Simultaneous Measurement of Photocurrent and Recombination Emission in Organic Solar Cell

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Abstract

Charge transfer (CT) state is a key intermediate to understand the recombination processes that induces a reduction of a power conversion efficiency in organic solar cells (OSCs). In this study, we measured the recombination emission from the CT state under different applied voltage in the OSC device and a photocurrent density flowing on the circuit simultaneously. By the experiment, we extracted only the information of CT state emission at the interface and proposed `PL-V plot` that is the voltage dependence of PL intensity of the CT state. The PL-V plot includes the information only from the radiative recombination at donor/acceptor interface, and is complementary to the `J-V plot` that is the most important information for evaluating OSCs. The result demonstrated that the fill factor of PL-V plot is definitely higher than that of J-V plot because the PL-V plot observes the CT state recombination only at the D/A interface, predicting the ideal FF of the device. Furthermore, the value of the activation energy for the non-radiative recombination is estimated by the temperature dependence of the CT state emission intensity. Our result demonstrated that the simultaneous measurement of photocurrent and recombination emission proposed in this study could be a strong tool for evaluating photoconversion characteristics at the D/A interface in OSCs.

Main text

Organic solar cells (OSCs) have attracted attention as a renewable energy source because of its low-cost and flexibility. However, in order to put OSCs to practical use, the power conversion efficiency (PCE) of OSCs that have exceeded over 18% should get close to crystalline silicon SCs[1,2]. In a typical donor/acceptor (D/A) type OSCs, an exciton that is generated by light absorption is dissociated into an electron-hole pair by utilizing an energy difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the D/A materials, and charge transfer (CT) state that is defined as a bounded charge pair by Coulomb attraction at the D/A interface forms. Free charges eventually form from the CT states after overcoming the Coulomb attraction[3]. On the other hand, a recombination process that is a deactivation from a generated free charge to a ground state occurs through the CT state. The recombination processes are mainly classified as a radiative and non-radiative recombination. Especially, the non-radiative recombination that is induced by a thermal vibration is a main problem that causes large energy loss in open-circuit voltage (V_{oc}) in OSCs[4,5]. Therefore, clarifying the mechanism that induces the recombination loss is an important for further improving the PCE of OSCs. Generally, the CT state that is a key intermediate for recombination processes is investigated by an electroluminescence (EL) measurement[6]. However, a large amount of charges have to be injected into the device by applying a relatively large forward voltage to measure EL of the CT state emission because the CT state has extremely low emission quantum yield as low as from 10^{-3} to $10^{-5}\%$ due to small overlaps of molecular orbital between D/A materials[6]. The character of the CT state should be investigated under similar condition with standard SC operation, namely light irradiation and moderate applied voltages.

In this study, we observed the radiative recombination emission from the CT state by simultaneously measuring the photocurrent density flowing on the OSC device under different applied voltage. Relationships between the amount of radiative recombination and extracted photocurrent density to the electrode under different applied voltages is as follows: in the open-circuit condition of the OSC devices, the photogenerated current density (J_{ph}) and recombination current density (J_{rec}) balances, namely all the generated charges are recombined via CT state[7]. Thus, photoluminescence (PL)

intensity of recombination emission from the CT state was maximized, and no net current flows on the circuit. When the applied voltage goes below the V_{OC} , some of free charges starts to be collected to the electrodes, but others recombined due to insufficient electric field in the device. Therefore, recombination emission decreases and photocurrent flowing in the circuit increases compared to the OC condition. In a short circuit condition, most of all CT state are separated and free charges are collected to the electrodes due to the enough large electric field. Thus, almost all of the recombination emission from the CT state is quenched. By subtracting PL spectra at short-circuit from open-circuit, we can extract only the information of CT state emission at the D/A interface by cancelling out a background signal that is independent on the bias voltage. Furthermore, we can introduce the concept 'PL- V plot' where the intensities of the recombination emission are plotted at different applied voltage from these observations. The plot includes the information only from the radiative recombination excluding the non-radiative recombination, and is complementary to the ' J - V plot' that is the most important information for evaluating OSCs but includes all the recombination events.

