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## Solution-processed broadband photodetectors without transparent conductive oxide electrodes

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Broadband photodetectors (PDs) have great applications in both industrial and scientific sectors. In this study, solution-processed broadband PDs with an “inverted” vertical photodiode device structure without incorporating transparent conductive oxides electrodes, fabricated by bulk heterojunction (BHJ) composites composed of a low optical gap conjugated polymer blended with highly electrically conductive PbS quantum dots (QDs), operated at room temperature, are reported. The low optical gap conjugated polymer incorporated with PbS QDs contributes to the spectral response from the ultraviolet (UV)-visible to the infrared (IR) range. To realize the IR spectral response and to circumvent the weak IR transparency of the transparent oxide electrodes, the implementation of a photodiode with an “inverted” vertical device structure with the Au anode and the Ba/Al bilayer semitransparent cathode passivated with the MgF<sub>2</sub> layer is demonstrated. Photoinduced charge carrier transfer occurring within the BHJ composite gave rise to decent photocurrent, resulting in detectivities greater than 10<sup>12</sup> Jones (cm Hz<sup>1/2</sup>/W) over the wavelength from the UV-visible to the IR range under low applied bias. Thus, our findings of the utilization of the BHJ composites and an “inverted” vertical photodiode without the incorporation of the transparent conductive oxide electrodes provide a facile way to realize broadband PDs.

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### 1. Introduction

Broadband photodetectors (PDs) have drawn great attention in both academic and industrial sectors due to their various applications including telecommunications, day/night surveillance, thermal imaging, chemical/biological sensing, and spectroscopic and medical instruments.<sup>1–4</sup> To realize broadband PDs, current PDs with different sub-bands were integrated to one electronic device to cover the spectral response from the ultraviolet (UV)-visible to the infrared (IR) range.<sup>1–5</sup> Moreover, InCaAs- and HgCdTe-based IR PDs require an extremely low operating temperature (4.2 K) and operate at high voltage to achieve reasonable detectivity.<sup>1,2</sup> In addition, expensive manufacturing processes are required to fabricate these IR PDs.<sup>1–3,6</sup> All these requirements restrict their application in biosensors and image sensors where both high sensitivity and low operating voltage are required.<sup>1–3</sup>

In the past years, inorganic quantum dot (QD)-based PDs with a planar device structure have been extensively studied to realize IR responsibility but high operation voltages were

required to achieve a decent detectivity.<sup>4,6–10</sup> Two-dimensional (2D) materials, such as graphene and transition metal dichalcogenides, have been studied as alternatives to demonstrate IR detection with high detectivities through PDs with the same device structure as that of thin-film transistors (TFTs).<sup>11–14</sup> However, their applications are restricted by the difficulty in the large-scale and high throughput fabrication of mono and multilayer 2D materials as well as the high gate (or drive) voltages to be used for TFTs.<sup>11–14</sup> In the past two decades, organic/polymer-based PDs have gained abundant attention due to their advanced features such as ease of processing, low cost, physical flexibility, and excellent optoelectronic properties.<sup>5,15–17</sup> In 2009, we reported polymer-based PDs with a spectral response from 300 nm to 1450 nm.<sup>5</sup> Recently, we demonstrated polymer-based PDs with spectral response from 300 nm to 2500 nm.<sup>17</sup> Various novel molecules were developed for extending the spectral response of polymer-based PDs.<sup>18–21</sup> Furthermore, film morphology evolution,<sup>22</sup> interfacial engineering,<sup>23,24</sup> molecular engineering and arrangement,<sup>25,26</sup> and the photomultiplication (PM) effect<sup>27–29</sup> have been used to enhance the detectivities of polymer-based PDs. However, it is still a challenge to realize polymer-based PDs with decent IR photoresponse because of their short exciton lifetime induced by phonon-exciton recombination.<sup>30–34</sup>

To circumvent the above challenges, either polymers or hybrid perovskites incorporated with inorganic QDs have been developed to realize broadband PDs.<sup>4,23,24,35–41</sup> In the past years, we have reported various room-temperature (RT) operated

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broadband PDs by conjugated polymers, inorganic QDs, conjugated polymers incorporated with inorganic QDs, and hybrid perovskites incorporated with inorganic QDs.<sup>4,23,24,35–41</sup>

