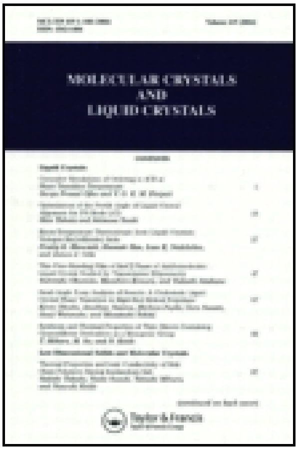

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# Electric Field Effect on The Charge Migration of Methylene-Linked Carbazole and Terephthalic Acid Methyl Ester in PMMA Polymer Films

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Photoinduced inter- and intramolecular electron transfer reactions of methylene-linked (n) carbazole and terephthalic acid methyl ester (abbreviated as D-(n)-A, n=4 and 12) have been examined by using external electro-modulated fluorescence spectroscopy and photocurrent measurement, which allow one to obtain information about the Stark shift and the efficiency of fluorescence quenching as well as photocarrier generation induced by an electric field. The action spectra of the photocurrent could be successfully measured at various concentrations in the absorption region of carbazole (240-365 nm). The obtained action spectra agree well with the simultaneously measured fluorescence excitation spectra, indicating that photocarrier generation occurs following the relaxations including internal conversion to $S_1$ and excitation energy migration among carbazole chromophores. Furthermore, the efficiency of photocarrier generation of D-(12)-A is higher than that of D-(4)-A, indicating that an intramolecular recombination process plays an important role in charge recombination of a photogenerated ion-pair state.

Keywords: intramolecular electron transfer; electric field effects; photocarrier generation; exciplex fluorescence quenching; charge recombination

## INTRODUCTION

The electric field effect on dissociation or recombination process of the produced radical-ion pair has been studied for photocarrier generation[1-3]. These processes lead to the fluorescence quenching by an applied electric field observed in poly (vinylcarbazole) in the presence of an electron acceptor[4].

In a previous paper[5], photoinduced inter and intramolecular electron transfer reactions of methylene-linked carbazole and terephthalic acid methyl ester (D-(n)-A, n=3 and 20) have been studied extensively. D-(n)-A exhibits inter-molecular exciplex fluorescence in PMMA films following excitation into carbazole chromophore along with the fluorescence emitted from the carbazole moiety, as the dopant concentration increases. While both the carbazole and the exciplex fluorescence are quenched by an external electric field at high concentration of D-(n)-A, exciplex fluorescence of D-(n)-A increases at low concentration and the amount of the field-induced enhancement divided by the total intensity decreases exponentially with increasing the chain length. The field-induced quenching of the exciplex fluorescence is considered to arise from the free carrier generation by the field-assisted dissociation of an electron-hole ion-pair state.

The present study extends our previous study in photodynamics of D-(n)-A, n=4 and 12, doped in PMMA polymer films in the presence and absence of an external electric field. Besides the fluorescence measurements, photocurrent measurements have been carried out with a series of excitation wavelengths to confirm the presence of photocarrier generation at high dopant concentrations of D-(n)-A, which was suggested by the electric-field induced quenching of the exciplex fluorescence.

## EXPERIMENTAL

A vacuum-evaporated aluminum (Al) thin film on a substrate was prepared using EG-240 (Tokyo Vacuum, Co. Ltd.) until the electrical conductivity of an Al layer was successfully achieved. The PMMA polymer film containing D-(n)-A, n=4 and 12, shown in Scheme 1 was prepared onto the semitransparent aluminum (Al) coated substrate by using spin-coating technique. The concentration of D-(4)-A or D-(12)-A ranges from 2 to 10 mol% in a ratio to the monomer unit of PMMA. Subsequently, a sample substrate was completely dried under vacuum followed by evaporation of Al as an additional electrode on the polymer coated film. The electrical contacts between these Al layers and the external electrical leads were made by means of small drops of silver paste. The thickness of the film was in the range 0.57-0.70 μm. Electromodulated fluorescence measurement has already reported elsewhere[6]. Fluorescence excitation spectra and action spectra of the photocurrent were simultaneously measured by a spectrofluorometer and an electrometer (model 617, KEITHLEY), respectively, applying 1.5 V dc supplied by the built-in generator. Incident light intensity was varied using neutral density (ND) filters. The optical cross section at the excitation wavelength was normalized both by ND filters and the optical transmittance of Al electrode on an illumination side

