Highly sensitive polymer photodetectors with a broad spectral response range from UV light to the near infrared region†

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Highly sensitive polymer photodetectors (PPDs) are successfully achieved with a broad spectral response range from UV light to the near infrared region (NIR) based on P3HT : PTB7-Th : PC71 BM as the active layer. The highest external quantum efficiency (EQE) values of the PPDs with P3HT : PC71 BM (100 : 1) as the active layer are 90 700% and 84 100%, corresponding to 390 nm and 625 nm light illumination under a −25 V bias, respectively. The spectral response range of the PPDs can be extended to the NIR by doping narrow band gap polymer PTB7-Th into P3HT : PC71 BM as the active layer. The highest EQE values of the PPDs with P3HT : PTB7-Th : PC71 BM (50 : 50 : 1) as the active layer are around 38 000% in the spectral range from 625 nm to 750 nm under a −25 V bias. The high EQE values of the PPDs should be attributed to three points: (i) the rather weak dark current due to the relatively large hole injection barrier; (ii) the enhanced hole tunneling injection due to the interfacial band bending, which is induced by trapped electrons in PC71 BM near the Al cathode; and (iii) the efficient hole-only transport in the active layers with the rather low PC71 BM content. The broad spectral response range is due to the contribution of PTB7-Th exciton dissociation on the number of trapped electrons in PC71 BM near the Al cathode.

1 Introduction

Polymer photodetectors (PPDs) have attracted more and more attention because of the rapid development of excellent polymer semiconducting materials, which are already used in polymer light emitting diodes and polymer solar cells.1–4 The polymer semiconducting materials can provide many choices for obtaining highly sensitive PPDs due to their high absorption coefficients, and adjustable energy levels and band gaps.5–9 Highly sensitive photodetectors should have more circuiting charge carriers per absorbed photon in the active layer, i.e. the external quantum efficiency (EQE) should be in excess of 100%.10–14 Photodiode type PPDs exhibit low EQE values, less than unity, based on electron donor/acceptor (1 : 1, w/w) blend films as the active layer, which can be explained by the limited photon harvesting efficiency, exciton dissociation efficiency, and charge carrier transport and collection.15–17 In fact, the mechanism of photodiode type PPDs is very similar to that of photovoltaic cells. Meanwhile, the working bias of photodiode type PPDs is relatively low due to the bicontinuous interpenetrating network for efficient charge carrier transportation in the active layer, resulting in a relatively large dark current.18 The optimized EQE values for photodiode type PPDs are lower than 75% based on p-DTS(FBTTh2)2 : PCBM (6 : 4, w/w) as the active layer.19 For inorganic photodetectors or photomultiplier tubes, a high EQE in excess of 100% can be easily achieved based on impact ionization triggered by hot carriers, the photoelectric emission effect or the secondary emission of electrons.20,21 However, most of the charge carriers in organic materials are localized in a single molecule and intermolecular charge carrier transportation occurs through thermal-activated hopping due to their disordered structure and large binding energy. Therefore, impact ionization and the photoelectric emission effect are hard to achieve in organic materials due to their relatively large binding energy.22,23 Trap-assisted charge tunneling injection or the photomultiplication (PM) phenomenon based on polymer or small molecule photodetectors may open a window to obtain high EQE values. The mechanism of the PM phenomenon in PPDs involves photogenerated holes or electrons becoming trapped or blocked in the active layers, while the oppositely charged carriers can continually pass through the active layers and are collected by the corresponding electrode.