On the other hand, transparent electrodes are required to realize PDs with IR spectral response. However, currently widely used transparent conductive oxides, such as indium tin oxide (ITO) and fluorine-doped tin oxide (FTO), as the transparent electrodes for various electronics including sensors and PDs possess very weak transmittance in the IR region.<sup>42–44</sup> Thus, PDs with a planar device structure and a TFT device structure were developed to avoid using neither ITO nor FTO electrodes, thus realizing IR spectral response.<sup>6–14</sup> Furthermore, carbon nanotubes (CNTs),<sup>45,46</sup> silver nanowires (Ag NWs),<sup>47</sup> and semiconducting polymers<sup>48–51</sup> were under intensive investigation for the substitution of ITO or FTO electrodes. However, CNTs and Ag NWs thin films possess poor electrical conductivity<sup>45–49</sup> and were required to be processed with complicated costly nanoimprint lithography as well.<sup>45–49</sup> Semiconducting polymer thin films as transparent electrodes have drawn much attention owing to their advanced features such as low cost, lightweight, mechanical flexibility, and compatibility with plastic substrates.<sup>50,51</sup> But the semiconducting polymer thin film with high electrical conductivities needs to be treated with strong acids,<sup>50,51</sup> which restrict its practical applications in electronics. Recently, we demonstrated flexible solution-processed broadband PDs with a “vertical” sandwiched device structure, made by hybrid perovskites incorporated with PdSe QDs, based on the solution-processed polymeric thin film as the transparent electrode.<sup>42</sup>

In this study, we report room-temperature (RT) operated solution-processed broadband PDs fabricated by the bulk heterojunction (BHJ) composites composed of a low optical gap conjugated polymer blended with highly electrically conductive PbS QDs and with an “inverted” vertical photodiode device structure without incorporating the transparent conductive oxide electrodes. The low optical gap conjugated polymer contributes to the IR photoresponse up to 1700 nm. PbS QDs further extend the IR photoresponse up to 2000 nm. To realize IR spectral response and circumvent the weak IR transparency of the transparent oxides’ electrodes, the implementation of a photodiode with an “inverted” vertical device structure with the Au anode and the Ba/Al bilayer semitransparent cathode passivated with the MgF<sub>2</sub> layer, is demonstrated. Photoinduced charge carrier transfer occurring within the PDDTT:PbS QDs BHJ composite gave rise to decent photocurrent, resulting in detectivities greater than 10<sup>12</sup> Jones (cm Hz<sup>1/2</sup>/W) over the wavelength region from 300 nm to 2000 nm under low applied bias. Thus, our findings of the utilization of the PDDTT:PbS QDs BHJ composites and an “inverted” vertical photodiode without incorporation with the transparent oxide electrodes provide a facile way to realize broadband PDs.

## 2. Experimental section

### 2.1. Materials

PbO (99.999%) was purchased from Alfa Aesar. Oleylamine (OLA) (90%), 1-octadecene (ODE) (90%), trioctylphosphine

(TOP) (97%), diphenylphosphine (DPP) (98%), selenium (99.99%), 1,2-ethanedithiol (EDT) (98%), methanol (99.8%), and acetonitrile (ACN) (99.8%) were purchased from Sigma Aldrich. All materials were used as received without further purification. PDDTT was synthesized in our lab following the procedures reported previously.<sup>5</sup>

**Synthesis of PbS QDs.** PbCl<sub>2</sub> (1 mmol, 0.28 g) was added to 5 mL of oleylamine (OLA) at RT, and then heated to 120 °C under vacuum and stirred vigorously until the PbCl<sub>2</sub>-OLA mixture turned into a homogeneous clear solution. Elemental sulfur (0.4 mmol, 14 mg) was dissolved in 2.5 mL of OLA by heating at 80 °C in an oil bath, which gave a deep red solution. The resultant sulfur solution was injected into the PbCl<sub>2</sub>-OLA solution at 140 °C, and then kept for 1 hour. The resultant solution was further centrifuged and purified to generate OLA-capped PbS QDs power. The OLA-capped PbS QDs thin film was spin-cast from the 50 mg mL<sup>-1</sup> OLA-capped PbS QDs octane solution, and the cast EDT acetonitrile solution on the top of the OLA-capped PbS QDs. Afterward, acetonitrile solvent was used to wash out the excess organic ligand. The above steps were repeated several times for obtaining the EDT-capped PbS QDs thin film.

### 2.2. Preparation and characterization of thin films

PDDTT and PbS QDs thin films, and PDDTT:PbS QDs BHJ composite thin film were fabricated through the spin-coating method from their corresponding solutions. The absorption spectra of the thin films were measured by a Lambda 750 UV/Vis/NIR spectrometer from PerkinElmer. The transmission electron microscopy (TEM) images were measured using a Model JEOL JSM-1230. The thin film thickness was measured on the DektakXT surface profile system. The transient absorption measurements were carried out using a dual-beam femto-second spectrometer utilizing the second harmonic of an OPA (optical parametric amplifier) as the pump and a white light continuum as the probe in Professor Alan J. Heeger’s laboratory at the University of California, Santa Barbara.

