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学位論文題目 Study of Charge Recombination in Organic Solar Cells

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## Summary of Doctoral Thesis

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Title Study of Charge Recombination in Organic Solar Cells

Organic solar cells (OSCs) are attracting considerable attention as renewable energy because of low-cost technology and flexible solar modules. However, to place OSC into practical use, the power conversion efficiency (PCE) is lower than that of Si. Therefore, improving PCE is the important theme of OSC research. The PCE of OSCs is produced of its short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), and fill factor (FF). High-performance OSCs show ~100% internal quantum efficiencies, which indicates that the devices can efficiently photogenerate charges. Thus, researchers have focused on enhancing  $V_{oc}$  to increase the efficiency of OSCs.  $V_{oc}$  decides charge transfer (CT), state energy, and energy loss. CT state is the important point to research the recombination process and charge recombination energy loss affects the voltage loss of OSCs. The development of organic solar cells requires explaining the mechanism of charge recombination. The author focused on charge recombination in OSCs. The primary objectives of this thesis are listed below.

(i) Photoconversion mechanism of *pn*-homojunction OSCs

The exciton is separated using the energy offset between the donor and acceptor molecules in OSCs. The author's primary question is whether a free charge formation is possible in single organic semiconductor material by light absorption compared with that in inorganic semiconductors. Recently, an organic *pn*-homojunction interface that achieves efficient charge separation has been reported. However, the author analyzed the doping concentration dependence on the photoconversion process in organic *pn*-homojunction OSC devices, primarily by temperature dependence measurement.

(ii) Simultaneous measurement of photocurrent and recombination Emission

Non-radiative recombination induced by thermal vibration causes considerable voltage loss in OSCs. Therefore, for improving  $V_{oc}$ , the recombination loss from the CT state is important. However, considerable amounts of charges must be injected into the device by applying a relatively large forward voltage to measure the electroluminescence of the CT state emission because the CT state has a low emission quantum yield of as low as  $10^{-3}$  to  $10^{-5}\%$  because of small overlaps of molecular orbitals between D/A materials. The character of the CT state should be investigated under a similar condition with standard SC operations such as light irradiation and moderate applied voltages. Thus, the author observed radiative recombination emission from the

CT state by simultaneously measuring the photocurrent density flowing on the OSC device under different applied voltages.

This thesis comprises four chapters.

In chapter 1, the fundamental knowledge of OSCs and the motivation of this study are introduced. Thus, the photoconversion process, the device performance of OSCs, and recombination issues are described.

In chapter 2, organic *pn*-homojunction solar cells are described. The author fabricated organic *pn*-homojunction solar cells using a single material. It was able to adjust that the Fermi level of organic semiconductors using the doping effect. It was able to adjust that the Fermi level of organic semiconductors using the doping effect. Organic *pn*-homojunction was produced by Fermi-level alignment when *p* and *n*-type doped layers were contacted. Ambipolar molecule: diindinoperylene (DIP) was used as a host material for *pn*-homojunction devices. The doping concentration was controlled between 1% and 5% by volume rate, and the same concentrations of dopants (both MoO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub>) were introduced in the *p* and *n* layers, respectively. Thus, the  $J_{SC}$  of the DIP device with 5% doping increased eight times from the undoped one; however,  $V_{OC}$  decreased from 1.13 to 0.83 V.

The temperature dependence of  $J$ - $V$  characteristics was measured to investigate the charge generation and recombination process. The activation energy during charge separation of 1% and 5% doped devices was calculated to be 110 and 74.4 meV, respectively. Moreover, the effective bandgap energy of 1% and 5% doped devices were calculated to be 1.95 and 1.75 eV, respectively. The result of the temperature dependence of  $V_{OC}$  shows that the decrease in  $V_{OC}$  due to increasing doping concentration can be caused by the reduction in the effective energy gap ( $E_g^{eff}$ ) at the interface.

