

# Photoconversion Mechanism at the *pn*-Homojunction Interface in Single Organic Semiconductor

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## Abstract

Clarifying critical difference of free charge generation and recombination process in between inorganic and organic semiconductor are important for developing efficient organic photoconversion devices such as solar cells (SCs) and photodetector to catch up inorganic devices. Recently, we have reported that *pn*-homojunction interface in a single organic semiconductor films formed by doping can achieve efficient charge separation. In this study, we analyzed the doping concentration dependence on the photoconversion process in the organic *pn*-homojunction SC devices mainly by a temperature dependence measurement.

## 1. Introduction

Free charge generation processes by light absorption in inorganic and organic semiconductors are completely different. Inorganic semiconductors have a large dielectric constant; thus, free charges are directly formed after the light absorption in a single semiconductor material. In contrast, a strongly bounded Frenkel type exciton forms after light absorption in organic semiconductors, because they generally have a smaller dielectric constant when compared with that of inorganic semiconductors. Recently, we have reported that *pn*-homojunction interfaces in a single organic semiconductor films formed by doping can achieve efficient charge separation [1]. The organic *pn*-homojunction solar cell SC device showed a high internal quantum efficiency of 30%.

In this study, we analyzed the doping concentration dependence on the photoconversion process in organic *pn*-homojunction SC devices mainly by a temperature dependence measurement.

## 2. Results and discussion

Fermi level of organic semiconductors was controlled by doping effect. *pn*-homojunction was produced by Fermi level alignment when the *p* and *n*-type doped layers were contacted. Ambipolar molecule: diindinoperylene (DIP: Fig 1a) was used as a host material for the *pn*-homojunction device. MoO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> dopants were introduced into the DIP layer via co-deposition techniques. (Fig 1b). Fig. 1c shows *J-V* characteristics of *pn*-homojunction device. The same concentrations

of MoO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> were introduced in the *p* and *n* layers, respectively. Short-circuit current density (*J*<sub>SC</sub>) of DIP device with 5% doping increased 8 times from undoped one. In contrast, open-circuit voltage (*V*<sub>OC</sub>) decreased from 1.13 V to 0.83 V.

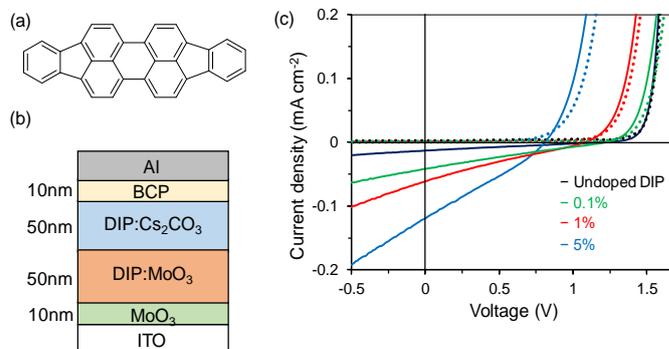


Fig. 1 (a) Chemical structure of DIP. (b) Schematic of the *pn*-homojunction device with the MoO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> doped layer. (c) *J-V* curves of *pn*-homojunction devices.

To investigate the charge generation and recombination processes, we measured the *J-V* characteristics of the devices at temperatures. Firstly, the temperature dependence of *J*<sub>SC</sub> is expressed by the following Arrhenius Equation (1):

$$J_{SC} = J_0 (P_{light}) \exp(-E_a / kT) \quad (1)$$

where  $J_0(P_{light})$  is the pre-exponential factor,  $E_a$  is the activation energy,  $k$  is Boltzmann constant, and  $T$  is temperature [2]. The origin of  $E_a$  was attributed to activation process during charge separation.  $E_a$  of the devices with 1% and 5% doping calculated from the Arrhenius plots is 110 and 74.4 meV, respectively (Fig 2a). A lower  $E_a$  of the 5% doped device than 1% doped device indicates that the charge separation was accelerated at higher doping concentrations.

Next, the temperature dependence of  $V_{OC}$  is expressed by the following equation:

$$qV_{OC} = E_g^{eff} + nkT \ln(J_{ph} / J_{00}) \quad (2)$$

where  $q$  is elementary charge,  $E_g^{eff}$  is effective bandgap energy at the interface,  $n$  is ideality factor,  $J_{ph}$  is the photogenerated current density, and  $J_{00}$  is the pre-exponential factor of the reverse saturation current density. Equation (2) represents

the  $V_{OC}$ , which is determined by the former energetic term and latter recombination loss term, which are dependent on the temperature [3]. The effective energy gap ( $E_g^{\text{eff}}$ ) of both devices calculated from temperature dependence of open-circuit voltage ( $V_{OC}$ ) is 1.95 and 1.75 eV, respectively (Fig 2b). The results indicate that the decrease in  $V_{OC}$  owing to an increase in doping concentration is the result of the reduction in the effective energy gap at the interface.

