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Computational Analysis of Electron Injection on Light-Emitting Polymer/Cathode Interface

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1. Introduction

Polymer light-emitting diodes (PLEDs) have been attracted much attention for next generation displays and illuminations. For PLEDs to become commercially available, it is required to improve their luminescence efficiencies and lifetimes.

It is known that device properties such as turn-on voltage, lifetime, and luminescence efficiencies are greatly affected by the structure of polymer/electrode interface [1]. Therefore, a study on the relationship between interface structure and carrier injection property is important for improving the performance of PLEDs.

We have developed a simulation method for the analysis of carrier transfers in light-emitting polymers based on quantum chemistry (QC) calculation and Monte Carlo (MC) method. By using this method, we have simulated the carrier transfers in poly-(9,9'-dioctylfluorene) (PDOF) which has pure blue luminescence and high stability [2]. In this study, we used this simulation method for the analysis of electron injection of the PDOF/Ca interface. We constructed two PDOF/Ca interface models which have different polymer orientations. We calculated the electronic structure of each model by using QC calculation. We simulated the electron injections by using QC calculation results obtained. We investigated the relationship between structure and carrier injection properties in the PDOF/Ca interface.

2. Computational Details

For the construction of each PDOF/Ca surface model, we used a molecular dynamics (MD) and MC simulation methods. In these simulations, we used a consistent valence force field to represent atomic interactions [3].

To calculate electronic structures, we used our tight-binding QC calculation program, "New-Colors" [4]. Parameters of New-Colors were adjusted so as to reproduce the shapes and energies of molecular orbitals determined by density functional theory for isolated fluorene monomer and Ca unit structure.

Carrier transfer simulation was performed according to the QC calculation results. In this simulation, calculation cell was divided into three dimensional meshes. The mesh size was set to $0.3 \times 0.3 \times 0.3$ Å^3. We simulated electron transfer in materials as virtual carrier transfers among meshes. Then, transfer probability to each mesh was determined from the electronic density of each mesh [2].

3. Results and Discussion

PDOF/Ca interface model

We built a PDOF chain model consisting of five repeated units of a DOF monomer. Six PDOF chains were inserted into the unit cell and the structure was relaxed by MD simulation. On the PDOF model, we added 300 Ca atoms by using MC simulation. Fig. 1 shows the models after MC simulation. Two types of interface models were built. One is upright model, whose PDOF chain's backbones are spreading in the direction normal to the Ca surface. The other is horizontal model, whose PDOF chain's backbones are spreading in the direction parallel to the Ca surface.

Electronic structure of interface

We calculated the electronic structure of PDOF and Ca bulk models by using TB-QC calculation. Fig. 2(a) shows the partial density of states (PDOS) of PDOF-bulk model. The energy level of LUMO was less than the Fermi level of Ca-bulk. Therefore, it was suggested that the electron injection from Ca to the PDOF layer is favorable.

We also simulated the electronic structures of the interface models. Fig. 2(b) and 2(c) shows the PDOS of each model. Ca-4*s* orbital affected the C-2*p* orbital, and the energy level of PDOF's LUMO shifted to the higher energy level. Moreover, the energy shifts in the upright model was larger than in the horizontal model. From these results, it is suggested that the C-2*p* orbital in the upright model more strongly affected Ca-4*s* orbital than the horizontal model

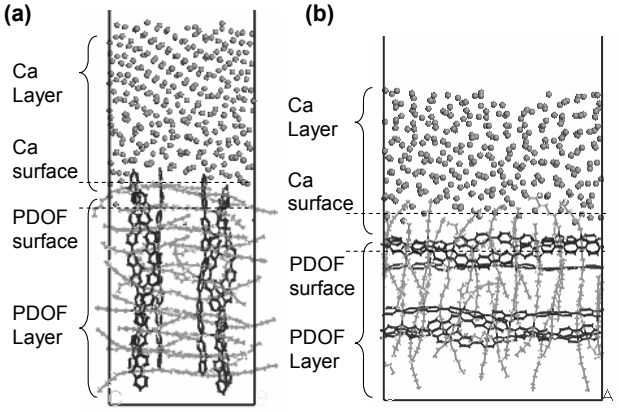

Fig. 1 Interface model, (a) upright model (b) horizontal model. The backbone atoms are emphasized in black. The dashed line shows each surface of the layer.

did. It is because of the difference in a distance between aromatic rings of PDOF chains and Ca atoms. As shown in Fig. 1, the distances between Ca atoms and aromatic rings are shorter in the upright model. Therefore, the interaction between Ca-4*s* orbital and C-2*p* orbital became stronger. However, in horizontal model, there are octyl side chains in the interface between Ca atoms and polymer backbones. Then, the octyl chains separated the Ca atoms from the aromatic rings and reduced the interaction between Ca-4*s* and C-2*p* orbitals.