The device of bulk heterojunction (BHJ) OSCs were fabricated in the configuration of inverted structure with well-studied combination of PTB7 as electron donor and PCBM as acceptor materials (**Figure 1a**): ITO/polyethylenimine ethoxylated (PEIE)/PTB7:PCBM/MoO₃/Ag. The BHJ layer were spin-coated from the mixed solution of PTB7:PCBM by using chloroform as a solvent and 3% of 1,8-diiodooctane (DIO) as an additive[8–10]. The J - V characteristics of the PTB7/PCBM device under simulated solar light were presented in **Figure 1b**. The value of V_{OC} , short circuit current density (J_{SC}), fill factor (FF) and PCE were obtained as 0.74 V, 13.54 mA/cm², 67.10% and 6.76%, respectively. Those performances are comparable to the previous report[11]. CT state absorption and emission spectra were measured by a highly sensitive EQE and EL measurements as presented in **Figure 1c**. The CT state absorption and the emission peaks could be fitted by a Gaussian function based on Marcus theory[6]. The peak centers of the CT state absorption and the emission were determined as 1.46 eV and 1.18 eV, respectively. As the result, CT state energy (E_{CT}) was determined as 1.32 eV by the intersection of the two Gaussian curves (**Figure 1c**) [6].

To investigate the radiative recombination from the CT state under different applied voltages, PL spectra of PTB7/PCBM device at near infrared region irradiated by 470 nm monochromatic LED light was measured under the open-circuit (0.75 V) to short-circuit (0 V) conditions in 0.01 V steps (**Figure 2a**). The reason for choosing excitation wavelength at 470 nm was that PTB7 had small absorbance at the wavelength to reduce a fluorescence signal and the wavelength was enough far to the NIR region where the CT state emission appears. The light intensity was set as 468 mW/cm² at which the device shows four times larger J_{SC} than 1 sun condition of solar simulator. The V_{OC} of the device in this excitation condition was 0.75 V. In the PL spectrum when the V_{OC} (0.75 V) was applied, small peaks at 1050 nm was observed in the emission tail of the fluorescence from PTB7. The peaks gradually decreased and disappeared with smaller applied voltage than 0.5 V. The PL emission was quenched by the internal electric field, and the EL spectrum of the device in **Figure 1c** revealed that the peak center of the CT state was 1050 nm. Therefore, we concluded the PL emission at 1050 nm was from radiative recombination from the CT state. To separate the emission tail of the fluorescence from PTB7 and the CT state emission, the PL spectra was subtracted by the spectrum at 0 V where almost all of the CT state was quenched and only the PTB7 fluorescence that is bias independent remains. The subtracted PL spectra as **Figure 2b** clearly exhibited the peak center of CT state emission was 1050 nm and the emission was quenched under smaller voltage than 0.5 V.

The intensity of the CT state emission irradiated by 470 nm LED under applied voltage was plotted with the photocurrent density flowing on the device during the PL measurement in **Figure 3**. We got the two plots: voltage dependence of photocurrent density (J - V plot), and the voltage dependence of the PL intensity from the CT state recombination that we call as PL- V plot. The J - V plot was the most important information for evaluating OSC performance but includes all the recombination events such as radiative and non-radiative recombination, whereas the PL- V plot includes the information only from the radiative recombination of the CT state. The two plots present the opposite voltage dependence, namely the photocurrent density increases from zero as the applied voltage decreases from V_{OC} , whereas The PL intensity decrease from V_{OC} . When the zero intensity of PL- V plot at 0 V is adjusted to J_{SC} of J - V plot and the maximum intensity of PL at V_{OC} is adjusted to

zero, we can compare the voltage dependence of the photocurrent and the intensity of the recombination emission, i.e. FF of these two plots. **Figure 3** exhibited that there was clear difference in the voltage dependence of the two plots: J gradually increased with the voltage decrease from V_{OC} to 0 V, whereas PL suddenly quenched from V_{OC} to 0.6 V. The J - V and PL- V plots are fitted by an equivalent circuit model of the diode[12], and the FF of the two plots were calculated as 49.81% and 71.73% in J - V and PL- V , respectively. The result indicated that additional recombination that PL- V plot cannot detect take place when the OSC device was operated.

