiOPc(I)/CTM1, whereas considerable dependence was observed in TiOPc(IV)/CTM1.

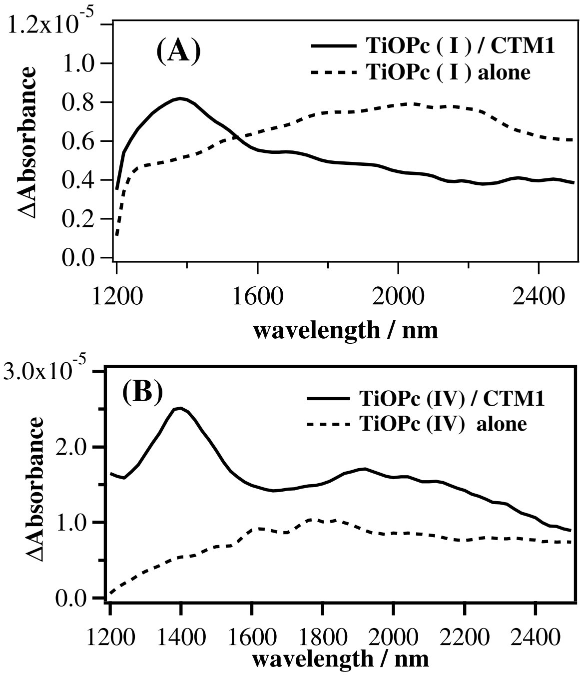

Figure 4. Comparison of transient absorption spectra between a TiOPc(I)/CTM1 layer (A) and a TiOPc(IV)/CTM1 layer (B) under the same experimental condition (bias = 400 V). The transient absorption spectra of TiOPc alone layers are also shown.

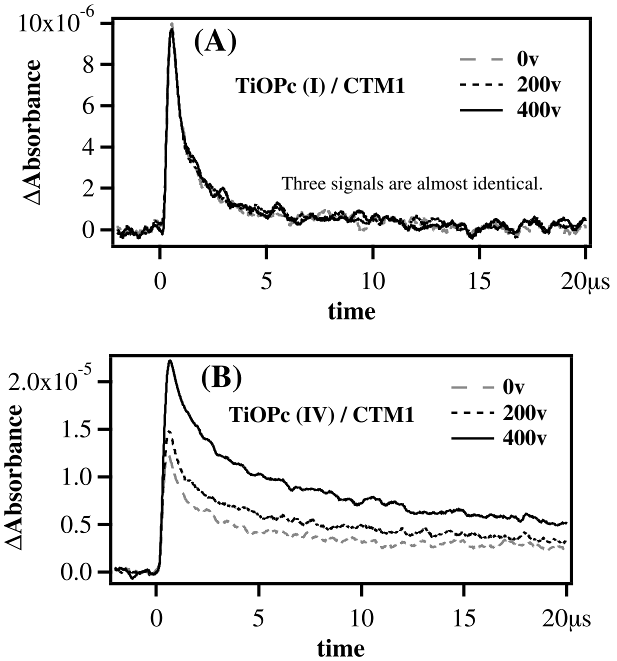

Figure 5. Transient absorption decay of a TiOPc(I)/CTM1 layer (A) and a TiOPc(IV)/CTM1 layer (B) at 1400 nm. The applied voltage was 0, 200, or 400V.

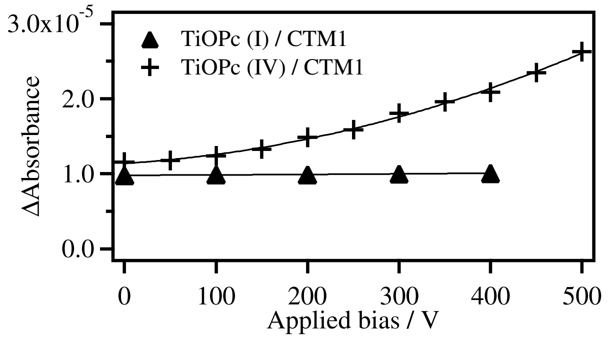

Figure 6. Dependence of the initial intensity of transient absorption on applied voltage for TiOPc(I)/CTM1 and TiOPc(IV)/CTM1 layers.

As the electric field increased, the transient absorption became larger and the decay became slower in TiOPc(IV). We show in figure 6 the dependence of the initial intensity on applied voltage for TiOPc(I)/CTM1 and TiOPc(IV)/CTM1. At zero voltage, the initial intensity of the transient absorption was nearly the same between these two layers. When we added the voltage to the layer, the intensity remained constant in TiOPc(I)/CTM1. In TiOPc(IV)/CTM1, the increment of initial intensity exhibited approximately quadratic dependence on applied voltage.

Figure 6 tells us the difference of the response to electric field between phase I and IV TiOPc. There are two components in the transient absorption; one is the component that is independent of electric field and another is the component that is quadratically dependent on electric field. The transient absorption is contributed from the both components in phase IV, but only from the first component in phase I. In the transient absorption measurement for a CGM/CTM combined layer, the signal intensity is proportional to the quantity of cationic species of CTM. Therefore, the intensity of transient absorption is a good indication of the degree of 'real' charge generation. From this point of view, figure 6 shows there are two components (paths) in charge generation; one is electric-field-unaided charge generation and another is electric-field-assisted charge generation. The difference in the degree of electric-field-assisted charge generation may be related to the fact that phase IV is much more sensitive than phase I as a photoreceptor. Now we are obtaining more experimental data for constructing the charge generation models to consistently explain our experimental results.

Summary

The transient absorption of photoreceptors using TiOPc as a CGM was measured to investigate photogeneration mechanism. In TiOPc/CTM layers, we obtained almost the same transient absorption spectrum as we had observed in azo-CGM/CTM layers. In addition, TiOPcs gave weak transient absorption even without CTMs. The most possible species that gave this transient absorption is cations of TiOPc. These observations clearly show the charge generation mechanism is different between azo-pigments and TiOPc.

We also found that the response to external electric field largely depended on the crystalline phase of TiOPc. The transient absorption signal was almost independent of the electric field in phase I, whereas considerable dependence was observed in phase IV. It was interesting that these results strongly correlated with the sensitivity of photoreceptor.

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Biography

Kan Takeshita received his M.S. degree in physical chemistry from Kyoto University in 2001. Subsequently, he joined the analytical service division of Mitsubishi Chemical Group Science and Technology Research Center, Inc.. He is also working as a visiting researcher at Kanagawa Academy of Science and Technology from 2002 to 2003. He has worked on physical chemistry, especially photo and electric properties, of important industrial materials, such as organic photoreceptors and photovoltaic cells by use of various techniques of laser spectroscopy.