Carrier transfer in interface

To analyze the carrier injection properties, we also simulated electron transfers in the interface models using the QC calculation results. Fig. 3 shows the distribution of carrier probability which is shown in color strength: the darker the more, and the lighter the fewer. In this carrier transfer simulation, we considered electron transfers from the injection plane to the PDOF surface shown in Fig. 3. As shown in Fig. 3(a), the electrons injected in the upright model stayed on the Ca surface and PDOF backbones. This result shows that the electron could transfer from the Ca to the PDOF layers along the polymer backbones in the upright model. On the other hand, the electrons injected in the horizontal model stayed only on the Ca surface. This means that the electrons injected in the horizontal model stopped near the Ca surface, and did not arrive on the PDOF layer.

Then, we counted the carrier numbers arriving on each surface of the models. Fig. 4 shows the ratio of arrived carrier numbers on each surface at each calculation step. The ratio was calculated from the counted numbers and total injected carrier numbers. As shown in Fig. 4, most of the electrons injected in the upright model arrived on the PDOF surface line at 500,000 simulation steps. However, in the horizontal model, injected electrons arrived only on the Ca surface, but hardly arrived to the PDOF surface at the same calculation step. From these results, we investigated that the electron transfer from Ca to PDOF layers is easier in the upright model than in the horizontal model. This difference should be caused by the strong interaction between Ca atom and aromatic ring in the upright model. Therefore, it is suggested that constructing a structure, which has close Ca atoms and aromatic rings, might be important to reduce electron injection barriers of PLEDs.

4. Conclusion

We analyzed the relationship between carrier injection properties and structures in the PDOF/Ca interface by using a carrier transfer simulation method. We found that the aromatic rings in the upright model, whose polymer chains oriented for the direction normal to the Ca surface, strongly interacted with Ca atoms. This interaction would cause easy carrier injection from Ca to PDOF layers. Therefore, it is suggested that controlling the orientations of polymer chains to upright models would reduce the electron injection barriers of PLEDs and improve the device properties.

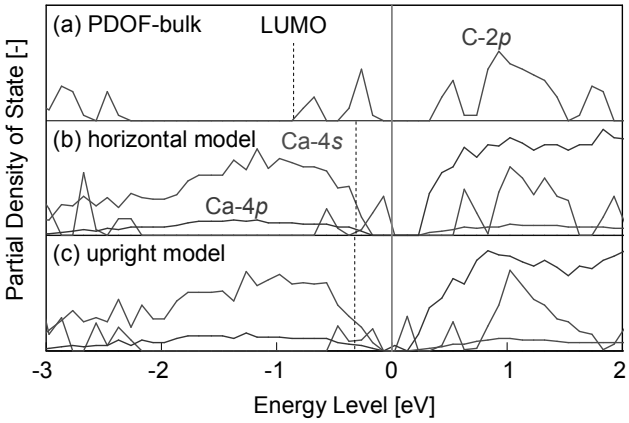

Fig. 2 Partial density of state. The dashed line shows LUMO of each model. The Fermi level of Ca-bulk was set as 0 eV.

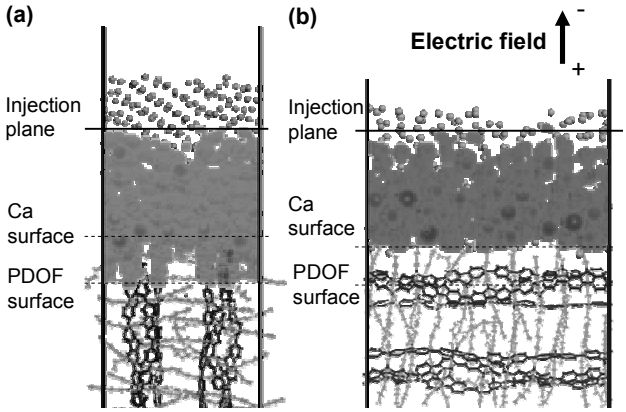

Fig. 3 Distribution of carrier probability: (a) upright model, (b) horizontal model. Solid lines show carrier injection planes. Dashed lines show Ca surface, and PDOF surface.

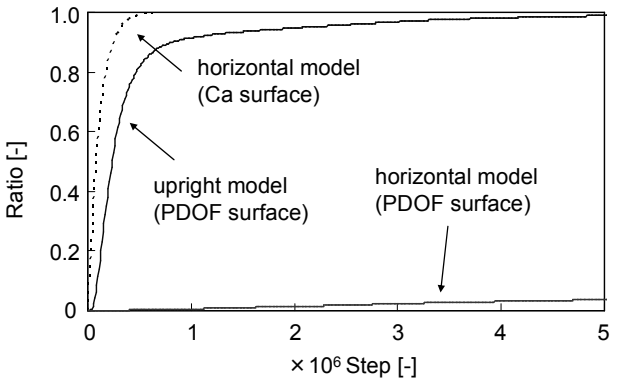

Fig. 4 Ratio of carrier numbers arriving on the each surface.

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