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Highly sensitive, low-voltage, organic photomultiple photodetectors exhibiting broadband response

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Highly sensitive polymer photodetectors exhibiting broad spectral responses, ranging from the ultraviolet to the near-infrared (NIR) region, are obtained after incorporating an organic NIR dye into the device active layer. As a result, high external quantum efficiencies ($>7000\%$) and high responsivities (32.4 A/W) are achieved at an extremely low operating voltage (-1.5 V). The high photomultiplication could be attribute to trapping of electrons, originating from the photogenerated electron/hole pairs, at the dye molecules, which effectively facilitates hole injection from the external circuit. The device preparation scheme presented herein opens up the possibility fabricating lost-cost, flexible organic photodetectors. © 2010 American Institute of Physics.

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Organic photodetectors (OPDs) are attracting considerable interest because they have many advantageous properties, including low-cost fabrication, light weight, large device areas, and mechanical flexibility.¹⁻⁵ More interestingly, they allow the realization of devices exhibiting unique functions, such as flexible sheet image scanners⁶ and hemispherical focal plane detector arrays that can mimic human eyes.⁷ Highly sensitive OPDs exhibiting broad spectral ranges, based on both polymers and small molecules, have been reported recently.^{8,9} To obtain highly sensitive photodetectors, a high photoconductive gain (electron-to-photon quantum efficiency $>100\%$) is desirable. For inorganic semiconductors, avalanche photodiodes, which usually exhibit high gains, are typically fabricated through impact ionization under a high reverse bias.¹⁰ The disordered structures of organic thin films usually result, however, in strong localized charge carriers. As a result, an electrical field that is several orders of magnitude greater is required to induce ionized states.¹¹ Nevertheless, photomultiplication (PM) in organic photodiodes have been observed; the authors attributed this phenomenon to a decrease in the charge injection barrier across the metal-organic contact after photoinduced charge trapping in the bulk of the active layer or at the contact.¹²⁻¹⁵ Herein, we report a simple approach toward achieving a PM effect in organic photodiodes. After adding a near-infrared (NIR) organic molecule into polymer/fullerene blends, we obtained an external quantum efficiency (EQE) greater than 7000% for the resulting device. More importantly, the NIR dye extended the spectral response range to approximately 1100 nm .

The conjugated polymer, fullerene derivative, and NIR dopant used in this study were poly(3-hexylthiophene) (P3HT), [6,6]-phenyl- C_{60} -butyric acid methyl ester (PCBM), and 4,5-benzoindotricarbocyanine¹⁶ (Ir-125; Exciton Corp.), respectively [Fig. 1(a)]. The optimized weight ratio of these three components was 1:1:1. The inset to Fig. 1(b) illustrates the energy levels of the materials.¹⁷ We determined the en-

ergy levels of Ir-125 from cyclic voltammetry data and the absorption edge of an Ir-125 thin film [Fig. 1(b)].^{1,18} The figure also shows that the optical absorption of the P3HT:PCBM thin films in the long wavelength regime increased in the presence of Ir-125. The OPDs were fabricated on indium tin oxide (ITO)-coated substrates. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was spin-cast onto the ITO substrates and the resulting film was baked at 120°C for 1 h. P3HT/PCBM blends dissolved in 1,2-dichlorobenzene were spin-coated onto the samples to form $80 (\pm 5)\text{-nm}$ -thick photoactive layers. To prepare the device exhibiting a high photoconductive gain,

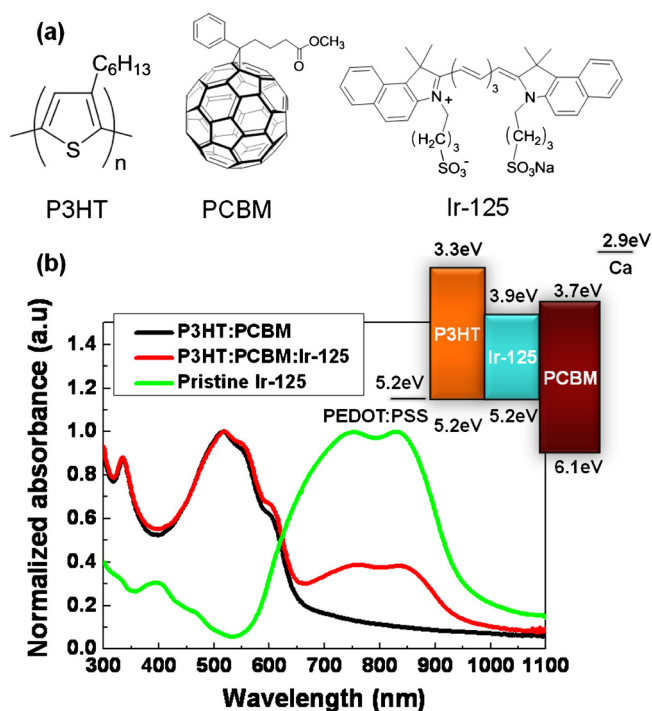


FIG. 1. (Color online) (a) Chemical structures of P3HT, PCBM, and Ir-125. (b) Absorption spectra of the P3HT:PCBM film, the P3HT:PCBM film containing Ir-125 [P3HT:PCBM:Ir-125, 1:1:1 (w/w/w)], and the pristine Ir-125 film. Inset: energy level diagram for the materials used in this study.