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In 1994, Hiramoto et al. first reported PM type organic photodetectors based on a simple structure of Au/perylene/Au. The PM phenomenon is attributed to the strong electron injection from the Au electrode to the perylene film, assisted by the accumulation of photogenerated holes trapped near the Au/perylene interface. A small amount of inorganic nanoparticles (CdTe) was doped into the poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PC61BM) (1:1, w/w) blend solution to prepare the active layers in the PPDs, and the PPDs exhibited a high EQE of 8000% at ~4.5 V, corresponding to 350 nm light illumination. The high EQE value of the photodetectors with P3HT:PC61BM: CdTe as the active layer can be attributed to the enhanced hole tunneling injection, assisted by trapped electrons in the CdTe nanoparticles. In fact, PC61BM in the blend films may not have a positive effect on the performance of the photodetectors due to the continuous electron transport channels formed by PC61BM, resulting in a relatively large dark current. Huang’s group also reported PM type UV-visible or UV photodetectors with nano-composite active layers of ZnO nanoparticles blended with P3HT or PKV. The ZnO nanoparticles were considered to be electron traps and the polymers were used to harvest photons and form hole transport channels in the blend films. The photodetectors with the nanocomposite as the active layer exhibited an excellent performance under a relatively high bias of ~9 V due to the efficient hole-only transport characteristics of the active layer. Dong et al. reported highly sensitive photodetectors with a broad spectral response range from UV light to the NIR by using PbS and ZnO quantum dots (QDs) doped into P3HT:PC61BM (1:1, w/w) as the active layer. Chen and Chuang successfully achieved PM type UV to NIR photodetectors based on the NIR dye 4,5-benzoindotricarbocyanine (Ir-125) doped into P3HT:PC61BM (1:1, w/w) as the active layer. They exhibited a maximum EQE value of ~7000% under a ~1.5 V bias at 510 nm light illumination, and the PM phenomenon is attributed to the enhanced hole injection, assisted by trapped electrons in the Ir-125 NIR dye. Meanwhile, the spectral response of the PPDs was further extended to longer wavelengths (~1200 nm) through codoping two NIR dyes (Ir-125 and Q-switch 1) into the P3HT:PC61BM (1:1, w/w) system. Narrow band gap materials can be used as low energy photon harvesting centers to improve the sensitivity of photodetectors in the longer wavelength region. Recently, we proposed a simple strategy to obtain PM type PPDs with P3HT:[6,6]-phenyl-C61-butyric acid methyl ester (PC71BM) (100:1, w/w) as the active layer. The highest EQE value was 16 700% under a ~19 V bias at 390 nm light illumination, which was attributed to the enhanced hole tunneling injection, assisted by trapped electrons in PC71BM near the Al cathode. Therefore, the spectral response of PPDs may be extended to the long wavelength region by incorporating narrow band gap materials, which can harvest low energy photons. This strategy has also been demonstrated as an effective method to improve the spectral response range of solar cells by doping narrow band gap materials as a second electron donor. This kind of solar cell is called a ternary solar cell.

2 Experimental section

The indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω square−1 were sequentially cleaned by ultrasonic treatment in detergent, deionized water and ethanol. The cleaned ITO substrates were dried by nitrogen gas and treated with UV-ozone for 10 min to increase the work function of the ITO surface. A solution of PEDOT:PSS was spin-coated onto the cleaned ITO substrates at a spin speed of 5000 rounds per minute (rpm) for 40 s. The PEDOT:PSS coated ITO substrates were baked at 120 °C for 10 min. Polymers P3HT and PTB7-Th (purchased from Organtec Material Inc.), and PC71BM (purchased from Luminescence Technology Corp.) were dissolved in 1,2-dichlorobenzene (o-DCB) to prepare separate 40 mg ml−1 solutions. Then, the mixed solutions were prepared with different doping weight ratios of P3HT:PTB7-Th:PC71BM (100:0:1, 90:10:1, 70:30:1, 50:50:1, 30:70:1, 10:90:1 and 0:100:1). The mixed solutions were spin-coated onto the PEDOT:PSS layers at 800 rpm for 30 s in a nitrogen-filled glove box. The thicknesses of the active layers were in the range of 280 nm to 300 nm. 100 nm thick aluminum was thermally evaporated on the active layers in a high vacuum (10−4 pa) chamber. The active area of each device was about 3.8 mm2, which is defined by the overlap of the Al cathode and ITO anode. The current density versus voltage (J−V) curves of the PPDs were measured by a Keithley 2400 source meter under 390 nm, 625 nm or 750 nm light illumination with intensities of 13.0 μW cm−2, 8.87 μW cm−2 or 6.85 μW cm−2, respectively. The monochromatic light was provided by a 150 W xenon lamp coupled with a monochromator. The monochromatic light intensity and wavelength were monitored and calibrated by a Newport 818-UV power meter and an Acton SpectraPro 2150i.
The absorption spectra of the active layers were measured by a SHINADZU UV-3101 PC spectrophotometer. The thicknesses of the active layers were measured by an AMBIOS technology XP-2 stylus profilometer. All the measurements were carried out at room temperature under ambient conditions. The light intensity spectrum of the monochromatic lights through a monochromator was measured and is shown in Fig. S1 (ESI†). The chemical structures of the used materials and the schematic device structure are shown in Fig. 1.