**Fabrication and characterization of TFTs.** The “bottom-contact” TFTs device structure was treated in hexamethyldisilazane before the deposition of the PbS QDs thin films. The TFTs device structures with different source-drain separations were fabricated on an n-doped Si wafer; the n-doped Si was used as the gate. The gate dielectric was a 200 nm film of SiO<sub>2</sub> thermally grown directly on the wafer. The source and drain electrodes (Au) were deposited on SiO<sub>2</sub> by e-beam evaporation. The channel lengths (source-drain separation) were 25 μm and the channel width was 1000 μm. Electrical measurements were carried out using a Keithley 4200 Semiconductor Characterization System in ambient conditions.

### 2.3. Fabrication and characterization of broadband PDs

Commercially available Au/Cr capped on the glass substrates were cleaned with deionized water, acetone, and isopropanol and then dried out in vacuum overnight. After UV ozone plasma treatment for 20 min (mins) in ambient atmosphere, ~30 nm MoO<sub>3</sub> layer was deposited on the top of the Au/Cr surface by the

spin-coating method from the  $\text{MoO}_3$  precursor solution, followed by thermal annealing at  $120^\circ\text{C}$  for 30 min.  $\sim 200$  nm PDDTT:PbS QDs BHJ composite thin film was spin-coated on the top of the  $\text{MoO}_3$  layer from the PDDTT:PbS QDs BHJ composite toluene solution. After that,  $\sim 10$  nm  $\text{BaO}$ ,  $\sim 5$  nm  $\text{Ba}$ ,  $\sim 20$  nm  $\text{Al}$ , and  $\sim 400$  nm  $\text{MgF}_2$  were thermally deposited consequently through a shadow mask under  $1 \times 10^{-6}$  mbar vacuum. The device area was measured to be  $0.16\text{ cm}^2$ .

The current density–voltage ( $J$ – $V$ ) characteristics of broad-band PDs were obtained using a Keithley model 2400 source measurement unit. A Newport Air Mass 1.5 Global (AM1.5G) full-spectrum solar simulator was applied as the light source. The light intensities for the wavelength ( $\lambda$ ) of  $800\text{ nm}$  was  $0.22\text{ mW cm}^{-2}$  and for  $\lambda = 1550\text{ nm}$  was  $0.05\text{ mW cm}^{-2}$ . The external quantum efficiency (EQE) spectra were measured by a quantum efficiency measurement system (QEX10) with a  $300\text{ W}$  steady-state xenon lamp as the source light. Transient photocurrent measurement was performed on a homemade setup using an optical chopper controlled using  $\lambda = 532\text{ nm}$  laser pulse at a frequency of  $2\text{ kHz}$ .

### 3. Results and discussion

To enhance the electrical conductivity of PbS QDs, 1,2-ethanedithiol (EDT), which has a short thiol (S–H) chain, is used to substitute OLA, which has a long carbon chain (C–C), through the ligand exchange process,<sup>52–55</sup> for generating the EDT-capped PbS QDs (termed as EDT-PbS QDs). After that, the EDT-capped PbS QDs were rinsed with  $\text{CH}_3\text{OH}$  and then treated with  $\text{NH}_3\cdot\text{H}_2\text{O}$ , followed by thermal annealing at  $150^\circ\text{C}$  for 10 min. The molecular structures of OLA and EDT are shown in Fig. 1a. The TEM images of the OLA-capped PbS QDs and EDT-capped PbS QDs thin films are presented in Fig. 1b and c.

Based on the TEM image, the average particle size of the OLA-capped PbS QDs is estimated to be  $\sim 9\text{ nm}$ , whereas the average particle size of the EDT-capped PbS QDs is estimated to be  $\sim 12\text{ nm}$ . Thus, the treatment described above could enlarge the particle size of the PbS QDs.

Fig. 1d presents the absorption spectra of PbS QDs. The absorption of the OLA-capped PbS QDs is extended to  $1900\text{ nm}$ , whereas the absorption of the EDT-capped PbS QDs is extended to  $2100\text{ nm}$ . Thus, the optical bandgap ( $E_g$ ) is estimated to be  $0.65\text{ eV}$  for the OLA-capped PbS QDs thin film and  $0.59\text{ eV}$  for the EDT-capped PbS QDs thin film. According to the quantum confinement effect,<sup>56</sup> the particle size of the OLA-capped PbS QDs is estimated to be  $\sim 9\text{ nm}$ , whereas the particle size of the EDT-capped PbS QDs is estimated to be  $\sim 13\text{ nm}$ . These results are in good agreement with the TEM images (Fig. 1b and c).