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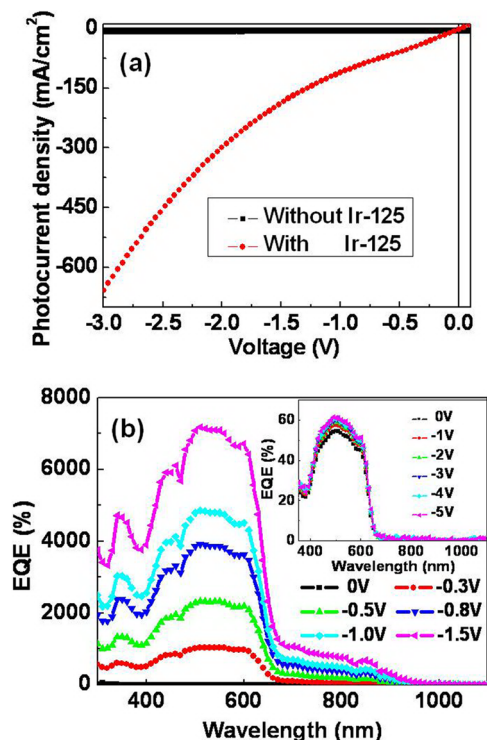


FIG. 2. (Color online) (a) J_{ph} - V curves of the devices prepared with and without Ir-125 under illumination (simulated AM1.5G, 100 mW cm⁻²). Device structure: ITO/PEDOT:PSS/P3HT:PCBM:Ir-125/Ca/Al. The light source was a Thermal Oriel solar simulator. (b) EQE spectra of the Ir-125-doped device. Inset: EQE spectra of the control device under short-circuit (0 V) and reverse bias conditions.

Ir-125 was added into the polymer blend. Finally, a bilayer metallic thin film of calcium (Ca: 50 nm) and aluminum (Al: 100 nm) thermally evaporated to form the cathode. The current density-voltage curves were measured using a Keithley 2400 source measurement unit. For the EQE measurements, a Xe lamp was used as the light source. The incident light passing through a monochromator was chopped at 100 Hz. By using a lock-in amplifier, the dc signal (dark current) was excluded and the ac signal (light-induced photocurrent) was transferred to an ac amplifier.¹⁵ A Si-based diode was used as a reference cell to calibrate the light intensity at various wavelengths. The morphological properties of the thin films were characterized using a DI 3100 series atomic force microscope (AFM).

Figure 2(a) displays the photocurrent density-voltage curves (J_{ph} - V) for the devices prepared with and without Ir-125 under illumination; hereafter, we consider the device prepared without Ir-125 to be the control. The value of J_{ph} was determined using the equation $J_{ph} = J_{light} - J_{dark}$, where J_{light} is the current density obtained under illumination and J_{dark} is the dark current density. Figure 2(a) reveals that the device containing Ir-125 had a photocurrent density almost four orders of magnitude greater than that of the control device. The photocurrent of the control device remained almost unchanged when the voltage was reverse-biased from 0 to -3 V. In contrast, the photocurrent of the device containing Ir-125 increased rapidly from -2.43 mA cm⁻² (at 0 V) to -658 mA cm⁻² (at -3 V).

To further evaluate the photoresponse of the photodiodes quantitatively, we performed spectrally resolved EQE measurements [Fig. 2(b)]. The results were quite consistent with

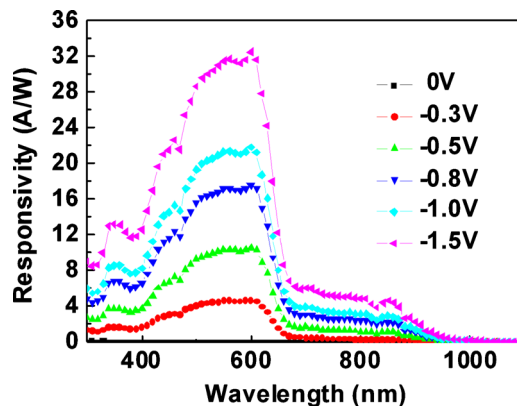


FIG. 3. (Color online) Plots of the responsivities (R) of the Ir-125-doped devices, recorded under various bias conditions.

