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Evidences of photocurrent generation by hole–exciton interaction at organic semiconductor interfaces

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ABSTRACT

The charge–exciton interaction at the donor/acceptor interface plays a significant role in the exciton dissociation processes, and thus influences the performance of organic solar cells. In this work, the evidences of photocurrent generation via hole–exciton interaction (HEI) at the organic semiconductor interface in organic solar cells, which is the counterpart of photocurrent generated by electron–exciton interaction, is demonstrated. A heterojunction, composed of copper phthalocyanine (CuPc) and fullerene (C_{60}), is used to provide free holes that interact with the excitons supplied by perfluorinated hexadecafluorophthalo-cyaninatozinc (F16ZnPc). The fact that photocurrent generation via HEI is well evidenced by: (1) a short circuit current of 0.38 mA cm^{-2}; (2) the jump of an external quantum efficiency (EQE) around 800 nm after adding a bias light; (3) the EQE variations under bias light of different wavelengths and light intensities; and (4) the superlinear dependence of the photocurrent on the light intensity.

1. Introduction

Organic solar cells (OSCs) are promising candidates for photovoltaic applications due to their potential advantages of light weight, low cost manufacture and flexibility [1–5]. Power conversion efficiencies (PCE) in the range of 9–10% for OSCs have been demonstrated [6,7], and are now comparable to inorganic photovoltaic cells, such as those based on amorphous silicon [8]. In order to further increase the solar cell efficiency, it is important to indentify and understand the factors that govern the performance of OSCs. An exciton (the excited electron–hole pair where the hole and electron are tightly bound together) is produced when a photon is absorbed in organic semiconductors. Although converting excitons to free carriers in OSCs is one of the basic photon-to-charge converting processes, it is still not fully understood. Generally, free charges can be generated in organic semiconductor devices by dissociating excitons at the donor/acceptor (D/A) interface [9–13]. Under ideal conditions, these free charges would be collected by the electrodes.

However, practically, these free electrons (which are transferred to the lowest unoccupied molecular orbital ($LUMO_A$) of the acceptor) or free holes (which are located on the highest occupied molecular orbital ($HOMO_D$) of the donor) cannot be completely collected by the electrodes. Therefore, these free charges could return to regenerate excitons, or recombine across the D/A interface [14–17]. Other physical mechanisms governing these excitons and free charges are exciton–exciton interaction (including singlet–singlet annihilation, triplet–triplet annihilation, exciton–exciton recombination across interface to generate free carriers [18,19]) and charge-exciton interaction [20–23] (electron–exciton interaction and hole–exciton interaction (HEI)).

These processes mentioned above coexist at the interface of organic semiconductor, which would have negative influence on the free charge generation and collection. However, they would have positive effect on photocurrent of OSC if they (exciton–exciton and charge–exciton interaction) are clearly understood and explored properly. As it is known, besides the exciton dissociation process at the D/A interface, the processes of charge–exciton interaction and exciton–exciton recombination across the interface have been proposed for the generation of free carriers [20,22,24]. If an OSC is designed to capture the carriers from these processes, a photocurrent can be detected [24,25]. For example, Song et al.

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have demonstrated that a photocurrent can be generated in an n–n type solar cell through intermolecular exciton recombination [24]. Chen et al. have shown that the interaction between electrons and excitons contribute to photocurrent generation [25]. Transient photovoltage measurement and phase change with chopper frequency were used to indirectly verify photocurrent generation by the interaction between electrons and excitons [25]. However, more direct evidences for photocurrent contribution from the electron–exciton interaction are still lack. More importantly, photocurrent generation due to the counterpart of electron–exciton interaction, namely, HEI, has not yet been reported. In this paper, we design OSC devices to confirm photocurrent generation through hole–exciton interaction at the organic semiconductor interface. Several evidences, including the external quantum efficiency (EQE) enhancement using a bias light, the EQE variation under a bias light of different wavelengths or intensities, and the superlinear dependence of photocurrent on the light intensity, are solid confirmations of photocurrent generation through HEI in OSC devices.

2. Experimental sections

2.1. Materials

The organic materials (their molecular structures are given in Fig. 1(a)) perfluorinated hexadecafluorophthalo-cyaninatozinc (F16ZnPc), phthalocyanine (CuPc), fullerene (C_{60}), tris-8-hydroxy-quinolinato aluminum (Alq3) were bought from Sigma Aldrich and used as received. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was bought from Heraeus.

