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Sakiyama, Shin

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Komura, Takuya

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Iwashita, Hirotaka

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Mizutani, Naoki

Institute for Materials Chemistry and Engineering, Kyushu University

他

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# Carrier Density and Mobility in n-Doped Poly(*p*-Phenylene Vinylene)

Shin Sakiyama<sup>1</sup>, Takuya Komura<sup>1</sup>, Hirotaka Iwashita<sup>1</sup>,  
Naoki Mizutani<sup>2</sup>, Katsuhiko Fujita<sup>1,2\*</sup>

<sup>1</sup>Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

<sup>2</sup>Institute for Materials Chemistry and Engineering, Kyushu University

\*Author to whom correspondence should be addressed,

E-mail: katsuf@asem.kyushu-u.ac.jp

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The conductivity of a polymer semiconductor, poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) was drastically improved by n-type doping with LiF. The improvement of the conductivity is mainly caused by the improved carrier mobility. This phenomenon is attributed to trap filling by doping. The carrier generation should take place at a trap level of the semiconductor and the trap level can be filled, resulting in carrier mobility improvement. Furthermore, we fabricated the organic Schottky solar cells with n-doped MEH-PPV. Open circuit voltage (Voc) was significantly increased as the doping concentration increased, indicating that LiF in MEH-PPV can change Fermi level.

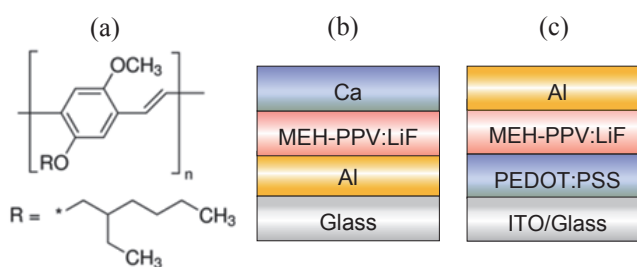
Keywords: organic electronics, polymer semiconductor, n-type doping, poly(*p*-phenylene vinylene).

## 1. Introduction

The doping for a polymer semiconductor has been widely studied over the two decades, with the purpose of enhancing the performance of organic devices such as organic solar cells (OPV), light-emitting diodes (OLED), thermoelectric conversion element, and thin film field effect transistors (OTFT). A number of approaches have been investigated, especially for p-type doping<sup>1-3</sup>. For example, the hole current of a polymer semiconductor can be enhanced by two orders of value upon the addition of Iodine, tetracyano-tetrafluoro-quinodimethane (F4TCNQ), and Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)<sup>1</sup>. Meanwhile, n-type doping for polymer semiconductor is still a challenge. In low molecular organic semiconductors, Cs, Cs<sub>2</sub>CO<sub>3</sub>, and Li, were utilized for n-dopants, however these dopants are not soluble in common solvent for organic semiconductors (toluene, THF, chlorobenzene, 1,2-dichlorobenzene)<sup>4-7</sup>. We screened various low work function materials which are soluble in a common solvent, and found that LiF was soluble in THF at required concentration. LiF has been used as the cathode buffer material for OPV and OLED. We report that, LiF doping in a polymer organic semiconductor, poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV, Aldrich, molecular weight: 10000) [Fig. 1 (a)], increases the electrical conductivity and open circuit voltage (Voc) in a Schottky solar cell.

## 2. Experimental

To investigate the electron current characteristics of MEH-PPV, an electron-only device (EOD), Ca/MEH-PPV:LiF/Al/Glass was fabricated [Fig. 1 (b)]. 6 mg/ml toluene solved MEH-PPV blended LiF in THF was spin coated at 2000 rpm, for 45 s (Mikasa spincoater 1H-D7), and metal electrode was deposited in vacuum. The current-voltage (J-V) characteristics were measured by Keithley 238 source meter without breaking vacuum after top electrode deposition. The electron density of the non-doped MEH-PPV was calculated from the I-V curves. A Schottky solar cell, Al/MEH-PPV:LiF/PEDOT:PSS/ITO/Glass was also fabricated [Fig. 1 (c)] to evaluate the effect of n-type doping in photoelectric conversion by using solar simulator (YSS-50A Yamashita Denso).



