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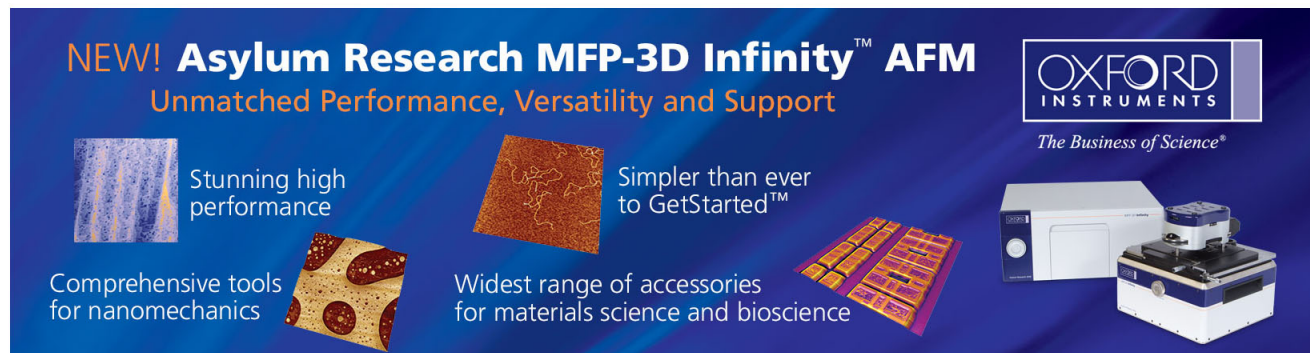
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Infrared photocurrent response of charge-transfer exciton in polymer bulk heterojunction

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We study the charge-transfer exciton absorption and photocurrent response in solution-processed bulk heterojunction based on poly(3-hexylthiophene) donor and (6,6)-phenyl-C₆₁-butyric acid methyl ester acceptor in the near-infrared wavelength region. While the exciton absorption exists only for wavelength below 650 nm, direct generation of charge-transfer exciton formed between the donor and acceptor extends the absorption wavelength to 950 nm. For films with micrometer thickness, the photon-to-electron conversion efficiency is about 60% at 750 nm wavelength under reverse voltage bias and the photocurrent to dark current ratio is about 8.6 at 900 nm and remains 3.6 even at 1000 nm. Photodetector with high sensitivity covering exclusively the 650–1000 nm near infrared region can therefore be made without a low bandgap material. The charge-transfer exciton absorption coefficient and photocurrent sensitivity depend on the annealing condition which controls the donor-acceptor morphology. © 2008 American Institute of Physics.

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Organic semiconductors have found applications in a wide range of optoelectronic and electronic devices. Most of the device operations are governed by the basic physics of excitons and charge carriers. In addition to exciton and carrier, charge-transfer exciton is another important type of excitation which can be viewed as a bound electron-hole pair where the electron and hole belong to two different semiconductors in close contact. Charge-transfer exciton is commonly observed in the blend of two organic materials forming type II semiconductor junctions between the electron donor and electron acceptor. In such donor-acceptor blend, the lowest excited state is the charge-transfer exciton, or exciplex, formed between them. There are, few reports on its effect on the absorption. So far, no device application is based on charge-transfer exciton except for emission spectrum tuning in some organic light-emitting diode.¹ But study on charge-transfer exciton in organic semiconductors remains mostly academic.

One of the most studied materials for donor-acceptor blend is poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl-C₆₁-butyric acid methyl ester (PCBM) developed for solar cell application.² P3HT and PCBM form bulk heterojunction with large interface area which favors the formation of charge-transfer exciton.³ In this work, we study the infrared

absorption as well as photocurrent of the P3HT:PCBM blend of thicknesses from 200 nm up to 14 μm. By comparing pure P3HT and PCBM samples with blends of various micromorphologies controlled by annealing conditions, we observe large infrared absorption and current responses due to charge-transfer exciton, which peaks at 750 nm and extends up to 950 nm. As the film is thick enough, the incident photon to current conversion efficiency (IPCE) under reverse voltage bias can be as high as 60% at 750 nm, where both P3HT and PCBM do not absorb at all.

