Time-Resolved Fluorescence Study on Primary Photocarrier Generation Process in Layered Organic Photoreceptors

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Abstract

We have been studying the photocarrier generation mechanism in layered organic photoreceptors comprised of bisazo pigment based carrier generation materials (CGMs) and carrier transport materials (CTMs) using thermally stimulated current (TSC) technique. And it was concluded that the formation yield of initial ion-pair -(CGM$^-$/CTM$^+$) mainly determined the photosensitivity. It is known that the carrier generation yield is greatly enhanced by the coexistent CTMs in this type of photoreceptors. In the present study, we examine the primary process just after photoexcitation by means of time-resolved fluorescence spectroscopy. We observed that the CTMs considerably shortened the lifetime of CGM exciton. We attempt to correlate the quenching rate of CGM fluorescence by CTMs with the sensitivity of the photoreceptors.

Introduction

We have already reported the TSC study on the carrier generation mechanism in layered photoreceptors.[1-3] In these studies, temperature and/or electric field dependence of the carrier generation, recombination and separation processes of ion-pairs were analyzed. It was concluded that the formation yield of initial ion-pairs determined the sensitivity of the photoreceptor. The amount of CGM exciton can be monitored by using fluorescence spectroscopy. Umeda *et al.* reported the steady state fluorescence study of bisazo-based photoreceptors and showed that the CGM fluorescence quenching efficiency by the CTM was well in accordance with the carrier generation efficiency.[4] Time-resolved fluorescence spectroscopy provides the direct information on the temporal evolution of exciton and makes it possible to distinguish the exciton having different lifetimes. We

have successfully applied this technique for investigating the primary process in titanyloxy phthalocyanines.[5-7]

In this paper, we report the time-resolved fluorescence study on primary process in the same bisazo-based photoreceptors as those studied by TSC measurement. We focus our attention on the fast process just after photoexcitation and discuss the relation between the exciton dynamics and the carrier generation.
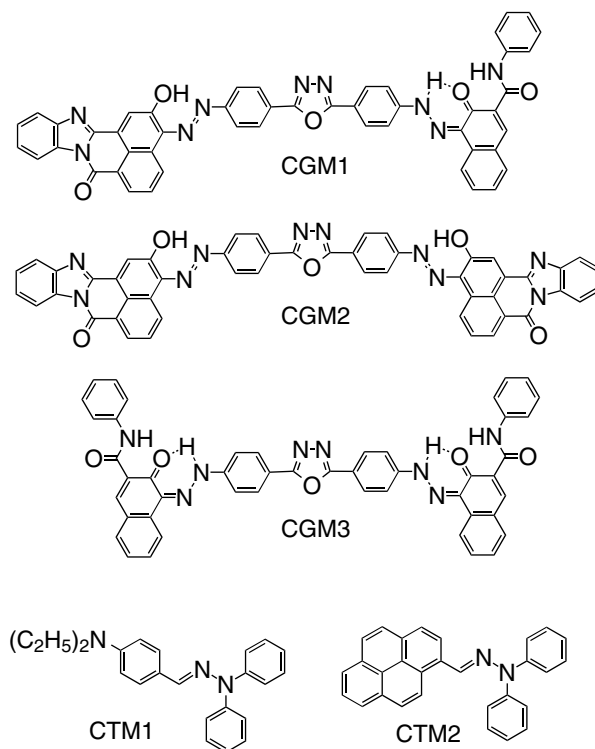

Figure 1.Molecular structures of three CGMs and two CTMs

Experimental

Molecular structures of bisazo pigments and CTMs are shown in Fig. 1. The charge generation layer (CGL) contains 50wt% bisazo CGM dispersed in poly(vinylbutyral). The charge transport layer (CTL) is a 50wt% solid solution of a CTM in polycarbonate. The CGL and the CTL were successively coated on a glass substrate. The samples were 15-18 μm in thickness. The drift mobility and the oxidation potential of CTM1 and CTM2 are listed in Table 1. The photoconductive sensitivity of each bisazo-CTM layered photoreceptor is shown in Table 2.

Picosecond time-resolved fluorescence apparatus was constructed in our laboratory (Fig. 2).[6] This system is based on a modelock Ti:sapphire oscillator (Coherent MIRA 900F) and a streak scope (Hamamatsu C4334). Second harmonic of the oscillator output (λ= 425 nm) was used for photoexcitation. Repetition rate of laser was reduced to 1MHz by using pulse picker. Streak scope was driven in a photon-counting mode. Temporal resolution of the system is 30 psec. We chose the back-illumination geometry, in which the excitation laser was irradiated onto the CGL from reverse side of samples, for avoiding the absorption of excitation light by the CTL.