2.2. Device fabrication

An OSC device was fabricated based on a structure consisting of indium tin oxide (ITO)/PEDOT:PSS/F16ZnPc/CuPc/C_{60}/Alq3/Ag, as shown in Fig. 1(a). A pre-patterned ITO glass substrate with a sheet resistance about 15 Ω/square was ultrasonically cleaned for 20 min by sequentially ultrasonic cleaning in detergent, acetone, and deionized water, respectively. After oxygen plasma treatment, the ITO was modified by adding a 40 nm thick PEDOT:PSS layer on top of it. Then, three organic layers, namely, F16ZnPc of thickness 20 nm, CuPc of thickness 15 nm and C_{60} of thickness 55 nm, were thermally evaporated onto the PEDOT:PSS in turn in vacuum. The thin film absorbance spectra of F16ZnPc, CuPc and C_{60} are shown in Fig. 1(b). All active layers were deposited under a pressure about 8×10^{-6} Pa with a deposition rate of 1.2 nm min^{-1}. A 10 nm thick Alq3 buffer layer was deposited at a rate of 0.9 nm min^{-1}. Finally a 100 nm Ag electrode was deposited under a vacuum of 2×10^{-5} Pa at a rate of 4 nm min^{-1} through a shadow mask to define an area around 9 mm^2. The deposition rate was monitored in situ by a calibrated quartz oscillator.

2.3. Device characterization

The current–voltage (*I*–*V*) measurements were carried out by Keithley 2400 under 100 mW cm^{-2} (AM 1.5 G) simulated sunlight from a Newport solar simulator (94043A). The EQE of the devices was calculated from the photocurrent measured by a lock-in amplifier (SR-830). A 150 W xenon lamp was used in conjunction with a monochromator to supply AC modulated monochromatic light. A tungsten lamp of intensity 40 mW cm^{-2} was employed as a DC white bias light. DC bias light with different wavelengths were realized by inserting an appropriate optical filter between

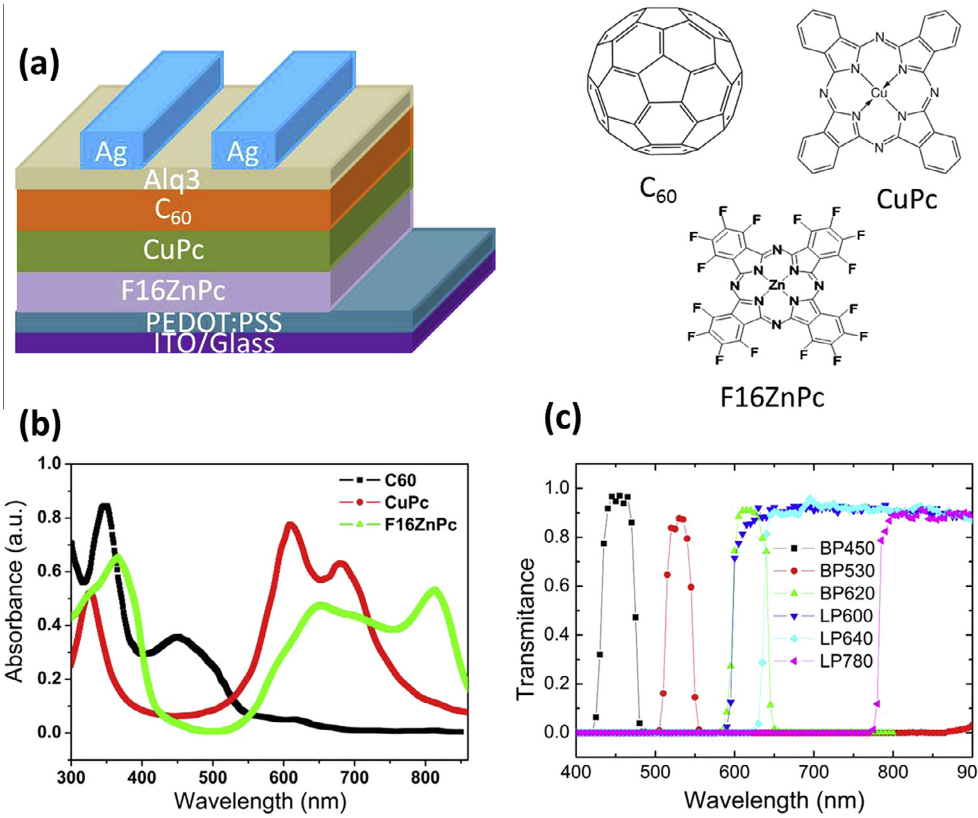

Fig. 1. (a) (left) The OSC device structure and (right) molecular structures of C_{60}, CuPc and F16ZnPc. (b) Absorbance spectra of C_{60}, CuPc and F16ZnPc thin films. (c) The transmittances of the various band pass and long-wavelength pass optical filters used in the experiments.