3 Results and discussion

A series of PPDs with P3HT$_{100}$ : PTB7-Th$_x$ : PC$_{71}$BM$_1$ as the active layers were fabricated under the same conditions. The doping weight ratio of the donors to acceptor was kept constant at 100 : 1 (w/w). The subscript $x$ represents the PTB7-Th doping ratio in the donors. The EQE spectra of all the PPDs were measured under different biases from −4 V to −25 V with an interval of 3 V. The EQE spectra of the PPDs with P3HT$_{100}$ : PC$_{71}$BM$_1$, P3HT$_{50}$ : PTB7-Th$_{50}$ : PC$_{71}$BM$_1$ and PTB7-Th$_{100}$ : PC$_{71}$BM$_1$ as the active layers are shown in Fig. 2a–c. The EQE spectra of the other PPDs with different PTB7-Th doping ratios in the donors are shown in Fig. S2 (ESI†). The EQE values of all the PPDs at different reverse biases and light illuminations are summarized in Table S1 (ESI†).

It is apparent that the EQE values of the PPD with P3HT$_{100}$ : PC$_{71}$BM$_1$ as the active layer are more than 100% in the spectral

Fig. 1 (a) Molecular structures of the organic materials P3HT, PTB7-Th, and PC$_{71}$BM; (b) device structure of the PPDs.

Fig. 2 EQE spectra of the PPDs under different biases from −4 V to −25 V with an interval of 3 V: (a) P3HT$_{100}$ : PC$_{71}$BM$_1$; (b) PTB7-Th$_{100}$ : PC$_{71}$BM$_1$; and (c) P3HT$_{50}$ : PTB7-Th$_{50}$ : PC$_{71}$BM$_1$ as the active layers. (d) The dependence of the EQE values of the PPDs on the PTB7-Th doping ratio in the donors at 390 nm, 625 nm and 750 nm light illumination under a −25 V bias.
range from 350 nm to 700 nm when the reverse bias is larger than 4 V, as shown in Fig. 2a. The highest EQE values of the PPD with P3HT:PC71BM as the active layer are 90 700%, 84 100% and 850% under 390 nm, 625 nm and 750 nm light illumination, respectively, and a −25 V bias. There is a distinct dip between 490 nm and 570 nm in the EQE spectra, which corresponds to the absorption spectrum of the P3HT film, as shown in Fig. S3a (ESI†). This phenomenon has been described in our previous paper, 33 and it can be attributed to the weakened trap-assisted hole tunneling injection resulting from fewer trapped electrons in PC71BM near the Al cathode. It is known that only PC71BM near the Al cathode can affect the interfacial band bending to assist the hole tunneling injection from the Al cathode onto the highest occupied molecular orbital (HOMO) of P3HT. There is also a distinct dip between 600 nm and 710 nm in the EQE spectra of the PPD with PTB7-Th100:PC71BM1 as the active layer, as shown in Fig. 2b. The characteristics of the EQE spectral dip are in accordance with the absorption spectral characteristics of PTB7-Th films. These fine characteristics are marked in Fig. S3b (ESI†). This phenomenon can further confirm that the EQE spectral dip should be attributed to the decreased number of trapped electrons in PC71BM near the Al cathode when the PPDs are illuminated by light in this spectral range. The trapped electrons should originate from the donor (P3HT or PTB7-Th) exciton dissociation around PC71BM near the Al cathode. It is known that more photons are harvested by the donor near the ITO cathode when light is irradiated from the ITO side, leading to fewer generated excitons in the donor and fewer trapped electrons in PC71BM near the Al cathode. Therefore, the trap-assisted hole tunneling injection is weakened, resulting in decreased EQE values in this spectral range.