The energy diagram and device structure of the bulk heterojunction are shown in Fig. 1(a). The electron affinity (EA) and ionization potential (IP) of the materials are labeled in eV. PEDOT is poly(3,4-ethylene dioxythiophene) doped by poly(styrene sulphonate). Because the energy difference between the donor and acceptor electron affinities is larger than the exciton binding energy of the donor, usually less than 0.5 eV, the lowest excited state of the donor-acceptor bulk heterojunction blend is expected to be the charge-transfer exciton which is a bound state of a hole in P3HT and an electron in PCBM. Since the intermolecular Coulomb attraction between these two particles is weak, the charge-transfer exciton energy is estimated to be close to the difference between the IP of P3HT and EA of PCBM. The charge-transfer exciton involves two different molecules and the Coulomb interaction depends on the details of the intermolecular geometry which has a wide statistic distribution in

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such a disordered system. In other words, the charge-transfer exciton does not have a definite energy but a broad distribution below the exciton. Since the P3HT exciton energy is 1.9 eV (650 nm), the charge-transfer exciton energy is expected to cover the highly desirable near infrared region for solar cell as well as photodetector applications.⁴ Once an exciton in P3HT is generated by photon absorption, it will quickly relax into an charge-transfer exciton in the bulk heterojunction because of the availability of an interface within the exciton diffusion length. The charge-transfer exciton can decay directly through radiative or non-radiative channels. It can also decompose into two free charge carriers.

The donor-acceptor blend with 1:1 weight ratio is used. P3HT concentration is 17 mg/ml in dichlorobenzene solution. The blend solution is spin coated at 450 rpm over PEDOT. The active layer thus made by spin coating is 200 nm thick. We also fabricate thicker films by multiple drop casting with thickness ranging from 1 to 14 μm , depending the times of drop casting. The samples are fabricated in the nitrogen environment. Ca(35 nm)/Al(100 nm) electrode is formed by thermal evaporation on top of the active layer. For photocurrent measurement, a continuous-wave white light beam generated by a 250 W quartz-tungsten-halogen lamp (Osram) plus monochromator is focused on the active layer of the sample as the excitation. The lamp power is calibrated by the Si photodiode (New Focus). In order to avoid the overtone effect of the monochromator, we use a high-pass filter to remove the wavelength lower than 550 nm.

The absorption spectra of the P3HT:PCBM blend are shown in Fig. 1(b) for various annealing conditions. The absorption of the pure P3HT, is also shown for comparison. For pure P3HT, there is no absorption beyond 750 nm (1.6 eV) within experimental accuracy while for the blend, there is a broad tail of absorption extended to as long as 900 nm (1.38 eV).⁵ We attribute this infrared absorption to the charge-transfer exciton for three reasons. First, the absorption exists only in the blend but not in the individual components. Second, the charge-transfer exciton is the only excited state of the blend with such a low energy. Third, the absorption is sensitive to the annealing condition which is known to control the microscopic morphology of the donor-acceptor blend, which in turn controls the total interface area and, therefore, the strength of the absorption. It is interesting that we get the highest absorbance without baking and vacuum where the solvent evaporation is the slowest. The slow evaporation is known to facilitate the self-assembly of the donor and acceptor into a closely interpenetrating networks at the nanometer scale with presumably the largest interface area.⁶ The interpenetration network gives large short circuit current for the solar cell by more efficient exciton dissociation and large infrared absorption for the photodetector by higher charge-transfer exciton density of state. The absorption from 600 to 900 nm corresponds to a energy range of 0.69 eV, which is close the difference of 0.62 eV between the Coulomb binding energy for electron-hole separations of 3 and 5 \AA assuming the dielectric constant is 3.

Figure 1(c) shows the absorption spectra and photocurrent conversion efficiency IPCE for 200 nm active layer thickness. The shape of IPCE is similar to the absorption spectrum. The maximal IPCE is 80% at 600 nm under -5 V bias. Let us turn to the infrared region. Even though small compared with the visible region, there is clearly a photocur-