To understand the origin of FF difference between the J - V and the PL- V plots, we investigated the light intensity dependence of those plots. Light intensity of 470 nm LED monochromatic light was fixed as 468 mW/cm² that was same condition as **Figure 2** and **3**, the irradiated light intensity to the device was controlled by neutral density filters from 100% to 10%. The photocurrent density and the PL intensity were measured at the different applied voltage and plotted in **Figure 4a** and **b**. The maximum PL intensity was normalized to the J_{sc} at each light intensity to compare the difference of the two plots clearly. The FF of all the fitting curves were calculated and plotted in **Figure 4c**. The FF of the J - V plots monotonically decreased from 66.73% to 49.81% when the light intensity was increased from 10% to 100%, whereas FF of the PL- V plots kept constant over 70% regardless of the light intensity. The result indicated that the recombination that causes FF difference between the J - V and the PL- V plots were sensitive to the light intensity and promoted at high carrier concentration condition. To closely evaluate the FF difference of the two plots, the photocurrent density and the PL intensity values at the different applied voltages are plotted as a function of the light intensity. The plots were fitted by power functions and the slope values (α_{JV} , α_{PL}) were summarized in **Table 1**. The slope is 1 when the photocurrent and the PL intensity has linear relationship with light intensity, but it decreases less than 1 when the recombination is promoted as high carrier concentration condition. α_{PL} s kept the value close to 1 regardless of the applied voltage, whereas α_{JV} monotonically decreased as the applied voltage approaching to the V_{OC} [13]. The results indicated that the recombination that can be observed in J - V plot has large influence at high carrier concentration and smaller internal electric field close to the V_{OC} .

Figure 5a and **b** are schematics of the different information detected by the J - V and PL- V plots, respectively. In the BHJ device, some of photogenerated charges recombine before they reach the electrodes, and only extracted charges are reflected in the J - V plots. The result of the light intensity dependence revealed that the recombination observed in the J - V plots is dominant at high carrier concentration and smaller internal electric field condition, indicating it occurs during charge transport[14]. On the other hand, the PL- V plot is a method that directly observes the CT state recombination only at the D/A interface. Thus, the PL- V plot is able to predict the ideal FF, which considers only the characteristics of charge separation and recombination near the D / A interface, is higher than that of the J - V plots.

The simultaneous measurement of photocurrent and recombination emission is a strong tool for extracting only the information of CT state emission at the interface. To investigate the origin of non-radiative recombination in OSCs, the CT state emission spectra extracted by subtracting PL spectra at short-circuit from open-circuit excited by 470 nm LED in the PTB7/PCBM device were observed under different temperature from 30 to -50°C in 5°C steps as shown in **Figure 6a**. The intensity of CT state emission increases with decreasing device temperature. This is because the non-radiative recombination induced by thermal vibration of the organic semiconductor molecules in the active layer was suppressed by cooling of the device temperature. The peak intensities of the CT state emission at the various temperature were plotted in **Figure 6b**. The temperature dependence of the PL intensity is expressed as the following thermal quenching formula because non-radiative recombination rates are thermally activated[15,16]:

$$I = I_0 / [1 + a \exp(-\frac{E_a}{kT})] \quad \text{eq. 1}$$

where I is PL intensity, I_0 is the PL intensity at $T = 0$ K, a is pre-exponential factor, k is Boltzmann constant, T is temperature and E_a is the thermal activation energy for inducing non-radiative recombination. The calculated E_a from the Arrhenius plot in **Figure 6b** is 64.9 meV. The intramolecular vibration energy of rubrene that is typical donor molecules in organic semiconductor has been reported as ~140 meV [17]. On the other hand, the energy of several intermolecular vibrational modes in a DNTT crystal that is a famous hole transporting material with high mobility

has been reported as ranging from 2 and 12 meV[18]. Our result of the excitation energy for thermal activation of non-radiative recombination from the CT state was in between the energy values of inter- and intra-molecular vibrations of organic semiconductors in the previous reports. This is possibly because the molecular vibration of both donor and acceptor materials contributed into the intermolecular vibration of the CT state.

In summary, we demonstrated the concept `PL-V plot` that includes the information only from the radiative recombination in the PTB7/PCBM device that is one of the most famous D/A combination in OSCs. The PL-V plots are clearly different from *I-V* plots in voltage dependence, resulting the FFs of *J-V* and PL-V plots were calculated as 49.81% and 71.73%, respectively. The light intensity dependence measurement revealed that the difference of FFs was caused by the recombination during charge transport, and the PL-V plot is able to predict the ideal FF, which considers only the characteristics of charge separation and recombination near the D/A interface. Furthermore, the value of the activation energy for the non-radiative recombination is estimated by the temperature dependence of the CT state emission intensity. Our result demonstrated that the simultaneous measurement of photocurrent and recombination emission proposed in this study could be a strong tool for evaluating photoconversion characteristics at the D/A interface in OSCs.