Based on the EQE spectral characteristics of the PPDs with P3HT:PC71BM or PTB7-Th:PC71BM as the active layers, it can be deduced that the dip in the EQE spectra of the PPDs is due to the relatively strong absorption intensity of the active layers in this spectral range. For the ternary P3HT50:PTB7-Th50:PC71BM1 blend films, there is a relatively broad absorption spectrum in the visible light range with two shoulder absorption peaks corresponding to the absorption peaks of P3HT and PTB7-Th. Therefore, the dip in the EQE spectra of the PPD with P3HT50:PTB7-Th50:PC71BM1 as the active layer should be not very obvious, which is confirmed from the experimental results shown in Fig. 2c. The corresponding characteristics in the EQE spectra of the PPDs and the absorption spectra of the ternary blend films have one-to-one relationships, as shown in Fig. S3c (ESI†). Meanwhile, the EQE values of all the PPDs rapidly increased along with the increase in the applied bias, which should be attributed to the enhanced charge carrier injection induced by interfacial band bending under a higher bias and the improved hole transportation in the active layers under a high electric field. The phenomenon can be explained by the following equation:

\[
\text{EQE} = \frac{\chi T^2}{\tau} = \frac{\chi \mu V}{L^2} \tag{1}
\]

where \(\chi\) is the fraction of excitons that dissociate into trapped electrons and free holes, \(\tau\) is the lifetime of the trapped electron, \(T\) is the hole transport time, \(V\) is the applied bias, \(L\) is the active layer thickness, and \(\mu\) is the field dependent hole carrier mobility. 34 It is apparent that the hole transport time \(T\) for passing through the whole active layer should be decreased under a higher applied bias, resulting in an increase in the EQE value.

To more intuitively display the effect of the PTB7-Th doping ratio in the donors on the EQE values, the dependence of the EQE values of the PPDs on the PTB7-Th doping ratio in the donors under a −25 V bias is shown in Fig. 2d. As we know, the major charge carrier in all the PPDs should be the holes due to the rather low PC71BM content in the active layers. The EQE values of the PPDs at 390 nm and 625 nm monotonously decreased along with the increase in the PTB7-Th doping ratio in the donors, which may be attributed to the disrupted hole transport channels in P3HT caused by doping PTB7-Th in the active layers and the weakened hole tunneling injection from the Al cathode into the active layers. However, the EQE values of the PPDs at 750 nm increased from 850% to 38 000% and then decreased to 130% along with the increase in the PTB7-Th doping ratio in the donors. According to the EQE spectra of the PPDs with PTB7-Th:PC71BM as the active layer (shown in Fig. 2b), the relatively large EQE values at 750 nm should also be attributed to the enhanced hole tunneling injection, assisted by trapped electrons in PC71BM near the Al cathode. The trapped electrons originate from exciton dissociation in PTB7-Th. The EQE values at 750 nm reach the maximum for the PPD with P3HT50:PTB7-Th50:PC71BM1 as the active layer, which should be attributed to the best trade-off between the hole tunneling injection and the hole transport in this active layer. The trap-assisted hole tunneling injection is codetermined by (i) the hole injection barrier from the Al cathode onto the HOMO level of P3HT or PTB7-Th; (ii) the trap depth corresponding to difference in the lowest unoccupied molecular orbital (LUMO) levels between PC71BM and P3HT or PTB7-Th. According to Fig. 2a and b, the EQE values of the PPD with P3HT:PC71BM (100 : 1) as the active layer are much larger than those of the PPD with PTB7-Th:PC71BM (100 : 1) as the active layer under the same reverse bias. It is known that the hole mobility of PTB7-Th is better than that of P3HT, 35,36 which means that the trap-assisted hole tunneling injection (dependent on the number of trapped electrons in PC71BM near the Al cathode, i.e. the trap depth) should play a vital role on the EQE values of the PPDs.