Table 1. Oxidation Potential and Drift Mobility of Each CTM in Bisphenol A Polycarbonate (50wt%).

	Oxidation Potential (vs. SCE)	Drift mobility[a] $(cm^2/(Vs))$
CTM1	0.52	1.55×10^{-6}
CTM2	0.92	8.51×10^{-6}

a) 307/cm, 25°C

Table 2. Photoconductive Sensitivity of Each Layered Photoreceptor.

	Photoconductive sensitivity[a] $(cm^2/\mu J)$
CGM1/CTM1	3.3
CGM1/CTM2	4.8
CGM2/CTM1	2.3
CGM2/CTM2	4.0
CGM3/CTM1	-
CGM3/CTM2	0.7

a) reciprocal half-decay exposure from 700V, by monochromated light (525nm)

Results and Discussions

As all the data were acquired in the back–illumination geometry, first we had to check the observed difference of quenching dynamics in front- and back-illumination. CTM1 has relatively weak absorption at 425 nm, then the quenching dynamics of CGM2 fluorescence by CTM1 was tested in both geometries. The fluorescence of CTM1 spectrally overlapped the CGM fluorescence in front-illumination condition. The time constants of CTM1 fluorescence are relatively long compared to those of CGM and CTM contribution was safely compensated. And we confirmed that the quenching dynamics are almost identical in both geometries.
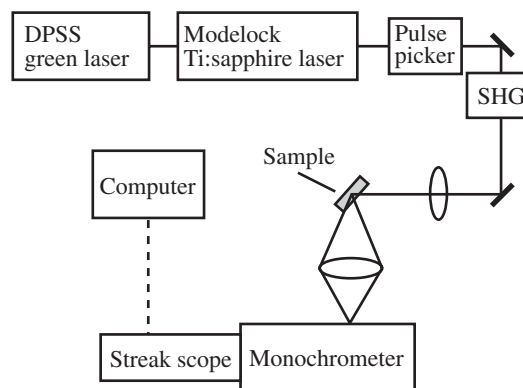

Figure 2.Picosecond time-resolved fluorescence apparatus.

Figure 3 shows the quenching dynamics of CGM exciton in all the combination of (CGM/CTM). Instrumental response function is also placed in this figure. These data were normalized, as a maximum intensity was unity. It was clearly observed that the CTM considerably quenched the CGM exciton. It is unlikely that the intersystem crossing rate from singlet to triplet exciton or the internal conversion rate from singlet exciton to ground state is remarkably altered by the small amount of CTM. Therefore this quenching phenomenon is thought to be ascribable to the ion-pair formation originating from the charge-transfer reaction between CGM and CTM. It should be noticed that quenching dynamics in CGMx/CTM1 and CGMx/CTM2 are quite identical even when changing CGMx. These results indicate that the ion-pair formation yield is same when changing CTMs. Hence we analyzed only the decay data of CGM/CTM1, by fitting the temporal profiles to a simple model function. The model function was the convolution of an instrumental response and a sum of two exponentials as Eq.1.