To verify the hypothesis that the EDT-capped PbS QDs thin film possess superior electronic properties than that of the OLA-capped PbS QDs, the TFTs are applied to study the field-effect mobilities of the two different PbS QDs thin films. The field-effect mobility in the saturation regime was extracted using the equation  $I_{\text{DS}} = C_i \mu (V_{\text{GS}} - V_{\text{Th}})^2 W/2L$ ,<sup>57</sup> under the condition of  $-V_{\text{DS}} > -(V_{\text{GS}} - V_{\text{Th}})$ , where  $I_{\text{DS}}$  is the source/drain current,  $\mu$  is the field-effect mobility,  $W$  is the channel width,  $L$  is the channel length,  $C_i$  is the capacitance per unit area of the gate dielectric layer, and  $V_{\text{GS}}$ ,  $V_{\text{Th}}$ , and  $V_{\text{DS}}$  are the gate, threshold, and source/drain voltages, respectively. Fig. 2a presents the  $I_{\text{DS}}$  vs.  $V_{\text{G}}$  characteristics of the TFTs made using two different PbS QDs thin films. The field-effect mobilities of  $\sim 1 \times 10^{-5}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  and  $\sim 2.2 \times 10^{-3}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  are observed from the OLA-capped PbS QDs thin film and the EDT-capped PbS QDs thin film, respectively. The field-effect hole mobility of the EDT-capped PbS QDs thin film is  $\sim 100$  times larger than that of the OLA-capped PbS QDs thin film.

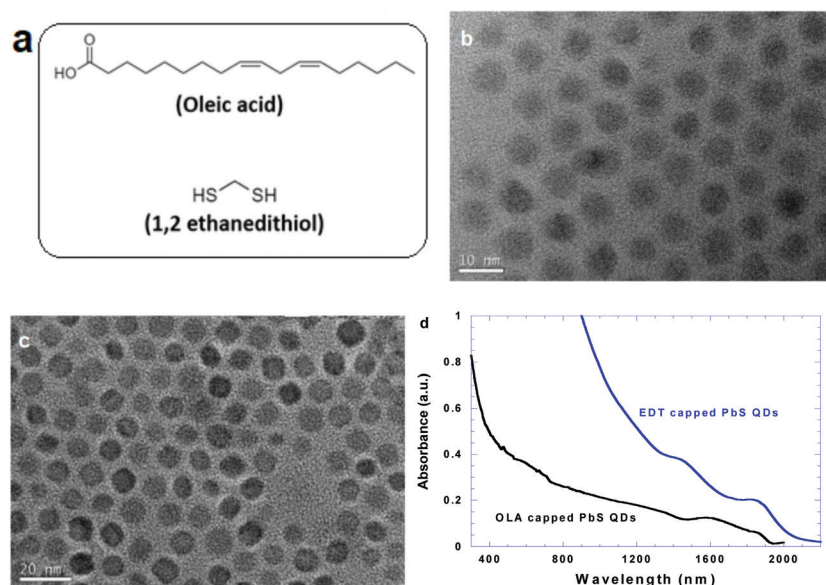


Fig. 1 (a) Molecular structures of OLA and EDT, the TEM images of (b) the OLA-capped PbS QDs thin film and (c) the EDT-capped PbS QDs thin film, and (d) the absorption spectra of two different PbS QDs thin films.

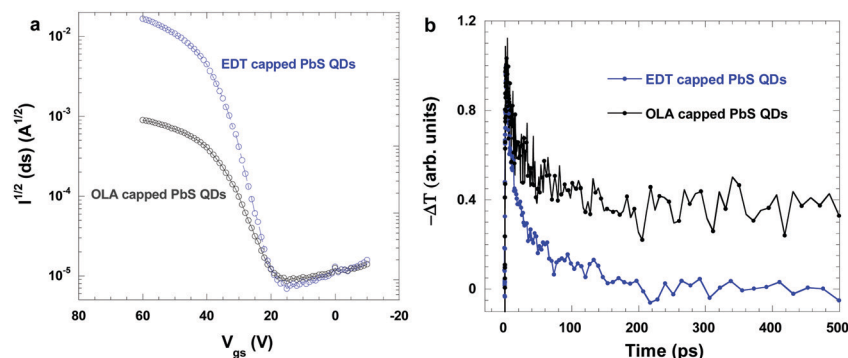


Fig. 2 (a) The  $I_{DS}$  versus  $V_G$  characteristics of thin-film transistors based on the PbS QDs thin films, (b) the transient decay dynamics of PbS QDs thin films probed at 4.7 mm.