**Fig. 1.** (a) The molecular structure of the MEH-PPV, (b) electron only device, (c) Schottky solar cell.

### 3. Result and Discussion

Fig. 2 (a) shows J-V characteristics of EODs with LiF doping at the concentration of 0, 0.01, 0.1, and 1.0 wt%. In the non-doped device, slope of J-V curve was changed from Ohmic behavior (slope=1) to SCLC behavior (slope=2) at an inflection point ( $V_T$ ). This is typical behavior in conjugated polymer. On the other hand, current density in doped device was increased. The conductivity calculated from the ohmic regions of I-V curves increases against dopant concentrations [Fig. 2 (b)]. These results show that increase of carrier density or mobility enhanced conductivity by LiF doping into polymer.

For this reason, we confirmed electron carrier density using  $V_T$  which are each dopant concentrations. From this  $V_T$ , carrier density can be calculated as following equation<sup>8,9</sup>.

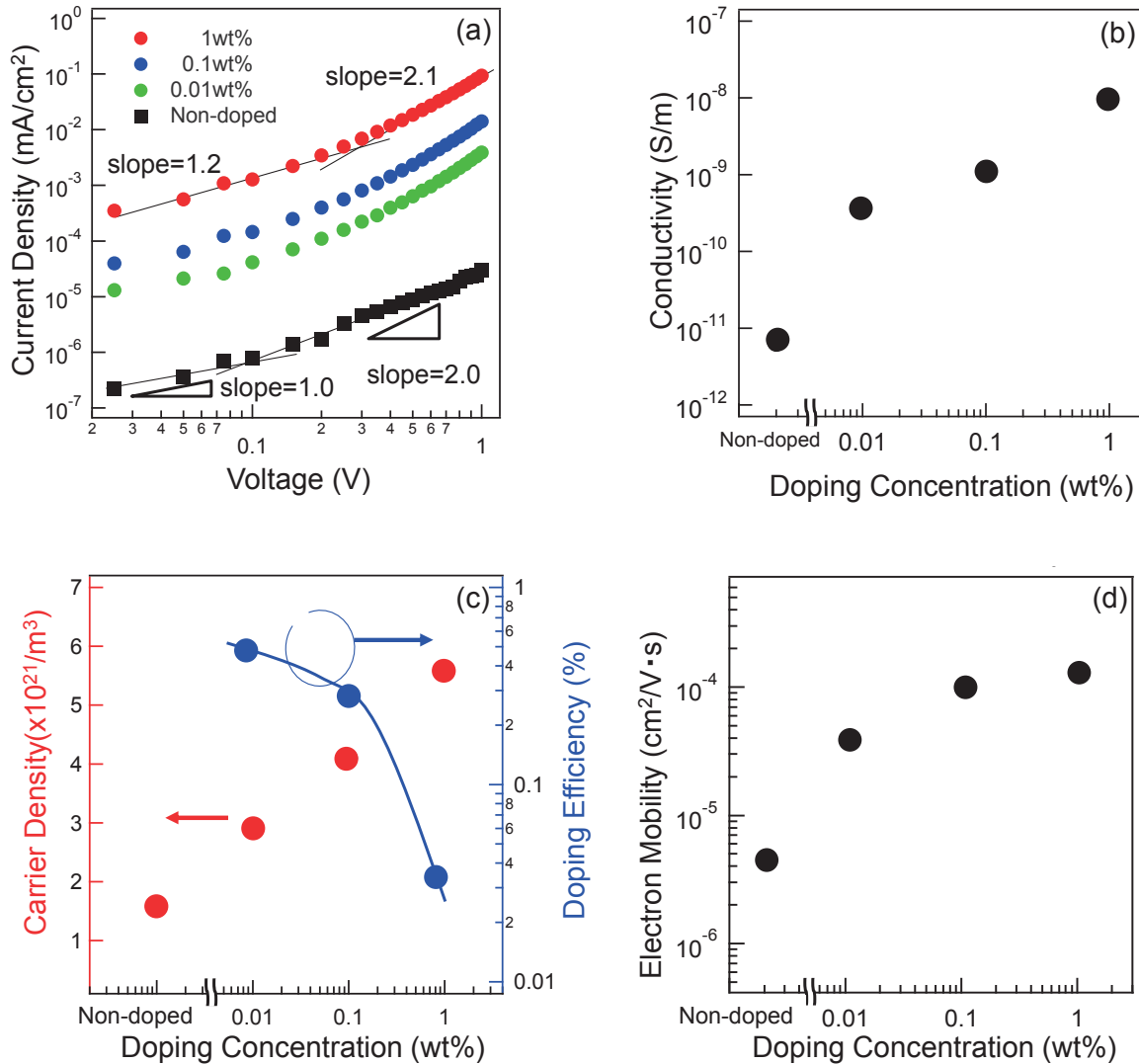
$$N = \frac{9}{8} \cdot \frac{\epsilon_0 \epsilon_r}{q} \cdot \frac{V_T}{d^2}, \quad (1)$$

where  $q$  is the charge of electrons,  $\epsilon_0$  is the permittivity of vacuum,  $\epsilon_r$  is the relative permittivity (MEH-PPV  $\approx 2.4$ ), and  $d$  is the thickness of the polymer layer. From carrier density, the doping efficiency (=number of generated carrier/ number of introduced dopants) was calculated. The carrier density increases with dopant concentrations, on the other hand, the doping efficiency was decreased with increasing doping concentrations [Fig. 2 (c)]. We assume that the low doping efficiency is due to the aggregation of dopants in polymer matrix.

