

Electronic structure of regioregular poly(3-hexylthiophene)

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1 Introduction

Organic semiconductors based on π -conjugated polymers are widely regarded as promising materials for low-cost fabrication of optoelectronic devices [1]. Currently some of the most intensely investigated applications are bulk heterojunction (BHJ) [2] photovoltaic devices (solar cells) and organic field-effect transistors (OFETs) [3] because of their potential for realizing low-cost, large-area, lightweight, and high-mechanical flexibility. The performance of these devices depends largely on the efficiency of interfacial charge transfer and charge generation which are influenced by morphology and molecular structure.

The BHJ solar cells are composed of blends of conjugated polymers such as poly(3-hexylthiophene) (P3HT) as an electron donor with fullerene derivatives as an electron acceptor [4,5]. Those components are commonly used in organic solar cells. The energy difference between the lowest unoccupied molecular orbital (LUMO) of the donor and the LUMO of the acceptor is very important factor to determine whether efficient charge transfer will take place.

2 Experiment

Experiments were performed using synchrotron radiation at the beamline BL-27A of the Photon Factory, High Energy Accelerator Research Organization (KEK-PF) in Tsukuba. The BL-27A is equipped with an InSb(111) double-crystal monochromator with energy resolution of ca. 0.8 eV around S *K*-edge. The XAS spectra were measured using monitoring sample drain current near the S *K*-edge (2465–2500 eV). Such energies were chosen to excite the S 1s core electron to unoccupied orbitals of Regioregular (RR)-P3HT.

3 Results and Discussion

Figure 1 shows unoccupied conduction band minimum near the Fermi level for π - π stacking film at the incidence angle of $\theta=55^\circ$ (magic angle) and polycrystalline powder of RR-P3HT as probed by S 1s XAS. Magic angle condition was used to eliminate the orientation effect for anisotropic systems. It was observed that the LUMO of π - π stacking film is lower in energy by 0.3eV than that of the polycrystalline powder, although these compounds are the same origin. They are chemically similar and have the same ionization potential for S 1s electron.

The lower energy shift of LUMO can be explained by the previous theoretical studies [6,7] that the interaction between the two molecules in cofacial leads to

splitting of the LUMO level to LUMO and LUMO+1, resulting in reduced LUMO energy. When a large number of stacked molecules interact, the conduction band is formed. This shift may also be explained by Davydov splitting that the interchain interactions in lateral aggregation of chains (π - π stacking) cause the splitting of the LUMO level.

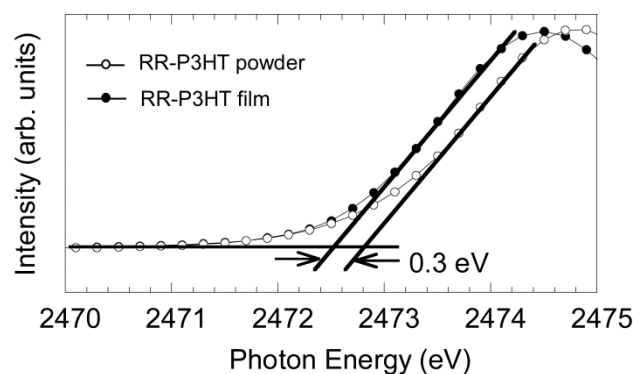


Fig.1 Unoccupied conduction band edge of RR-P3HT π - π stacking film and RR-P3HT polycrystalline powder.

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