Methods

Device fabrication

The ITO substrate was pre-cleaned in UV ozone cleaner for 20 min. A thin layer of polyethylenimine ethoxylated (PEIE) was prepared by spin-coating at 5000 rpm for 60 s on the ITO substrate. Immediately, PEIE film was annealed at 200 °C for 10 min in the air. The PTB7:PCBM (5:7.5 g/L) was dissolved in chloroform (CF) with the solvent additive of 1,8-diiodooctane (DIO) (3%, v/v). The solution was spin-coated at 1000 rpm for 120 s onto the PEIE layer and the thickness of the active layer was about 120 nm. The MoO₃ hole transporting layer (10 nm, 0.1 nm/s), and Ag electrode (100 nm, 0.3 nm/s) were deposited via thermal evaporation under high vacuum ($\sim 10^{-5}$ Pa) in a vacuum evaporation system (VTS-350M, ULVAC) housed in a glove box (UNICO). The devices were

encapsulated in the glove box by a glass substrate and epoxy resin, and characterized without exposure to air. The devices were placed in a cryostat for temperature dependence measurement.

Evaluation for the device performance

The *J-V* characteristics of the devices were measured under simulated solar light illumination (AM 1.5, 100 mW/cm²) from a solar simulator based on a 300 W Xe lamp (Hal-320, Asahi Spectra) using source meter (R6243, Adventest). The light intensity was calibrated with a standard silicon solar cell (CS-20, Asahi Spectra). The active area of the devices was defined using a 0.126 cm² photomask. The light intensity was controlled by neutral density filter (AND-50S, SIGMAKOKI) in the measurement of the light intensity dependence. The highly sensitive EQE of the devices was measured on a Hypermonolight SM 250F system with NF LI5640 lock in amplifier (Bunkoh Keiki).

Optical measurements

The UV-vis absorption spectra were measured on a spectrometer (V-570, JASCO). The near-IR PL spectra were measured by SPEX Fluorolog 3-21 (HORIBA) with InGaAs detector. The excitation light source was the 470 nm monochromatic LED light (LED470L, THORLABS). The bandwidth of monochromatic LED light was 22 nm. The active area of the devices was defined using a 0.126 cm² photomask. The *J-V* characteristics of the devices during PL experiments were measured using source meter (Model 2450, KEITHLEY).

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Figure 1. (a) Chemical structure of the donor (PTB7) and acceptor (PCBM) materials. (b) *J-V* curves of the PTB7/PCBM device under A. M. 1.5, 100 mW cm⁻² irradiation and dark. (c) EQE (red) and

reduced EL (blue) spectra of the PTB7/PCBM. (d) Absorption spectra of PTB7 (black), PCBM (blue) pristine film and PL spectra of PTB7 (red).

Figure 2. (a) PL spectra of the PTB7/PCBM device irradiated by 470 nm monochromatic LED under different applied voltages. (b) CT emission of PTB7/PCBM device under monochromatic light (470 nm) irradiation.

Figure 3. J - V and PL - V plots with the approximate curves of the PTB7/PCBM device under 470 nm monochromatic LED light irradiation.

Figure 4. Light intensity dependence of (a) J - V and (b) PL- V plots with approximate curve of the PTB7/PCBM device. (c) Fill Factor of the approximate curve of J - V (black) and PL- V (red) plots. The photocurrent density and the normalized PL intensity at the different applied voltage as a function of the light intensity.

Table 1. summary of the slope of J - V curve (α_{JV}) and PL- V plot (α_{PL}) with the injection voltage.

Injection voltage $/V$	α_{JV}	α_{PL}
0.1	0.9626	0.9627
0.2	0.9612	0.9585
0.3	0.9444	0.9565
0.4	0.9229	0.9548
0.5	0.8732	0.9565
0.6	0.7774	0.9675
0.65	0.7249	1.0345

Figure 5. A simplified schematic of (a) the photoconversion process from CT state formation to charge extraction and (b) radiative recombination at D/A interface in as OSCs.

Figure 6. Temperature dependence of (a) CT emission spectra and (b) CT emission intensity of PTB7/PCBM device.