## RESULTS AND DISCUSSION

Figure 1 shows the fluorescence spectra of D-(12)-A at concentrations of 2, 5 and 10 mol%. While the fluorescence of carbazole moiety dominates at 2 mol%, the formation of the exciplex fluorescence peaking near 440 nm becomes dominant at 10 mol%. Figure 1 also exhibits fluorescence excitation spectrum of 10 mol% of D-(12)-A monitored at 450nm along with the action spectrum of the photocurrent under an applied dc electric field (1.5 V). The action spectrum agrees well with the simultaneously measured fluorescence excitation spectrum, indicating that photocarrier generation occurs following the relaxation that includes both internal conversion to $S_1$ and excitation

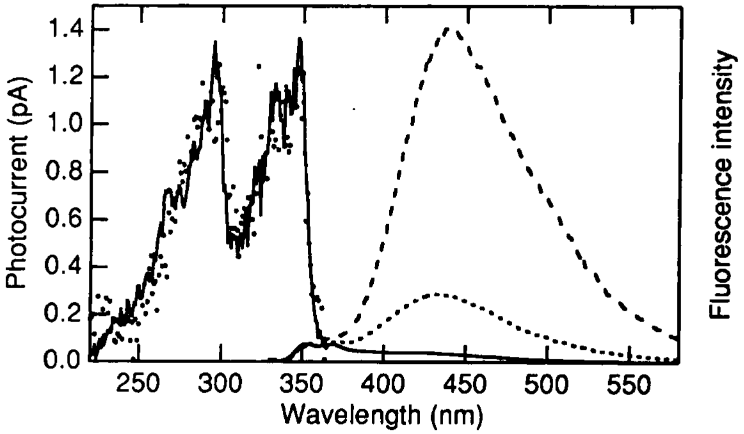


FIGURE 1 Fluorescence spectra of D-(12)-A at concentrations of 2 (—), 5 (···) and 10 (- -) mol% normalized at 354nm. Excitation wavelength is 294 nm. The action spectrum of photocurrent (•) of D-(12)-A at 10 mol% applied by 1.5 V dc along with fluorescence excitation spectrum (—) monitored at 450 nm.

energy migration among carbazole chromophores. Figure 2 shows the incident light intensity dependence on photocurrent with corrections for the transmittance of Al electrodes and ND filters. The phorocurrent at every concentration increases linearly with increasing incident light intensity per a D-(n)-A molecule. In addition, the efficiency of photocarrier generation increases with the concentration. It is worthwhile to note that slopes of photocurrent versus light intensity drastically increase in comparison with the increase of D-(n)-A concentrations. Furthermore D-(12)-A generates photocurrent more effectively than D-(4)-A does. This result will be discussed later. Figure 3 shows the quenching ratio of exciplex fluorescence observed at 438 nm where the Stark shift gives no contribution to electromodulated fluorescence spectrum as reported previously[5]. The values of $\Delta I_F/I_F$ are found to decrease as a function of the square of an applied electric field (F) since the solid lines fitted by functions of $F^2$ are in good agreement with measured data as also shown in Figure 3. The magnitude of quenching at the same field strength increases with the concentration of D-(n)-A.

The field-assisted thermal dissociation of an electron-hole ion pair is considered to cause the electric-field-induced quenching of the exciplex fluo-

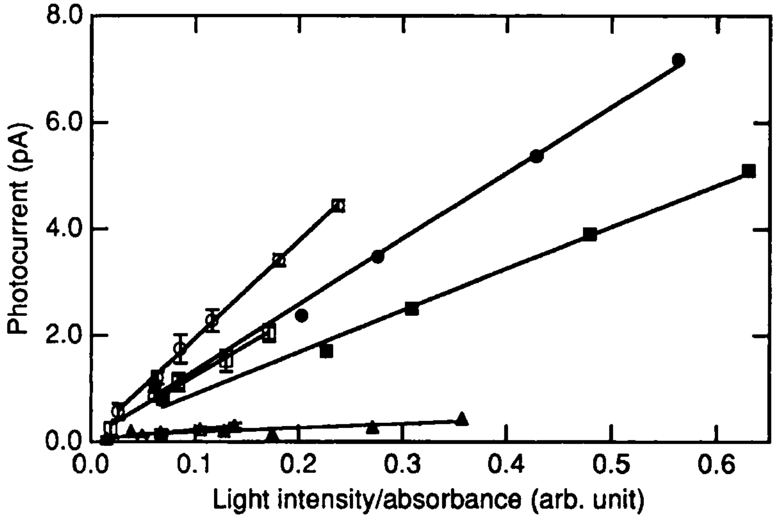


FIGURE 2 Plots of photocurrent as a function of light intensity normalized by absorbance at 347 nm of D-(n)-A. [D-(4)-A] : (▲) 2 mol%, (■) 5 mol% and (●) 10 mol%. [D-(12)-A] : (△) 2 mol%, (□) 5 mol% and (○) 10 mol%.