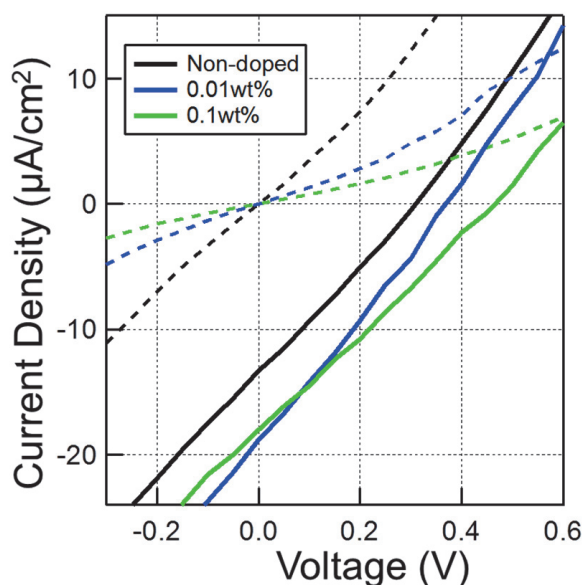
Then, we confirmed electron mobility by LiF doping effect. The electron mobility was calculated in the SCLC region using below.

$$J = q\mu N \frac{V}{d} \quad (2)$$

$J$  is the current density,  $N$  is the electron density,  $\mu$  is the electron mobility, and  $d$  is the thickness of the polymer layer. The calculated carrier mobility is shown in Fig. 2 (d). These results indicate that LiF doping in MEH-PPV



**Fig. 2.** EODs of MEH-PPV with LiF of (a) current-voltage characteristics, (b) conductivity, (c) carrier density and doping efficiency, (d) electron mobility at doping concentrations of 0, 0.01, 0.1 and 1.0 wt%.



**Fig. 3.** J-V characteristics and with LiF at the doping concentration of 0, 0.01, and 0.1 wt% (dotted line: dark current, solid line: photo current).

**Table 1.** Open circuit voltage ( $V_{OC}$ ), short circuit current ( $J_{SC}$ ), and fill factor (FF) of OPVs with LiF at the dopant concentrations of 0, 0.01, and 0.1 wt%.

	$V_{OC}$ (V)	$J_{SC}$ ( $\mu A/cm^2$ )	FF (%)
Non-doped	0.31	13.5	26.2
0.01 wt%	0.39	18.5	26.9
0.1 wt%	0.48	18.1	25.9

increases the electron mobility. Whereas the electron mobility shows a significant increase in two orders of magnitude, the carrier density increased by only three times. The improvement of the conductivity is mainly caused by the improved mobility. The work function of LiF is 3.5 eV,<sup>10)</sup> larger than the LUMO of MEH-PPV (3.1 eV). The carrier generation should take place at a trap level of the semiconductor and the trap level can be filled, resulting carrier mobility improvement<sup>11-13)</sup>.

We assumed that these improvements of polymer performance affect the photoelectric conversion. To study the influence of LiF doping on the photoelectric conversion of the polymer, Schottky solar cells (Al/MEH-PPV:LiF/PEDOT:PSS/ITO/Glass) were fabricated at the various doping concentrations of 0, 0.01, and 0.1 wt% (Fig. 3). Schottky solar cells are driven by a built-in potential difference of metal / semiconductor

interface.  $V_{oc}$  was increased as the concentration increased (Table. 1). This should be caused by the upper shift of the Fermi level by the n-doping.

#### 4. Conclusion

We have investigated the n-doping of MEH-PPV by blending LiF in the solution. LiF doping improved electric conductivity of MEH-PPV drastically. This increase is mainly caused by the carrier mobility improvement. Furthermore,  $V_{oc}$  of LiF doped Schottky solar cells were increased. These results indicate that the Fermi level of the polymer semiconductor can be shifted to the vacuum level surely by the n-doping.

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