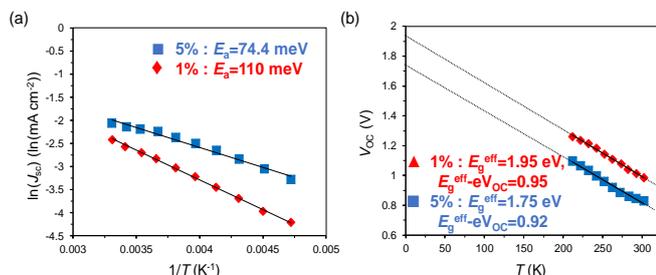


Fig. 2 Temperature dependence of (a)  $J_{SC}$  and (b)  $V_{OC}$  for the 1% doped (red) and 5% doped (blue)  $pn$ -homojunction devices.

The energy diagrams of the active layer in the  $pn$ -homojunction devices were estimated based on the result of the Kelvin Probe (KP) measurement. To estimate the energetic structure of whole films, we calculated the electric potential distribution derived from Poisson's equation [4]. Fig. 3 shows the calculated energy diagram of the active layer in the  $pn$ -homojunction devices. The total depletion width ( $W$ ) and built-in-potential ( $V_{bi}$ ) values of the 5% and 1% doped DIP devices are 20 nm and 1.40 eV and 60 nm and 0.99 eV, respectively. The result of energy diagrams suggests that the offset in adjacent molecules increases with increasing doping concentration.

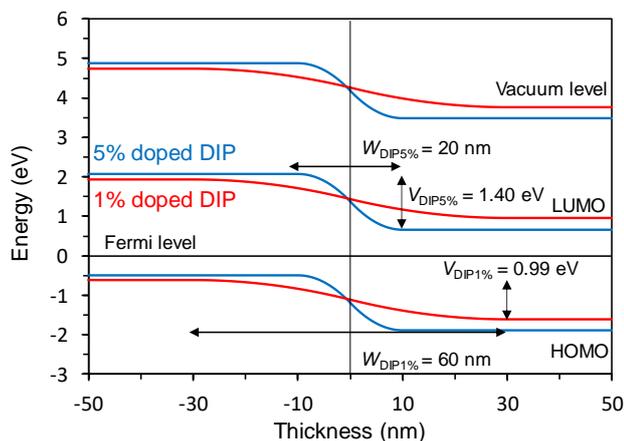


Fig. 3 Vacuum level, HOMO, and LUMO energy levels relative to the Fermi level in the 1% doped DIP (red) and 5% doped DIP (blue) devices as a function of film thickness.

The reason for the smaller  $E_a$  in the 5% doped device, compared with that in the 1% device, was that larger energy offset not only accelerated exciton dissociation, but also suppressed geminate recombination from the charge transfer (CT) state. In contrast, temperature dependence of  $V_{OC}$  revealed that the  $V_{OC}$  difference in the doping concentration was attributed to

the  $E_g^{\text{eff}}$  difference, not to the recombination loss difference.  $E_g^{\text{eff}}$  reflects the energy of charge recombination center. In the case of inorganic SCs,  $E_g^{\text{eff}}$  corresponds to the energy of the bandgap of the semiconductor material because the charge recombination happens from delocalized charges on the conduction and valence bands. In contrast,  $E_g^{\text{eff}}$  in the conventional D/A-type OSCs corresponds to the CT state energy because localized electrons on the lowest unoccupied molecular orbital (LUMO) of the acceptor and holes on the highest occupied molecular orbital (HOMO) of the donor recombine. The result of this study indicates that the charge recombination in the organic  $pn$ -homojunction SCs happens from localized holes and electrons at the two adjacent molecules and this mechanism is similar to that of the conventional D/A type OSCs.

### 3. Conclusions

In this study, we used the same host material, and only the interfacial energetics were modified by doping. the temperature dependence of  $J$ - $V$  characteristics and energy structure measurement revealed that the increase in  $J_{SC}$  and decrease in  $V_{OC}$  with an increase in doping concentration in the organic  $pn$ -homojunction SC devices was the result of the acceleration of charge separation and the change in energy of the recombination center. The charge separation mechanism in the device is that the localized exciton and CT state are separated by the energy offset between adjacent molecules, and the recombination happens from the localized charge carrier at two adjacent molecules, similar to those of D/A type OSCs. The primordial difference in the photoconversion process between inorganic and organic  $pn$ -homojunction SCs comes from the delocalized and localized nature of charges in inorganic and organic semiconductors, respectively.

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