Based on the detailed characterization of the PM type PPDs, the dependence of the responsivity \(R\) and detectivity \(D^*\) values of the PPDs on the photon wavelength were calculated under different biases, and the results are shown for −25 V and −10 V biases in Fig. 3 and Fig. S4 (ESI†), respectively. The detailed calculations of these values are expressed in the following equations:

\[
\text{EQE} = \frac{J_{ph\ h\nu}}{L^2 e} \tag{2}
\]
Here, \( J_{\text{ph}} \) is the photocurrent density, \( h \nu \) is the photon energy, \( I_{\text{in}} \) is the incident light intensity, \( J_d \) is the dark current density and \( e \) is the absolute value of the electron charge.

It is known that the responsivity and detectivity of photodetectors strongly depend on the photon wavelength. The best responsivity and detectivity values of the PPD with P3HT : PTB7-Th : PC71BM (100 : 0 : 1) as the active layer were 284.9 A W\(^{-1}\), 423.4 A W\(^{-1}\) and 5.2 A W\(^{-1}\), and \( 2.28 \times 10^{13} \) Jones, \( 3.39 \times 10^{13} \) Jones and \( 4.12 \times 10^{11} \) Jones, corresponding to 390 nm, 625 nm and 750 nm light illumination under a \(-25 \) V bias, respectively. The best responsivity and detectivity values of the PPD with P3HT : PTB7-Th : PC71BM (50 : 50 : 1) as the active layer were 229.5 A W\(^{-1}\) and \( 1.91 \times 10^{13} \) Jones at 750 nm light illumination under a \(-25 \) V bias. The responsivity and detectivity improvements should be attributed to the contribution of PTB7-Th photogenerated exciton dissociation to the increased number of trapped electrons in PC71BM near the Al cathode. Meanwhile, the relatively high responsivity and detectivity are also attributed to the rather low dark current due to (i) the relatively large hole injection barriers of 0.8 eV from the Al cathode onto the HOMO of P3HT or 1.15 eV from the Al cathode onto the HOMO of PTB7-Th; (ii) the hole-only efficient transport in the active layers due to the rather low PC71BM content. Under illumination and bias, the interfacial band bending and band tilting of the polymer materials will open the valve of the hole tunneling injection, and the injected holes will be effectively transported in the active layers. Therefore, the performances of the PM type PPDs exhibit a strong relationship dependence on the bias. The PM type PPDs also show a good stability under a high bias due to the single charge carrier transport characteristics of the active layers.

As we know, the energy levels of the donors become more curved near the interfaces between the active layers and the Al cathode when more electrons are trapped in PC71BM near the Al cathode due to the stronger Coulomb field. To further investigate the effect of the trap-assisted hole tunneling injection on the EQE values of the PPDs, the EQE spectra of all the PPDs with different PTB7-Th doping ratios in the donors were investigated under a relatively low bias (\(-10 \) V), as shown in Fig. 4a and b. Under the low bias, injecting holes from the Al cathode onto the HOMO level of the donors is very difficult under dark conditions due to the relatively large hole injection barriers of 0.8 eV for P3HT and 1.15 eV for PTB7-Th. This is demonstrated in the current density–voltage (\( J-V \)) curves for all the PPDs in the dark, as shown in Fig. S5 (ESI†).