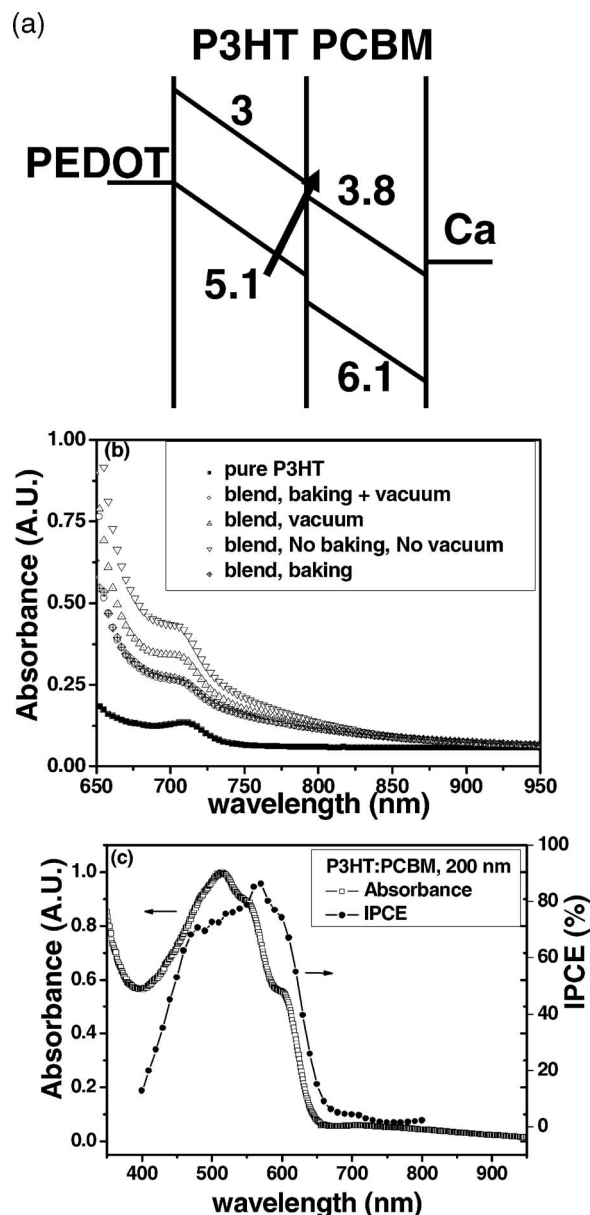


FIG. 1. (a) The device structure and energy diagram under reverse bias of P3HT and PCBM bulk heterojunction. The electron affinity and ionization potential are given in eV. (b) The absorption spectrum of pure P3HT and P3HT:PCBM blend at different baking and vacuum conditions. (c) The absorption spectra of P3HT:PCBM and the incident photon to current conversion efficiency (IPCE) of the device of ITO/PEDOT/P3HT:PCBM/Ca/Al, the active layer is 200 nm.

rent response of up to 800 nm for the 200 nm sample.

The photocurrent response of 14 μm thick sample is shown in Fig. 2(a). Voltage biases at 0, -100 , and -200 V are used. The bias is high but the electric field is not strong. In 200 nm sample, the electric field is 25 V/ μm at -5 V, while the field is 14 V/ μm for 14 μm sample at -200 V. For 14 μm sample, there is pronounced photocurrent response from 650 to 900 nm. The photon energy in this region (1.9–1.38 eV) is well below the bandgap of P3HT. Interestingly, the photocurrent response at the visible region below 650 nm now become negligible for this thickness in sharp contrast to Fig. 1(c). In 200 nm thin film, the film thickness is about the same as the penetration depth of the visible light, so, the visible light will create a uniform distribution of photocarriers throughout the thickness. In 14 μm

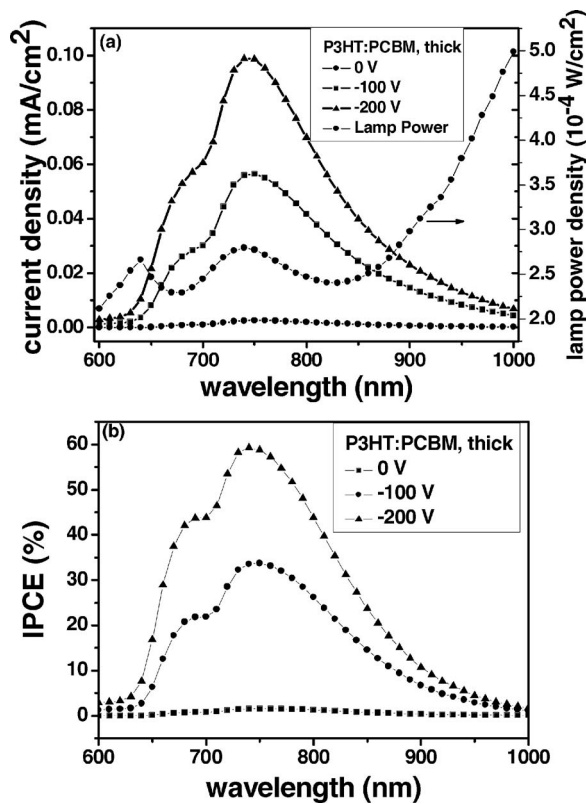


FIG. 2. (a) The lamp power density of quartz-tungsten-halogen lamp and the current density of ITO/PEDOT/P3HT:PCBM (14 μm)/Ca/Al under 0, -100, and -200 V reverse biases as functions of the incident photon wavelength. (b) The IPCE of ITO/PEDOT/P3HT:PCBM (14 μm)/Ca/Al under 0, -100, and -200 V biases.