the J_{ph} - V curves [Fig. 2(a)]. We observed nearly unchanged EQE spectra for the control device under various biased voltages [inset to Fig. 2(b)]. In contrast, the device prepared with Ir-125 exhibited much higher EQEs. Although the device had nearly no photoresponse (EQE < 10%) under short-circuit conditions, the EQEs increased dramatically upon increasing the reverse biases. In the visible region, the EQEs were greater than 100% when the applied voltage was less than -0.15 V. At a bias of -1.5 V, the highest EQE was approximately 7200% ($\lambda = 510$ nm)—approximately 1400 times higher than that obtained under the short-circuit conditions. In addition, the spectral response region was extended from 650 nm (the upper cut-off wavelength of the absorption of the P3HT:PCBM blend) to 1050 nm. Further, high EQEs in the NIR region were achieved (up to 100%) at a sufficiently low reverse-bias (-0.5 V). At a bias of -1.5 V, we observed a pronounced PM effect (EQE=757%) in the NIR region (800 nm). Note that we obtained even higher EQEs in the NIR region when we increased the reverse bias further (to less than -1.5 V). The magnitude of the largest negative applied voltage, however, was limited by the photocurrent that the lock-in amplifier could tolerate in the visible range [Fig. 2(b)].

According to the energy level diagram in Fig. 1, we suspected that the mechanism of photocurrent multiplication involved the presence of trap states induced after doping with the Ir-125 molecules. Under illumination, the photogenerated holes were transported through the P3HT molecules. In contrast, electrons would most likely be trapped at the Ir-125 molecules, thereby resulting in their accumulation in the device. The resulting build-up of space charges would induce a high electric field, eventually leading to the injection of holes through the contact barrier from the external circuit. As a result, we could obtain EQEs greater than 100%.

We calculated the detector responsivity (R , in units of A/W), defined as the ratio of photocurrent to incident-light intensity, using the equation $R = J_{ph} / L_{light}$, where L_{light} is the incident optical power.¹⁹ Fig. 3 reveals that the calculated spectrally resolved responsivities increased upon increasing the reverse bias. We observed a high responsivity (32.4 A/W) in the visible region (550 nm) under a reverse bias of -1.5 V. This value is among the highest reported for a photodiode prepared solely from organic materials.¹⁵ In addition, the responsivity remained high in the NIR region. For example, at

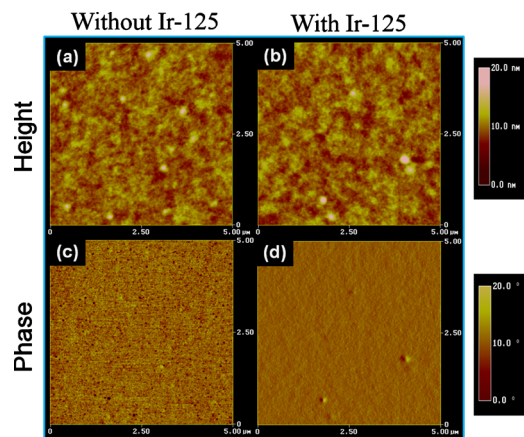


FIG. 4. (Color online) Tapping-mode AFM images ($5 \times 5 \mu\text{m}^2$) of the photoactive polymer films [(a) and (c)] before and [(b) and (d)] after the blending of the Ir-125 molecules. [(a) and (b)] Height-mode images; [(c) and (d)] phase-mode images.

a wavelength of 800 nm, the responsivity was as high as 4.9 A/W.

We used AFM to further characterize the photoactive films prepared with and without Ir-125 (Fig. 4). The height-mode images of the active layer prepared without Ir-125 [Fig. 4(a)] and with Ir-125 [Fig. 4(b)] both revealed rather flat surfaces, with root-mean-square (rms) roughness of 1.215 nm and 1.366 nm, respectively. We observed no significant differences in these two images. In the phase-mode images, however, we observed morphological changes after Ir-125 had been incorporated [cf. Figs. 4(c) and 4(d)]. The phase image of the active layer of the control device exhibited a phase roughness of 1.324° . We assign the evenly dispersed black dots to PCBM clusters.²⁰ The image of the active layer prepared with Ir-125 exhibited an even-more-homogenous surface; the phase rms roughness decreased to 0.438° . These AFM images suggest that no serious phase separation occurred in the photoactive layer after blending with an extremely high concentration of Ir-125. Therefore, we infer that the contribution to the PM effect might occur mainly from the molecules in the bulk.

In summary, we have developed highly sensitive all-organic PM photodetectors with spectral bandwidths extending from the UV to the NIR region. After doping an

organic NIR dye into the device, we achieved high EQEs ($>7000\%$) under extremely low bias conditions (< -1.5 V). We attribute the high photoconductive gain to the trapping of electrons at the NIR dopants, thereby facilitating hole injection into the device from the external circuit. The device preparation scheme presented herein opens up the possibility fabricating lost-cost, flexible organic detectors exhibiting high sensitivity for various photosensing applications.

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