The enhanced charge carrier mobility of the EDT-capped PbS QDs thin film is ascribed to the short-chain of the EDT molecule.

Fig. 2b compares the dynamics of the photoinduced absorption in the OLA-capped PbS QDs thin film and the EDT-capped PbS QDs thin film probed at 4.7 mm. Compared to the OLA-capped PbS QDs, a fast decay from the EDT-capped PbS QDs thin film was observed. A slow decay indicates that the traps induced by the insulating OLA restrict electron hopping from one PbS QD to another. On the other hand, a fast decay observed from the EDT-capped PbS QDs reveals that the electron can hop from one PbS QDs to another with less restriction. These results demonstrate that the charge carrier mobility of the EDT-capped PbS QDs is higher than those of the OLA-capped PbS QDs.

Fig. 3a presents the molecular structures of PDDTT with different side chains, where PDDTT is poly(5,7-bis(4-decanyl-2-thienyl)-thieno(3,4-b)diathiazole-thiophene-2,5). PDDTT is selected as the electron donor to form the bulk heterojunction (BHJ) composite with PbS QDs since it has a p-type low optical gap-conjugated polymer with decent charge carrier mobility.<sup>5</sup> Moreover, PDDTT exhibits optical response up to the near-infrared (NIR) region, which could certainly contribute to the NIR spectral response for broadband PDs based on PDDTT composites.<sup>5</sup> However, PDDTT with  $C_{10}H_{21}$  side chain (PDDTT-C10) possesses poor solubility in typical organic solvents.

To enhance its solubility, a side chain with a long carbon chain, such as  $C_{12}H_{25}$  was incorporated with PDDTT. The synthetic procedures of PDDTT with the  $C_{12}H_{25}$  side chain (PDDTT-C12) were the same as PDDTT-C10, which was reported previously.<sup>5,58</sup> The absorption spectra of the PDDTT-C10 and PDDTT-C12 thin films are shown in Fig. 3b. Due to polymer aggregation,<sup>59</sup> PDDTT-C12 thin film possesses extended absorption compared to the PDDTT-C10 thin film. Thus, PDDTT-C12 was used as the electron donor to form a BHJ composite with the EDT-capped PbS QDs for the development of broadband PDs.

Scheme 1a displays the device architecture of the broadband PDs. In this broadband PDs, neither ITO nor FTO, which are currently used as the transparent electrodes for various electronics, are used as the electrodes due to their very weak transmittance in the IR region.<sup>43–45</sup> Moreover, carbon nanotubes (CNTs),<sup>45,46</sup> silver nanowires (Ag NWs),<sup>47</sup> and semiconducting polymers<sup>48–51</sup> were also not utilized as the transparent electrodes since they possess poor electrical conductivity and are required to be processed with complicated costly nanoimprint lithography.<sup>45–49</sup> Towards the end, an “inverted” device architecture, as shown in Scheme 1a, was developed. In this device structure, the Au/Cr bilayer is the anode, solution-processed  $MoO_3$  thin layer acts as the hole extraction layer (HEL), the PDDTT:PbS QDs BHJ composite thin film is the photoactive layer, the vacuum-deposited BaO thin layer acts as the electron