films, the thickness is much larger than the penetration depth so the visible photons are all absorbed very near to the PEDOT electrode and the photocarriers are difficult to travel across the thick film without recombination. On the other hand, the infrared photons have weaker absorption coefficient and are able to penetrate into the thickness to generate a uniform distribution of photocarriers for 14 μm films. We therefore make an exclusive infrared photodetector based on two materials which absorb only at the visible and ultraviolet by themselves. The increase of the infrared absorption with the film thickness also shows that the absorption is a bulk effect instead of interface effect caused by, say, PEDOT. The infrared absorption as well as photocurrent both require the existence of the acceptor, indicating its origin of charge-transfer exciton absorption. The power density of the output of the monochromator as a function of the selected wavelength is also shown in Fig. 2(a). In Fig. 2(b), we divide the photocurrent by the lamp photon flux to obtain the conversion efficiency IPCE for the 14 μm sample. The IPCE achieves 60% at 750 nm at reverse bias of 200 V and remains 10% even at 900 nm. In addition to IPCE, the sensitivity of the photodetector is also characterized by the ratio between the photocurrent to the dark current I_p/I_d . In Fig. 3(a), the photocurrent for sample with 1 μm active layer thickness is shown as a function of the negative voltage. The absolute value for the voltage is used for clarity. At 900 nm photocurrent, I_p is much larger than I_d at lower voltage but approaches I_d at higher voltage, causing the smaller I_p/I_d

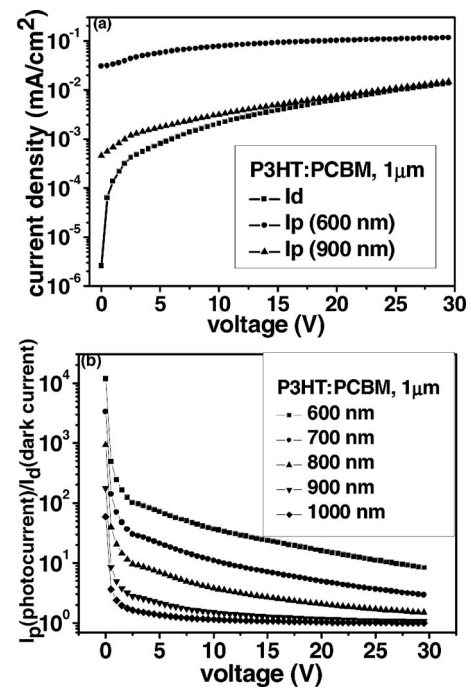


FIG. 3. (a) The photocurrent density and dark current density of the photodetector ITO/PEDOT/P3HT:PCBM (1 μm)/Ca/Al at 600 and 900 nm. (b) The current ratio I_p/I_d of ITO/PEDOT/P3HT:PCBM (1 μm)/Ca/Al at 600–1000 nm excitation wavelength under 0 to -30 V reverse biases.

ratio. The photocurrent of 600 nm is much higher than dark current even at higher bias. The current ratio is shown in Fig. 3(b) for excitation wavelengths with varied bias. At -0.5 V bias and under lamp power after the monochromator, the current ratio reaches 489 for the maximal P3HT absorption at 600 nm. Even at 1000 nm, the lamp light can be detected with current ratio of 3.6.

In conclusion, it is demonstrated that high sensitivity infrared photodetector covering 650 to 1000 nm spectral region can be made based on the direct photogeneration of intermolecular excited state charge-transfer exciton, which usually manifests itself only in the decay of the photoexcitations and is rarely involved in the absorption and device applications. Using solution-processed donor-acceptor bulk heterojunction developed by organic solar cell, the charge-transfer exciton infrared photodetector is made simply by increasing the film thickness to several microns without involving any low bandgap material.

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