

Driving Energy for the Formation of Molecular Bulk Heterojunction in Small Molecule based Organic Photodiode

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Molecular bulk heterojunctions have been introduced to organic opto-electronic devices such as organic solar cells and organic photodiodes to improve the device efficiency [1-3]. In organic bulk heterojunctions formed by interfacing a donor and an acceptor material, the driving force for exciton dissociation is provided by the energy offset between the molecular orbitals of the donor and acceptor [4]. Therefore, many studies have been made on the exciton dissociation dynamics as a key process that governs the power conversion efficiency of the organic opto-electronic devices [5]. On the other hand, a fundamental understanding of the major factors that control the formation of organic bulk heterojunction, or intermolecular packing structures, is still unsatisfactory and ambiguous, despite the exciton dissociation dynamics is affected greatly by the intermolecular packing structure also. Here, we address this issue by applying vibrational spectroscopic experiment performed on green-sensitive organic photodiodes with varying the composition ratio of donor to acceptor.

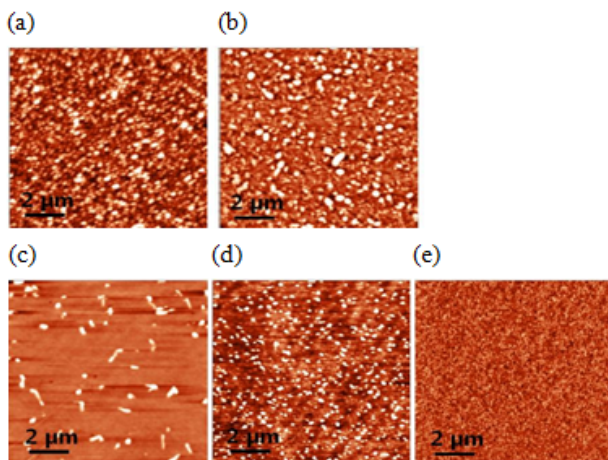


Fig. 1. AFM morphologies of vacuum evaporated (a) DMQA and (b) DCV3T films. (c)-(e) are those of blend films: the composition ratios of DMQA:DCV3T are 3:1 (c), 1:1 (d), and 1:3 (e), respectively. The rms roughness is 28.29 ± 4.39 nm, 17.36 ± 0.98 nm, 0.66 ± 0.03 nm, 1.02 ± 0.03 nm, and 11.44 ± 0.84 nm, respectively.

We examine the role of hydrogen bonding in the molecular packing and domain structures of the organic donor-acceptor bulk-heterojunction (BHJ) films, composed of N,N'-dimethyl-quinacridone (DMQA) as a donor and a dicyanovinyl terthiophene derivative (DCV3T) as an acceptor. In XRD experiments, all blend films show amorphous structures and thermal annealing does not change their crystallinity, although the donor-only and the acceptor-only films show the crystalline phases after thermal annealing (Fig.2).

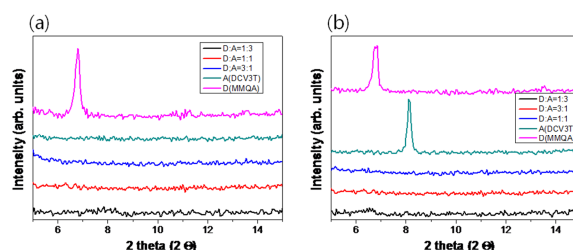


Fig. 2. XRD spectra of each blend film before (a) and after thermal annealing (b). ('A' denotes acceptor molecule and 'D' denotes donor molecule in legend)

Raman and FT-IR spectral changes show that the BHJ forms interpenetrating network efficiently between donor and acceptor molecules for the case of low composition ratio of donor, while acceptor molecules are thought to aggregate again each other to form a domain structure with increasing the relative composition of donor (Fig. 3). We provide also that the competition of CH---NC hydrogen bonding with butyl---OC hydrogen bonding in DMQA-DCV3T binary system decides the intermolecular packing structures of the blend film to affect on domain size. DFT and molecular mechanics calculations for stabilization energy and geometry optimization for several binary systems support these experimental results.

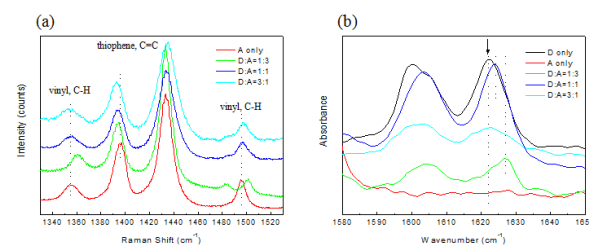


Fig. 3. Raman (a) and FT-IR (b) spectra of each film ('A' and 'D' in legend denotes acceptor and donor molecule, respectively. The peak marked by arrow near 1620 cm^{-1} in FT-IR spectra corresponds to C=O stretching vibrational absorption.)

In summary, we propose that hydrogen bonding is the one of the key driving force for forming nanoscale morphology in bulk heterojunction of organic semiconductors. For the understanding of the packing structure in molecular level, vibrational spectroscopy supported by DFT calculation is a very promising method. We may use these approaches to develop a molecule or a material combination as a kind of material design or selection guide to express higher quantum efficiency for organic opto-electronic devices with bulk heterojunction.

References

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