It is apparent that the EQE values of the PPDs decrease along with the increase in the PTB7-Th doping ratio in the donors over the spectral range from 350 nm to 650 nm. However, the EQE values in the longer wavelength region (at 750 nm) increase from \( \sim 76\% \) to \( \sim 1200\% \) along with PTB7-Th doping ratios up to 50 wt%, as shown in Fig. 4a. The EQE values of the PPDs are lower than 100% over the whole spectral range when the PTB7-Th doping weight ratio is more than 70% in the donors, as shown in Fig. 4b. The dip in the EQE spectral range from 490 nm to 570 nm becomes less and less obvious along with the increase in the PTB7-Th doping ratio in the donors, which should be attributed to the decreased photon harvesting by P3HT in this range. However, the dip in the EQE spectral range from 600 nm to 710 nm becomes more and more obvious along with the increase in the PTB7-Th doping ratio in the
donors. To further confirm the underlying reason for the dip in the EQE spectra, the absorption spectra of the blend P3HT100−x : PTB7-Thx : PC71BM1 films were measured and are shown in Fig. 5a. The subscript refers to the PTB7-Th doping weight ratio in the donors, x = 0, 10, 30, 50, 70, 90 or 100. It is apparent that the dip in the EQE spectra for each kind of PPD well matches with the strong absorption peak of the active layer. There are two absorption peaks at 635 nm and 700 nm accompanying a valley at 668 nm in the absorption spectra of the neat PTB7-Th films. These characteristics are finely projected in the EQE spectrum of the PPD with PTB7-Th : PC71BM (100 : 1) as the active layer, as marked in Fig. 4b. In the EQE spectral dip regions, the EQE values of the PPD with PTB7-Th : PC71BM (100 : 1) as the active layer are much smaller than those of the PPD with P3HT : PC71BM (100 : 1) as the active layer. Therefore, the trap-assisted hole tunneling injection of the PPD with PTB7-Th : PC71BM (100 : 1) as the active layer should be significantly weaker due to fewer electrons trapped in PC71BM surrounded by PTB7-Th. The electron-trapping ability of PC71BM depends on the energy levels of the donors surrounding it, which can be investigated from the energy levels of the used materials.

It is known that the photogenerated excitons on P3HT or PTB7-Th should be effectively dissociated into charge carriers at the interfaces with PC71BM. The electrons will be trapped in the PC71BM molecules due to the absence of electron transport channels in the active layers with rather low PC71BM content. The number of trapped electrons in PC71BM should be determined by the LUMO difference between PC71BM and P3HT or PTB7-Th. The depths of the electron traps are 0.76 eV or 1.4 eV, corresponding to PC71BM surrounded by PTB7-Th or P3HT according to their energy levels, as shown in Fig. 5b. Therefore, more electrons can be trapped in PC71BM surrounded by P3HT due to the deep trap (1.4 eV), leading to the more curved energy levels of P3HT near the interface between P3HT and the Al cathode, and the enhanced hole tunneling injection. However, relatively few electrons can be trapped in PC71BM surrounded by PTB7-Th due to the shallow trap (0.76 eV), which will limit the trap-assisted hole tunneling injection. Meanwhile, the hole injection barrier is 0.8 eV or 1.15 eV from Al onto the HOMO of P3HT or PTB7-Th, respectively. The relatively large hole injection barrier from Al onto the HOMO of PTB7-Th is not conducive to the hole injection, which can be demonstrated from the J–V curve in dark conditions. For the PPDs with ternary materials as the active layers, the hole transport in the ternary films should also be limited due to the different HOMO levels of P3HT and PTB7-Th.

The current density–voltage (J–V) curves for all the PPDs were measured in dark conditions or under 625 nm light illumination with an intensity of 8.87 μW cm−2 or 750 nm light illumination with an intensity of 6.85 μW cm−2, as shown in Fig. S5 (ESI†). It is apparent that the dark current density of the PPD with PTB7-Th : PC71BM (100 : 1) as the active layer is much less than that of the PPD with P3HT : PC71BM (100 : 1) as the active layer. The photocurrent density (Jph) curves of the PPDs were calculated according to the J–V curves in dark conditions and under light illumination, and are shown in Fig. 6. It is apparent that the Jph values of the PPDs under 625 nm light illumination decrease along with the increase in the PTB7-Th doping ratio in the donors, which is in accordance with that observed from the EQE spectra of all the PPDs. For the PPDs under 750 nm light illumination, the Jph values increase and then decrease along with the increase in the PTB7-Th doping ratio in the donors. For the PPDs with a relatively low PTB7-Th doping ratio in the donors, P3HT can provide effective hole transport channels to improve the EQE values in the longer wavelength range. The Jph values of the PPDs decrease along with the increase in the PTB7-Th doping ratio in the donors, which should be attributed to the following points: (i) fewer injected holes due to the large hole injection barrier of 1.15 eV from the Al cathode onto the HOMO of PTB7-Th compared with the barrier of 0.8 V from the Al cathode onto the HOMO of P3HT; (ii) the decreased interfacial contact area of P3HT/Al along with the increase in the PTB7-Th content in the active layer, (iii) the limited hole transport in the blend films due to the different HOMO levels of P3HT and PTB7-Th, resulting in increased charge carrier recombination in the active layers.

