Electroabsorption Study of Charge-Transfer Excited State in Donor-Acceptor-Type Polymer

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The origin of relaxed exciton formation and its effect on photocarrier generation were examined for a typical donor-acceptor (DA)-type polymer, poly{[9-(1-octylnonyl)-9*H*-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-1,2,5-thiophenediyl} (PCDTBT), with a focus on the two unique photoabsorption bands that originate from charge-transfer (CT) and main-chain (MC) excitations, respectively. The results of electroabsorption measurements showed that the CT excitation spatially localizes more than the MC excitation, which plays a crucial role for the relaxed exciton formation. The photocarrier generation characteristics are discussed in terms of the spatial localization of the CT and MC excitations.

Key words: Organic solar cell, donor-acceptor-type polymer, charge-transfer excitation, electroabsorption

1. INTRODUCTION

Donor-acceptor (DA)-type polymers, composed of alternating electron-donor and electron-acceptor units, are key materials for recent major development of organic solar cells (OSCs) and organic thin film transistors (OTFTs): they allow the realization of a power conversion efficiency higher than 9% for OSCs and a mobility higher than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for OTFTs [1-7]. They have two unique photoabsorption bands in the visible and near-infrared regions, i.e. the charge-transfer (CT) excitation between the donor and acceptor units and the spatially extended main chain (MC) excitation that is usually observed in conventional homopolymers such as poly(3-hexylthiophene-2,5-diyl) (P3HT) [8-9]. The former allows wide range photoabsorption in the near-infrared range, which should be crucial for high efficiencies in the DA-type polymer OSCs [10]. It has been recently pointed out that the efficiency of photocarrier generation is lower for the CT excitation than for the MC excitation and that this is associated with the formation of bound electron-hole pairs with strong lattice relaxation, referred as relaxed excitons [8,9,11,12]. However, it has been yet unclear what induces the formation of relaxed excitons.

In this study, we investigated the photoexcited-state properties of DA-type polymers by the electroabsorption measurements. The study was conducted for a typical DA-type polymer, poly{[9-(1-octylnonyl)-9*H*-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl} (PCDTBT [2,3]; Fig. 1(a)). From the results, it was found that the CT excited state is spatially more localized than the MC excited state. We demonstrated that this localized character is closely correlated with the formation of relaxed excitons and the photocarrier generation characteristics.

2. EXPERIMENTAL

Electroabsorption measurements were carried out for the stack cells composed of successive layers of semitransparent Al (4.5 nm), the active polymer (10-50 nm) on a tin-doped indium-oxide (ITO)-coated glass substrate. All fabrication processes and measurements were conducted under an inert atmosphere of nitrogen. The active polymer layer was fabricated by spin coating of a pristine DA-type polymer and then annealed at 423 K for 30 min. Monochromated light from a halogen lamp was focused onto the semitransparent Al electrodes and the transmitted light was detected by a Si photodiode. Sine-wave bias with the peak voltage of 0 V and V_{bias} was applied at frequencies of 10 Hz, and the modulated transmittance signal (ΔT) was detected by lock-in technique to obtain the electroabsorption signal, $\Delta A d = -\Delta T/T$, where A , d , and T are absorption coefficient, film thickness, and transmittance, respectively. To obtain the pure electroabsorption signal without the contribution of injected carriers, the sample cells were connected in a reverse bias condition during the electroabsorption measurements.

3. RESULTS AND DISCUSSION

Figure 1(b) and 1(c) show the photoabsorption and electroabsorption spectra measured for the pristine polymer film of PCDTBT. The electroabsorption spectrum was measured under the electric field of 2.3 MV cm^{-1} . The two unique photoabsorption bands can be clearly seen in the photoabsorption spectrum. The low-energy photoabsorption at around 2.2 eV corresponds to the CT excitation, while the high-energy photoabsorption at around 3.1 eV corresponds to the MC excitation [12]. In the electroabsorption spectrum, the spectral shape of both excitations are quite similar to the

first derivative of the ordinary photoabsorption spectrum. This indicates that the transition energy of both excitations are shifted by the applied electric field. According to the Stark effect, if the molecular polarizability and molecular dipole moment in the photoexcited state are respectively changed by $\Delta\alpha$ and $\Delta\mu$ from the ground state, the transition energy should be shifted in the presence of electric field F as [13]

$$\Delta E = -\frac{1}{2}\Delta\alpha F^2 - \Delta\mu F. \quad (1)$$

This energy shift ΔE causes the change of absorption coefficient ΔA expressed by

$$\Delta A = \frac{1}{2}\left(\frac{\partial A}{\partial E}\right)\Delta\alpha F^2 + \frac{1}{6}\left(\frac{\partial^2 A}{\partial E^2}\right)\Delta\mu^2 F^2. \quad (2)$$

Note that the eq. 2 assumes the simplified model system with random orientation of molecules. The eq. 2 indicates that the first derivative component ($\partial A/\partial E$) originates from the polarizability change $\Delta\alpha$ between the ground and photoexcited states, whereas the second derivative component ($\partial^2 A/\partial E^2$) originates from the change of molecular dipole moment $\Delta\mu$. Therefore, the electroabsorption spectrum with the spectral shape of the first derivative indicates that the polarizability change is dominant both for the MC and CT excitations. When we compare the electroabsorption spectrum with the first derivative of photoabsorption spectrum, we can find that the MC excitation contains 2.3 times larger contribution of the first derivative component than the CT excitation. This indicates that the MC excitation demonstrates larger polarizability change than the CT excitation. It should be noted that the second derivative component cannot be found in the CT excitation despite of its large $\Delta\mu$. The possible origin is that the $\Delta\mu$ axis orients perpendicular to the electric field, which corresponds to parallel orientation of polymer backbone with respect to the substrate surface.