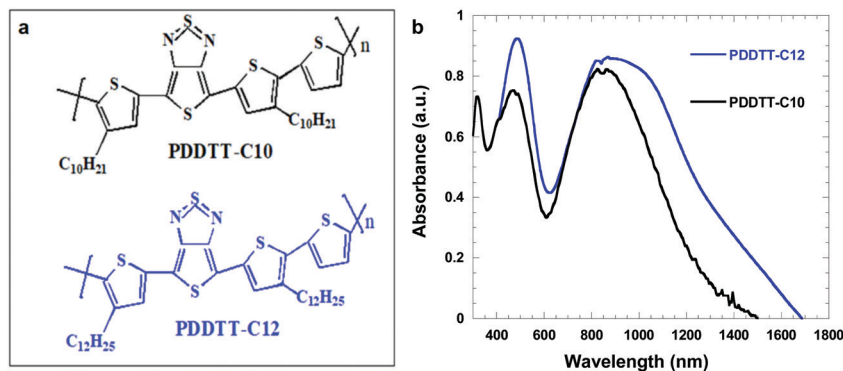
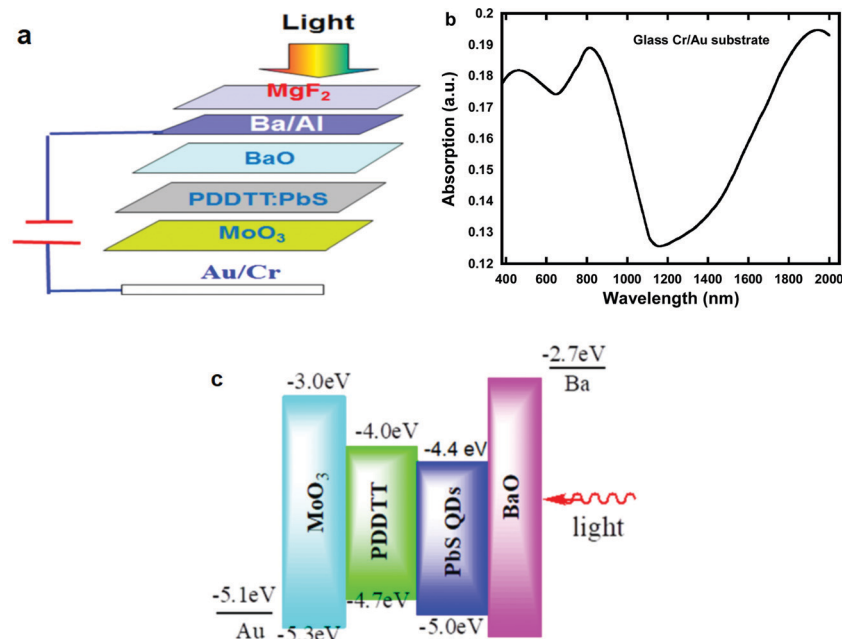


Fig. 3 (a) Molecular structures and (b) absorption spectra of PDDTT with different side chains.



**Scheme 1** (a) Device architecture of broadband photodetectors, (b) the absorption spectrum of glass Cr/Au thin film, and (c) the LUMO and HOMO energy levels of MoO<sub>3</sub>, PDDTT, PbS QDs, BaO, and the work functions of the Au and Ba electrodes.

extraction layer (EEL), thin Ba covered with Al bilayer acts as the cathode, and the transparent MgF<sub>2</sub> layer is used as the passivation layer since it has excellent transparency from the UV-visible to the IR region.<sup>60</sup> The Ba/Al (5 nm/20 nm) bilayer has decent transparency from the UV-visible to the IR region as well.<sup>61</sup> BaO is a wide optical gap oxide. The light passing through the BaO EEL will be absorbed by the PDDTT:PbS QDs BHJ composite thin film. Moreover, smooth Au layer typical can reflect 30% of light.<sup>62</sup> Scheme 1b displays the absorption spectrum of the glass Cr/Au thin film. It is clear that the smooth Au thin layer could reflect light from 300 nm to 2000 nm. This reflected light can be further reabsorbed by the PDDTT:PbS QDs BHJ composite thin film, resulting in boosted photocurrent. As a result, a decent photocurrent is expected to be observed from the broadband PDs with a device structure shown in Scheme 1a.

Scheme 1c displays the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energy levels of MoO<sub>3</sub>, PDDTT, PbS QDs, BaO, and the work-functions of the Au and Ba electrodes. Without illumination, the Schottky barrier formed between the Au anode and the MoO<sub>3</sub> HEL, and the Ba cathode and the BaO EEL could result in suppressed dark current density for broadband PDs. Under illumination, the excitons generated within the PDDTT:PbS QDs BHJ composite photoactive layer would dissociate into separated charge carriers under an external electric field created by the work function difference between the Au and Ba electrodes. Based on the band alignment, the separated electrons within the PDDTT:PbS QDs BHJ composite could transfer from PDDTT to PbS QDs due to a large LUMO offset between PDDTT and PbS QDs. These separated electrons are further extracted by the BaO HEL, and then collected by the Ba cathode. Meanwhile, the separated holes within the PDDTT:PbS QDs BHJ composite could transfer from PbS QDs

to PDDTT due to a large HOMOs offset between the PbS QDs and PDDTT. These separated holes are further extracted by the MoO<sub>3</sub> HEL, and then collected by the Au anode. Therefore, broadband PDs with a device structure shown in Fig. 1a would exhibit boosted  $R$  and  $D^*$ .<sup>5</sup>

