Development of Computational Analysis Method for Carrier Transport Pathway in Light-Emitting Polymers

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1. Introduction

Polymer light-emitting diodes (PLEDs) based on conjugated polymers are under development for applications such as new generation displays and illuminations. For commercial use of PLEDs, it is required to improve the luminescence efficiency and life time of blue light-emitting polymers [1]. Controlling mobility of electrons and holes in organic layers is a key factor to improve the luminescence efficiency. This is because PLEDs emit the visible light by recombination of electron and hole in organic layers. Carrier mobility difference would cause less efficiency and degradation of PLEDs [2]. There are many studies about carrier transportation in PLEDs. It is known that the electron transport properties strongly depend on the morphology in the organic layers [3]. To construct a guideline for development of high efficiency materials, it is necessary to investigate the relationship between the morphology and carrier transport properties of conjugated polymers.

In this study, we developed the analysis method of carrier transport pathways in PLEDs by using quantum chemistry calculation and Monte Carlo method. We also applied it to the analysis of electron transport pathway in poly-(9,9'-dioctylfluorene) (PDOF) which is known as a good blue light emitting polymer. We investigated the effects of the morphology on the electron transport properties of PDOF.

2. Computational Details

Tight-binding quantum chemistry calculation

We have developed a tight-binding quantum chemistry calculation program, “New-Colors” [4]. This program was used for electronic structure calculations. The total energy is calculated from following equation,

$$E = \sum_{k} \epsilon_{k} + \sum_{i} \sum_{j \neq i} \frac{Z_{i}Z_{j} \epsilon^{2}}{R_{ij}} + \sum_{i} \sum_{j} \sum_{\nu} \frac{\rho^{\nu}}{R_{ij}} (R_{ij})$$

where $\epsilon_{k}$ and $R_{ij}$ is the elementary electric charge and the inter-nuclear distance, respectively. In order to decrease the computation time, parameters for ionization potential, $\zeta$ values of Slater-type orbital, resonance integrals, two-center electron repulsion integrals, and exchange repulsion integrals are used. They were determined on the basis of the density functional theory.

Carrier transport simulation

We assumed transportation of excited carriers as that of virtual carriers. We considered two types of virtual carrier transportation. One is migration to the nearby spatial points. The other is energy transfer to other MOs. Then, we also assumed that transportation of virtual carriers depended on the electron density, $\rho$, and energy level, $E$, of each spatial point and MO. We divided the calculation cell into $101 \times 101 \times 101$ meshes and calculated $\rho$ of each mesh. Carrier transport probability from mesh $i$ to mesh $j$, $P_{ij}$, was calculated by following equation,

$$P_{ij} = \rho \exp \left( \frac{E_{i} - E_{j}}{kT} \right)$$

where $k$ and $T$ are Boltzmann constant and temperature, respectively. $U$ is the constant value which presents the electron field. We selected the meshes which had large $\rho$ as the start points for the carrier transport simulation. We used Monte Carlo method to select a transportation trial of the virtual carrier. We obtained the trajectory of the electron transportation using this method. $\rho$ and $E$ are determined by quantum chemistry calculation.

3. Results and Discussion

Electronic structure of PDOF

A PDOF model was made of nine PDOF chains which were constructed of five repeat units shown in Fig.1(a). The model was relaxed by using our molecular dynamics calculation program, “NEW-RYUDO” [5]. The density of the model was almost same as the experimental density of PDOF films [3]. Octyl group in the model was replaced by hydrogen, because the octyl group doesn’t affect electronic structure. Fig.1(b) shows the PDOF model without octyl group. We calculated electronic structure of this model by using New-Colors. We focused on the MOs in bottom of the conduction band (CB), because these MOs strongly affect electron transport properties. Fig.2 shows the lowest unoccupied molecular orbital (LUMO)+3 and LUMO+8. As shown in Fig.2, the MOs of PDOF were not distributed over the cell, but localized only on one chain. This result suggests that to transport electrons along PDOF chains is easy, but between PDOF chains is very difficult.

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In order to investigate the electron transportation between PDOF chains, we injected 1,000 virtual electrons into each chain, and moved them at 500,000 steps according to calculated probabilities. Then, we counted the number of electrons in each MO, and calculated the rate of changes of electron number (CR) from following equation:

\[
CR = \frac{\text{last carrier number} - \text{1000}}{1000}
\]  

(3)

Fig.3 shows the CR of each MO. As shown in encircled area of Fig.3, there are some MOs whose CR are near zero. It suggests that electron transportation between the chains would be difficult. However, the CR of other MOs are very high or low. This result shows that there is significant electron transportation among these orbitals. In order to investigate the reason for this, we focused on the electron transportation between LUMO+3 and LUMO+8. Fig.4 shows the geometry structure and trajectory of the electron transportation. The showing range is the encircled area in Fig.2. In Fig.4, there are two polymer chains in which different MOs are spreading: (1)LUMO+8 spreads in the lower chain, (2)LUMO+3 spreads in the upper chain. As shown in Fig.4, the electron which was injected into LUMO+8 moved only along the chain with electric field. When the electron reached to the close aromatic rings, it transferred from LUMO+8 to LUMO+3 through the rings. After the transportation to LUMO+3, the electron didn’t return to LUMO+8 and moved along the chain with electric field. It suggested that electron transportation between two PDOF chains mainly occur in the very close aromatic rings.

The electrons which were injected into LUMO+5 and LUMO+7 could transfer to the LUMO through the close aromatic rings. However, it should be noted that the CR of LUMO+7 is slightly larger than LUMO+5 and LUMO+8. In the case where the electron can transfer from LUMO+7 to LUMO, there are close aromatic rings, but the distance between the rings is 3.96 Å. It is a little longer than the distance of the other places where the electron could be transported between the chains. In our simulation, we observed the electron transportation in the different polymer chains where the distance between two aromatic rings is within 4.0 Å.

4. Conclusion

In this study, we developed an analysis method of carrier transport pathway in PLEDs by using quantum chemistry calculation and Monte Carlo method. We also applied it to the analysis of electron transport pathways in PDOF films. As a result, we were able to investigate the effects of the morphology on the electron transport properties of PDOF. This method for the analysis of carrier mobility or light-emitting centers could be used as a guideline for development of high performance materials in PLEDs.

References