Fig. 1. (a) Molecular structure of PCDTBT. The red and blue parts correspond to electron donor and acceptor units, respectively. (b) An electroabsorption spectrum (black line) and a first derivative of photoabsorption spectrum (red line) measured for a pristine polymer film of PCDTBT. The red broken line corresponds to a first

derivative of photoabsorption spectrum multiplied by the factor of 2.3. (c) Photoabsorption (black line) and photocurrent action (red line) spectra measured for a pristine polymer film of PCDTBT [12].

To obtain $\Delta\alpha$ for the CT and MC excitations, we measured the electric-field dependence of electroabsorption spectra (Fig. 2(a)). As seen, the signal intensities for both excitations increase as increasing the applied electric field. On the basis of the eq (2), it is expected that the electroabsorption spectra show increased contribution of the first derivative component in proportion to $1/2\Delta\alpha F^2$. So, we fitted the electroabsorption spectra by using the first derivative of photoabsorption spectrum and extracted $1/2\Delta\alpha F^2$ at respective electric fields. Note that the fitting was separately conducted for the CT (1.7–2.7 eV) and MC (2.8–3.8 eV) excitations. The fitting result is shown in Fig. 2(b) where the values of $1/2\Delta\alpha F^2$ are plotted as a function of F^2 . As seen, the values of $1/2\Delta\alpha F^2$ are reasonably proportional to F^2 . From the slope of figure, we estimated $\Delta\alpha$ at $1.2 \times 10^{-39} \text{ C V}^{-1} \text{ m}^2$ and $2.7 \times 10^{-39} \text{ C V}^{-1} \text{ m}^2$ for the CT and MC excitations, respectively. Since the polarizability is proportional to the spatial extension of electron cloud, $\Delta\alpha$ can be regarded as the degree of spatial delocalization of photoexcited state [14]. Therefore, the difference of $\Delta\alpha$ between the CT and MC excitations indicates that the CT excited state spatially localizes more than the MC excited state.

Fig. 2. (a) Electric field dependence of electroabsorption spectra measured for a pristine polymer film of PCDTBT. (b) Values of $1/2\Delta\alpha F^2$ for CT and MC excitations, plotted as a function of F^2 . These values were obtained from the fitting of electroabsorption spectra at respective electric field with using the first derivative of photoabsorption spectrum.

Here we discuss the correlation between the photocarrier generation and the spatial localization of photoexcited states. Figure 1(c) shows the photocurrent action spectra of the pristine PCDTBT film [cited from the reference 12]. In the spectra, the low-energy CT

photoabsorption band exhibits a lower photocurrent yield than the high-energy MC photoabsorption band. Furthermore, the activation energy of photocurrent, estimated by the Arrhenius-type temperature dependence (Fig. 3), is larger in the CT photoabsorption band than in the MC photoabsorption band. The internal quantum efficiency (IQE) and activation energy required to generate photocurrent for both excitations are summarized in Table I together with the value of $\Delta\alpha$ obtained from the electroabsorption measurements. From the comparison of these parameters, we can find clear correlation among them: the spatially localized CT excitation with small $\Delta\alpha$ demonstrates lower photocurrent yield and larger activation energy than the MC excitation with large $\Delta\alpha$. As the origin of this trend, it is considered that the spatial localization of the CT excited state enhances the exciton-phonon coupling. Actually, the strong lattice relaxation was confirmed for the CT excited state on the basis of the Stokes shift of the photoluminescence [12]. The strong exciton-phonon coupling should promote the formation of bound excitons associated with lattice relaxation. Thus, $\Delta\alpha$ provides a reasonable explanation of why the CT excitation demonstrates lower photocurrent yield than the MC excitation. It should be noted that the partial charges induced by the CT excitation should also enhance the exciton-phonon coupling [12].

Fig. 3. Temperature dependence of photocurrent yield for CT and MC excitations, measured for a pristine polymer film of PCDTBT [12].

Table I. Polarizability change $\Delta\alpha$, activation energy required to generate photocurrent E_a , and internal quantum efficiency (IQE) for CT and MC excitations in a pristine polymer film of PCDTBT.

	$\Delta\alpha / \text{C V}^{-1} \text{m}^2$	E_a / eV	IQE
CT	1.2×10^{-39}	0.09	0.004
MC	2.7×10^{-39}	0.06	0.010

In conclusion, we have studied the origin of relaxed exciton formation induced by the CT excitation for a typical DA-type polymer, PCDTBT. From the electroabsorption measurements, we obtained polarizability change $\Delta\alpha$ for the CT and MC excitations, which allowed us to examine the degree of spatial delocalization for them. We found that the values of $\Delta\alpha$ were clearly correlated with photocarrier generation characteristics: the spatially localized CT excited state with small $\Delta\alpha$ value demonstrates lower photocurrent yield and larger photocurrent activation energy than the MC excited state with large $\Delta\alpha$ value. These results

indicate that the spatial localization of the CT excited state enhances the exciton-phonon coupling and leads the formation of relaxed exciton. Thus, the spatial localization of CT excited state is crucial for efficient photocarrier generation in DA-type polymer OSCs.

ACKNOWLEDGEMENT

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) through its Innovative Solar Cell Program and by the Japan Society for the Promotion of Science (JSPS) through its Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program) and KAKENHI for Young Scientists (B) (24750190).

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(Received March 17, 2014; Accepted April 19, 2014)