To verify the photoinduced charge transfer occurring within the PDDTT:PbS QDs BHJ composite, the dynamics of the photoinduced absorption in the PDDTT:PbS QDs BHJ composite thin film probed at 4.7  $\mu\text{m}$  is investigated and further compared with those of pristine PDDTT and PbS QDs. The polarons from the conjugated polymers could be detected in the mid-IR spectral region.<sup>63–65</sup> As indicated in Fig. 4a, a fast decay observed from the pristine PDDTT thin film indicates that the lifetime of the polarons from PDDTT is very short. A relatively slow decay observed from the EDT-capped PbS QDs indicates that the charge carrier is trapped due to the insulation of the EDT molecule. However, a much longer polaron lifetime, which is up to a nanosecond, is observed from the PDDTT:PbS QD BHJ composite thin film as compared to those from the pristine PDDTT thin film and the pristine PbS QD thin film. These results reveal that the long-lived mobile carriers show the integration of PDDTT and PbS QDs, and further demonstrate the efficient charge transfer from PDDTT to PbS QDs with inhibited back-transfer. Thus, as expected, broadband PDs based on the PDDTT:PbS QD BHJ composite thin film would exhibit high photocurrent.

The current density *versus* voltage ( $J$ - $V$ ) characteristics of broadband PDs operated at RT and measured in dark and under a monochromatic light at a wavelength ( $\lambda$ ) of 800 nm with a light intensity of 0.22 mW cm<sup>-2</sup>, and at a  $\lambda$  of 1550 nm with a light intensity of 0.05 mW cm<sup>-2</sup>, are shown in Fig. 4b. In dark, the broadband PDs exhibit asymmetric  $J$ - $V$  characteristics with the rectification ratio of  $2.5 \times 10^4$  at  $\pm 1$  V. These results indicate

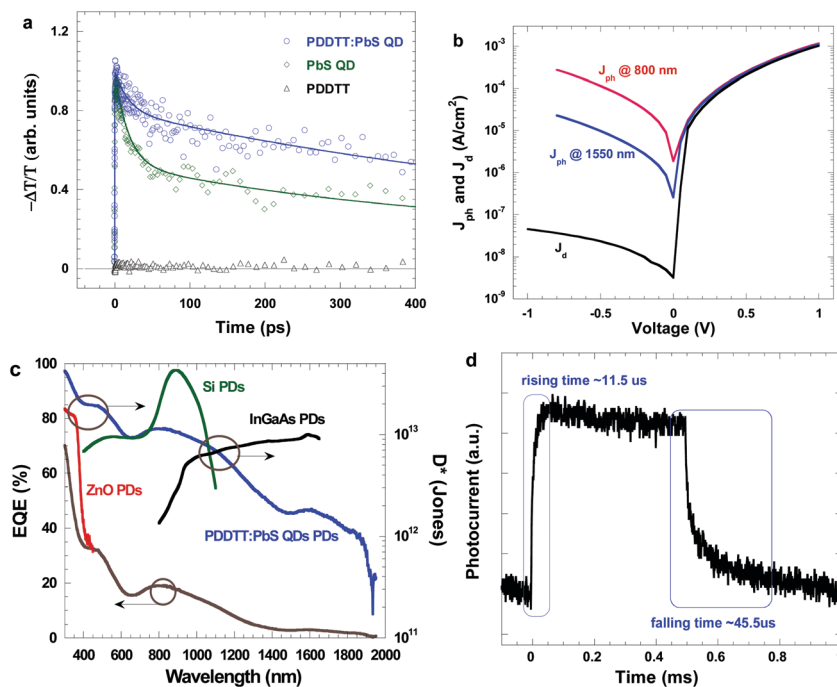


Fig. 4 (a) The transient decay dynamics of PDDTT and PbS QDs thin films and PDDTT:PbS QDs BHJ composite thin film, (b) the  $J$ - $V$  characteristics of broadband PDs, (c) the EQE spectrum of the broadband PDs and the projected detectivities of the broadband PDs versus wavelength compared with ZnO-based PDs, Si-based PDs, and InGaAs-based PDs, and (d) the photocurrent response time of broadband PDs.

that the broadband PDs possess excellent photodiode behaviors.<sup>66</sup> Different photocurrent densities observed from the broadband PDs under different monochromatic light illumination are ascribed to different light intensities, which indicate that the broadband PDs possess different photoresponsibilities.