To further clarify the working mechanism of the PPDs with the active layers containing different PTB7-Th doping ratios, the transient photocurrents of the PPDs were measured at −10 V under 625 nm or 750 nm light illumination, which was modulated by an electronic shutter with a modulation period of 20 s, as shown in Fig. 7. The rise and fall processes of the
transient photocurrents became faster along with the increase in the PTB7-Th doping ratio in the donors. It is known that the transient photocurrent will become saturated when the number of trapped electrons in PC 71BM arrives at a certain saturation state corresponding to a dynamic balance. In fact, there may be three kinds of electron traps for PC 71BM in the blend films, P3HT/PC 71BM/P3HT, PTB7-Th/PC 71BM/PTB7-Th and P3HT/PC 71BM/PTB7-Th. The shallow electron traps can be quickly filled in or emptied when the light is turned on or turned off. The number of trapped electrons in deep traps will take more time to arrive at the dynamic balance under the same conditions when the light is turned on or turned off. As we can envisage, the number of traps formed by P3HT/PC 71BM/P3HT, P3HT/PC 71BM/PTB7-Th or PTB7-Th/PC 71BM/PTB7-Th is altered along with the increase in the PTB7-Th doping ratio in the donors. The rise and fall processes of the transient photocurrent should be quicker due to the increased number of shallow traps formed by PTB7-Th/PC 71BM/PTB7-Th or P3HT/PC 71BM/PTB7-Th along with the increase in the PTB7-Th doping ratio in the donors. The transient photocurrent, in turn, further demonstrates that the PM phenomenon should be attributed to the enhanced hole tunneling injection assisted by trapped electrons in PC 71BM near the Al cathode.

Another interesting phenomenon is that the transient photocurrent of the PPDs with P3HT:PC 71BM (100:1) as the active layer exhibits very slow rise and fall processes under 750 nm light illumination, as shown in Fig. 7b. This phenomenon can also be understood from the number of trapped electrons in PC 71BM surrounded by P3HT near the Al cathode under 750 nm light illumination. According to the absorption spectrum of the blend P3HT:PC 71BM film (Fig. 5a), the blend film exhibits rather weak light absorption at 700 nm. This means that the deeper electron traps (P3HT/PC 71BM/P3HT) are hardly filled in under 750 nm light illumination. Therefore, the transient photocurrent of the PPDs with P3HT:PC 71BM (100:1) as the active layer shows rather slow rise and fall processes under 750 nm light illumination. This phenomenon further demonstrates the working mechanism of PM type PPDs based on the enhanced hole tunneling injection with the assistance of
trapped electrons in PC$_{71}$BM near the Al electrode. The accelerated response speed of PM type PPDs should be one of the key issues for its potential application, which may be resolved by controlling the photogenerated electron distribution in the active layers.

4 Conclusions

In summary, we have successfully developed highly sensitive PPDs with a broad spectral response range from UV light to NIR by using P3HT$_{100-38}$ : PTB7-Th$_{50}$ : PC$_{71}$BM$_{1}$ as the active layer. The highest EQE values of the PPDs with P3HT : PTB7-Th : PC$_{71}$BM (100 : 0 : 1) as the active layer are 90 700% and 84 100%, corresponding to 390 nm and 625 nm light illumination under a $-25$ V bias, respectively. The PM phenomenon should be attributed to the enhanced hole tunneling injection assisted by trapped electrons in PC$_{71}$BM near the Al cathode. The high EQE values of the PPDs are extended to the NIR by doping narrow band gap polymer PTB7-Th into P3HT : PC$_{71}$BM. The highest EQE values of the PPDs with P3HT$_{50}$ : PTB7-Th$_{50}$ : PC$_{71}$BM$_{1}$ are about 38 000% in the spectral range from 625 nm to 750 nm under a $-25$ V bias. This strategy may provide an effective method for organic photodetectors to achieve the PM phenomenon with a broad spectral response based on the trap-assisted charge tunneling injection.

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Notes and references