rescence of D-(n)-A at high concentrations[5]. Scheme 1 is likely to provide a reasonable explanation of the experiment. The electron transfer from $D_j^*$ to the neighboring electron acceptor $A_i$ leads to the formation of radical ion-pair state, $D_i^+$—$A_j^-$, followed by three processes; dissociation to free carriers, charge recombination and exciplex formation corresponding to $k_{DIS}$, $k_{CR}$ and $k_{GR}$ , respectively. The field-induced quenching of the exciplex fluorescence as shown in Figure 3 has been well explained by the field assisted thermal dissociation of an electron-hole ion-pair state[5]. This explanation is supported by the present study that successfully observed photocurrent attributed to the photogeneration of free carriers. Since the free carriers generated by the dissociation of ion pair become more spread to neighboring D-(n)-A molecules at higher concentrations, the efficient free-carrier photogeneration at 10 mol% allows us to explain exciplex quenching and remarkable increase of photocurrent as shown in Figure 2.

It was found that the photocurrent as well as exciplex quenching depends on methylene chain length as shown in Figure 2 and 3. Photocurrent generation and exciplex quenching of D-(12)-A occur more efficiently than those of D-(4)-A in the same condition. An applied electric field increase

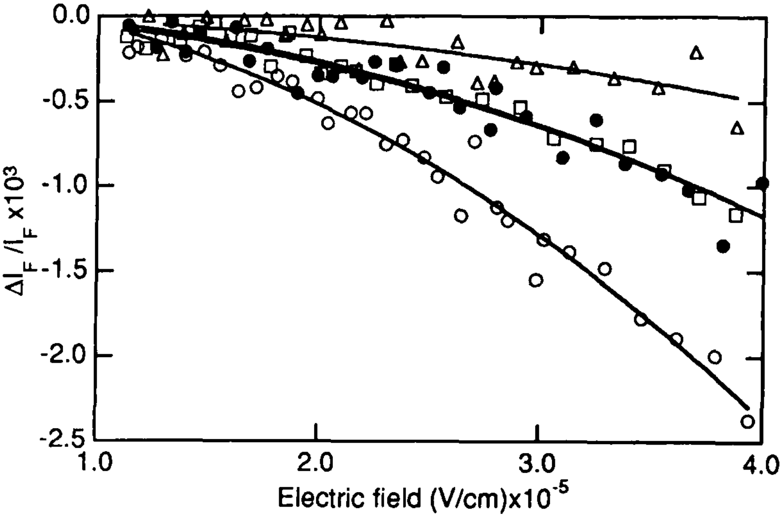
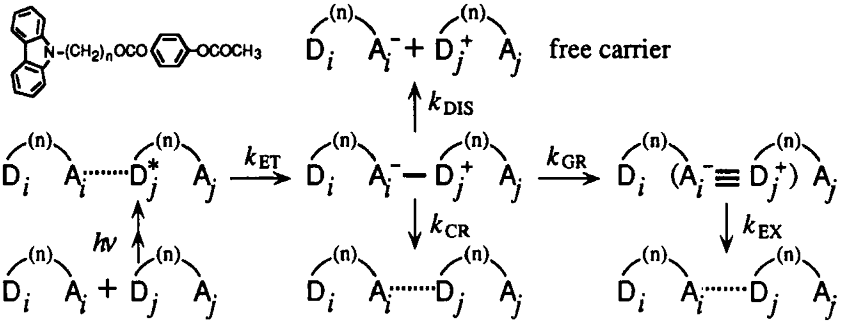


FIGURE 3 The quenching of exciplex fluorescence observed at 438 nm by the applied electric field. [D-(4)-A]: (●) 10 mol%. [D-(12)-A] : (▲) 2 mol%, (□) 5 mol% and (○) 10 mol%.

SCHEME 1



exciplex fluorescence of D-(n)-A at low concentration and the ratio of the field-induced enhancement to the total intensity decreases exponentially with increasing the chain length[5]. The magnitude of this enhancement decreases monotonically with the concentration of D-(n)-A and diminishes at high concentrations due to the free carrier generation. The field-induced enhancement of the exciplex fluorescence at low concentration is interpreted as follows: If the ion-pair state is quenched by a intramolecular charge recombination at zero field, the applied field seems to inhibit the charge recombination through the methylene chain followed by the recovery of the exciplex fluorescence quenched by the charge recombination. However, since the intramolecular recombination competes with photocarrier generation even at high concentration, the difference in $k_{CR}$ between D-(4)-A and D-(12)-A provides a reasonable explanation of the present photocurrent measurement.

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