The concentration dependence of energy diagrams suggests that the offset in adjacent molecules increases with increase in doping concentration. The larger energy offset both accelerated exciton dissociation and suppressed geminate recombination from the charge transfer (CT) state. Furthermore, the temperature dependence of  $V_{OC}$  revealed that the  $V_{OC}$  difference in the doping concentration was attributed to the  $E_g^{eff}$  difference, and not to the recombination loss difference.  $E_g^{eff}$ , which is the primary difference between inorganic and organic semiconductors, reflects the energy of the charge recombination center. However, this study shows that the charge recombination in the organic *pn*-homojunction SCs occurs from localized holes and electrons at the two adjacent molecules.

In chapter 3, the radiative recombination emission from the CT state under different applied voltages was measured at the same time as the photocurrent density

flowing over the OSC device. The author introduced the concept “PL- $V$  plot” in which the intensities of the recombination emission are plotted at a different applied voltage. The plot includes information from the radiative recombination, excluding the non-radiative recombination, and is complementary to the “ $J$ - $V$  plot.” The bulk heterojunction (BHJ) devices were fabricated by a well-studied combination of PTB7 as an electron donor and PCBM as an acceptor material.

Under the open-circuit to short-circuit, the radiative recombination from the CT state was estimated. The CT state emission spectra gradually decreased and disappeared with an applied voltage of  $<0.5$  V. The CT state emission was quenched by the internal electric field.

The FF of the two plots was calculated as 49.81% and 71.73% in  $J$ - $V$  and PL- $V$ , respectively. Thus, the result indicated that additional recombination that the PL- $V$  plot cannot detect occurs when the OSC device was operated.

The FF of both plots shows different behavior when the irradiated light intensity was controlled from 100% to 10%. The FF of the  $J$ - $V$  plots monotonically decreased from 66.7% to 49.8% when the light intensity was increased from 10% to 100%, whereas the FF of the PL- $V$  plots remained constant at  $>70\%$  regardless of light intensity. The result shows that the recombination that causes FF difference between the  $J$ - $V$  and the PL- $V$  plots was sensitive to the light intensity and promoted at a high carrier concentration condition and the  $J$ - $V$  plot has a large influence at a high carrier concentration and smaller internal electric field close to the  $V_{OC}$ . Furthermore, the PL- $V$  plot is a method that directly observes the CT state recombination only at the D/A interface. Therefore, the PL- $V$  plot could predict the ideal FF, which considers only the characteristics of charge separation and recombination at the D/A interface and it is higher than that of  $J$ - $V$  plots.

The temperature dependence of the CT state emission intensity has expressed the thermal quenching formula because non-radiative recombination rates are thermally activated, and the calculated activation energy from the Arrhenius plot is 64.9 meV. This result shows the vibration modes of the CT state existed between intermolecular and intra-molecular vibration.

In Chapter 4, a summary of this thesis, the conclusion, and prospects drawn from it are presented.

This thesis can be summarized as follows.

- 1) Using an ambipolar molecule, an organic  $pn$ -homojunction solar cell was realized. As the doping concentration of  $p$ - and  $n$ -layer increased, the energy offset of  $pn$ -interface increased, and the current-voltage characteristics changed. First, a large energy offset between adjacent molecules accelerated the charge separation; therefore, the photocurrent was promoted. However, the HOMO-LUMO gap

between adjacent molecules decreased and it affected voltage drop. This result indicates that the charge recombination in organic *pn*-homojunction solar cells occurs from localized charge carriers at the adjacent molecules. The mechanism is compared with the CT state recombination in conventional D/A type OSCs, although the devices in this study were fabricated using a single host material and a doping technique resembling the inorganic *pn*-homojunction SCs.

- 2) As a method for directly measuring the recombination of the CT state, we simultaneously measured the photocurrent and radiative recombination of the CT state under an electric field. CT state emission represents the maximum intensity in the open-circuit condition of the device. However, it quenches in the short-circuit conditions. The new concept, PL- $V$  plot, contains only information about the radiative recombination and the FF is high from  $I$ - $V$  characteristics. The result shows that additional recombination that the PL- $V$  plot cannot occur when the OSC device was operated. The light intensity dependence measurement revealed that the difference in FFs was attributed to recombination during charge transport. Moreover, the activation energy for the non-radiative recombination is estimated from the temperature dependence of the CT state emission intensity. For evaluating photoconversion characteristics, the simultaneous measurement of photocurrent and recombination emission could be a useful method.