$$A_1 exp(-\frac{t}{\tau_1}) + A_2 exp(-\frac{t}{\tau_2}) \qquad (1)$$

The amplitudes (A_1, A_2) and the time constants (τ_1, τ_2) were fitting parameters. It was found that (τ_1, τ_2) did not depend on wavelength but (A_1, A_2) did depend. Excitons having longer lifetime showed longer wavelength fluorescence. We integrated the intensity in the wavelength range 630-720nm, for CGM1 and CGM2, 610-700 nm, for CGM3. All the fitting procedure converged properly. The obtained fitting parameters are summarized in Table 3. We
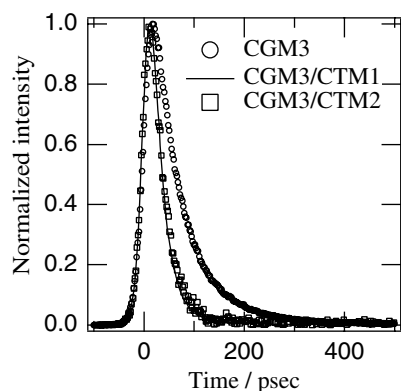
assumed that the intensity at time 0 after photoexcitation was unity ($A_1+A_2=1$). The integrated fluorescence intensities ($A_1\tau_1+A_2\tau_2$) are also indicated in Table 3.
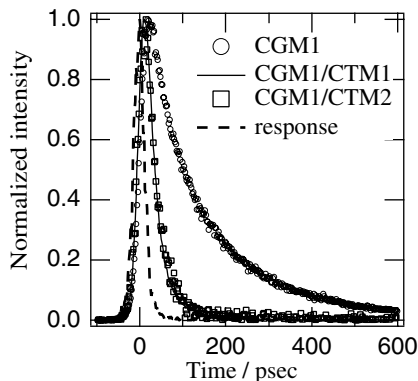
(a)
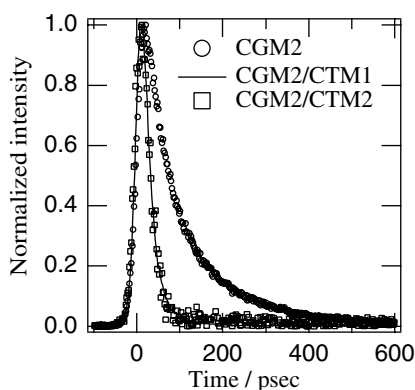
(b)

(c)

Figure 3. Fluorescence quenching dynamics in each photorecep-tor. (a) CGM1, (b) CGM2, (c) CGM3.

Table 3. Fitting Parameters.

	CGM1		CGM2		CGM3	
	-	CTM1	-	CTM1	-	CTM1
τ_1(psec)	61	18	50	18	49	21
τ_2(psec)	202	61	167	63	130	95
A_1[a]	0.55	0.91	0.71	0.95	0.89	0.98
A_2[a]	0.45	0.09	0.29	0.05	0.11	0.02
$A_1\tau_1+A_2\tau_2$	120	22	84	20	58	22

a) assuming ($A_1+A_2=1$)

Quenching efficiencies of CGM exciton calculated from integrated fluorescence intensities ($A_1\tau_1+A_2\tau_2$) are 0.82, 0.76, and 0.62 for CGM1, CGM2 and CGM3 respectively. This calculation is based on the assumption that both of short-lived and long-lived excitons contribute to the ion-pair formation. These values are qualitatively in accordance with the sensitivities of photoreceptors shown in Table 2. However the sensitivity difference when changing CTMs is not consistent with the results of fluorescence quenching as mentioned above.

In this way, the fluorescence quenching efficiency can be qualitatively correlated with the photosensitivity when changing CGMs. However the CTM dependence of the sensitivity is considered to be caused by the factors other than initial ion-pair formation. It was suggested that the factors determining the photosensitivity includes (i) the recombination rate of generated ion-pairs (lifetime of ion-pairs) and (ii) the rate of charge separation.

We observed two excitons having different lifetime and energy level. The successful fitting to the simple model function means that there are two singlet excitons, both of which show monomeric decays. The most tenable diagram of the exciton dynamics is schematically shown in Fig. 4. Exciton 1 corresponds to short-lived exciton and Exciton 2 to long-lived exciton. If we suppose that exciton 2 generated from exciton 1 via internal conversion and that only exciton 1 contribute to the ion-pair formation, we can calculate the ion-pair formation efficiency from the change in time constants τ_1 as 0.70, 0.64 and 0.57 for CGM1, CGM2 and CGM3 respectively. Again these values are qualitatively in accordance with the sensitivities of photoreceptors. We would like to characterize these two excitons more precisely in the future.
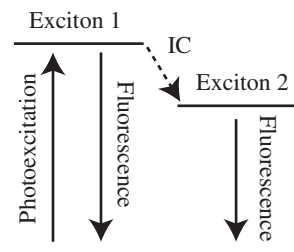

Figure 4. Schematic Diagram of Exciton Dynamics.

Conclusion

We have studied the primary photocarrier generation process using time-resolved fluorescence spectroscopy. Fluorescence quenching efficiency can be qualitatively correlated with the CGM dependence of carrier generation efficiency. However we can ascribe the CTM dependence of the sensitivity to the process after the ion-pair formation. It was suggested that other factors as the ion-pairs lifetime and the rate of charge separation were associated with the sensitivity of photoreceptors.

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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 the subsidiary company of MCC in 2000 (CACs). His work has focused on the application of laser spectroscopy, including time-resolved spectroscopy, to industrially important materials.