## 博士論文審査結果

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有機太陽電池の効率は近年 18% を越え、短絡光電流は  $20 \text{ mAcm}^{-2}$  以上となり、光電流量子効率 は理論的限界に近い 80% に達している。さらに効率を向上させるためには、開放端電圧と曲線因子の増大が必要であるが、この 2 つの性能はキャリアの再結合と深く関係している。出願者は有機太陽電池における複雑な各界面について、適切な試料系を選定することで、界面におけるキャリア再結合過程の機構を詳細に解明し、開放端電圧と曲線因子との新たな相関関係を明らかにしている。

第 1 章では、有機太陽電池の動作原理、電荷再結合の基礎について述べられている。また、本研究において、電荷再結合に着目した動機が述べられている。

第 2 章では、両極性有機半導体薄膜に、ドーピングによって pn ホモ接合を形成した系について述べられている。試料には diindenoperylene (DIP) 分子を用い、ドーパントとして  $\text{MoO}_3$  と  $\text{Cs}_2\text{CO}_3$  を用いて pn ホモ接合界面を作製した。X 線回折の結果から良質な結晶状態がドーピング後にも保持されていることを確認した。ドーピング濃度を増大させると、光電流が増大し、開放端電圧は減少するが各ドーパントに対して 5% 濃度で最大値を得た。温度依存性による電荷分離、再結合の解析、バンドマッピングによるエネルギー構造の解析から、pn 界面においては、隣接分子がドナー・アクセプター型のエネルギー関係となり、電荷移動(CT)状態が形成されていることが分かった。ドーピング濃度増大によって pn 界面での電界が増大するため、エネルギーオフセットが増大して光電流が増大し、CT 状態エネルギーが減少するため開放端電圧が減少する。さらにキャリア再結合は、この CT 状態の再結合によって起こっているという一連の変換メカニズムを明らかにすることに成功した。

第 3 章では、ドナーとアクセプターを混合した、バルクヘテロ接合を持つ有機太陽電池において、電荷移動(CT)状態からの CT 発光の電圧依存性 (PL-V プロット) と光電流の電圧依存性を同時測定する手法を初めて開発した。試料は典型的な有機太陽電池用のアクセプター (フラーレン誘導体; PCBM) とドナー (poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl) carbonyl]thieno[3,4-b]thiophenediyl; PTB7) を用いた。太陽電池特性の一般的な指標である光電流-電圧 (J-V) 特性の曲線因子は 0.5 であった。一方、本研究で初めて検討された PL-V プロットの曲線因子は 0.72 とかなり大きい値が得られた。これは、理論モデルから再結合のない理想的なセル特性に近いと推定される。CT 発光強度の最大値を開放端電圧に掃引することで照射光強度依存性を検討した結果、光電流-電圧特性の曲線因子を低下させているのは、自由になったホールと電子がセル内で会合し無輻射再結合を起こしているためであることが明らかになった。有機太陽電池の曲線因子が無輻射再結合によ

って低下しているのを、観測によって実証した例は、これまでにない。以上の結果は、電流値と電圧減少要因の一つとして無輻射再結合の寄与が示唆され、その再結合を抑制することで、有機太陽電池の効率向上の可能性を示している。

第4章では、本論文の結論と今後の展望が述べられている。

以上のように、本論文は、有機太陽電池の性能とキャリア再結合についての関係を詳細に解明しており、特に、再結合が曲線因子に及ぼす影響を、初めて観測することに成功していることから、基礎学術的、応用的に非常にレベルの高い研究であると判断できた。

博士論文は英語で記述され、出願者が第1著者の、審査のある国際誌の論文1報としてすでに掲載されている。審査員から指摘のあった、論文の修正にも適切に対応した。以上のことから、本博士論文は、博士（理学）の授与に値すると審査員全員一致で判断した。