Responsivity ( $R$ ), described as  $R = J_{ph}/L_{light}$ <sup>5,66</sup> (where  $J_{ph}$  is the photocurrent density and  $L_{light}$  is the light intensity), is often used to evaluate the device performance of the PDs. Under a bias of  $-0.1$  V,  $R$  of  $73 \text{ mA W}^{-1}$  and  $28.8 \text{ mA W}^{-1}$  at  $\lambda$  of  $800 \text{ nm}$  and  $1550 \text{ nm}$ , respectively, are observed from the broadband PDs. Moreover, under a bias of  $-0.5$  V,  $R$  of  $545 \text{ mA W}^{-1}$  and  $195 \text{ mA W}^{-1}$  at  $\lambda$  of  $800 \text{ nm}$  and  $1550 \text{ nm}$ , respectively, are observed from the broadband PDs.

If the dark current is only considered as the major contributor to the noise current,<sup>5,36,37</sup> the project detectivity ( $D^*$ ) can be described as  $D^* = R/\sqrt{2qJ_d}$  (where  $J_d$  is the dark current density,  $q$  is the elementary electric charge,  $q = 1.6 \times 10^{-19} \text{ C}$ , respectively). Thus, at RT,  $D^*$  at  $\lambda$  of  $800 \text{ nm}$  and  $1550 \text{ nm}$  are calculated to be  $1.6 \times 10^{13}$  Jones and  $6.4 \times 10^{12}$  Jones ( $\text{cm Hz}^{1/2}/\text{W}$ ), respectively, for the broadband PDs operated at a bias of  $-0.1$  V. Moreover, at RT and under a bias of  $-0.5$  V,  $D^*$  at  $\lambda$  of  $800 \text{ nm}$  and  $1550 \text{ nm}$  was calculated to be  $1.2 \times 10^{14}$  Jones and  $4.3 \times 10^{13}$  Jones, respectively, for broadband PDs. These  $D^*$  values are compatible with those observed from 2D metal dichalcogenide-based PDs.<sup>11–14</sup> All these results certainly demonstrate that broadband PDs with a vertical device structure exhibit high  $R$  and  $D^*$ , indicating that the broadband PDs have great potential applications.<sup>1–3</sup>

Fig. 4c presents the EQE spectrum of the broadband PDs. It is clear that the EQE spectrum of the broadband PDs is the

superposition of the absorption spectra of the EDT-capped PbS QDs thin film (Fig. 1), PDDTT thin film (Fig. 3), and the reflection spectrum of the Au thin layer (Scheme 1b).

Based on the EQE spectrum and  $D^*$  value at  $\lambda$  of  $800 \text{ nm}$  and  $1550 \text{ nm}$  for the broadband PDs,  $D^*$  values versus wavelength are calculated based on  $R = \text{EQE} \times \frac{q}{h\nu} = \text{EQE} \times \frac{\lambda}{1240}$ .<sup>5,66</sup> Fig. 4c presents  $D^*$  versus wavelength for the broadband PDs. Under a bias of  $-0.1$  V, the broadband PDs exhibit over  $10^{12}$  Jones from  $300 \text{ nm}$  to  $2000 \text{ nm}$  at RT. Such decent  $D^*$  over the broadband spectral region are ascribed to novel device architecture and the PDDTT:PbS QDs BHJ composite thin film.

The response time is another important parameter used to evaluate the device performance of the PDs. Fig. 4d presents the transient photocurrents of the broadband PDs. The rise time was defined as the time required for the output signals to increase from 10% to 90% of the saturated photocurrent. Similarly, the fall time was defined as the time required for the output signal to decrease from 90% to 10% of the saturated photocurrent.<sup>67,68</sup> A rise time of  $11 \mu\text{s}$  and a fall time of  $45 \mu\text{s}$  was observed from the broadband PDs. Such slow response time is probably originated from the relatively poor electrical conductivity of the EDT-capped PbS QDs thin film.

## 4. Conclusion

Room-temperature operated, solution-processed broadband photodetectors (PDs) based on low optical gap conjugated polymer incorporated with highly electrically conductive PbS

quantum dots (QDs) bulk heterojunction (BHJ) composite and inverted photodiode device structure without the incorporation of the transparent oxide electrodes, with the spectral response ranging from 300 nm to 2000 nm, were demonstrated. The low optical gap conjugated polymer, PDDTT, contributes to the IR photoresponse up to 1700 nm. PbS QDs further extend the IR photoresponse up to 2000 nm. The implementation of a photodiode with an “inverted” vertical device structure with the Au anode and the Ba/Al bilayer semitransparent cathode passivated with the MgF<sub>2</sub> layer realize IR spectral response and circumvent the weak IR transparency of the transparent oxide electrodes. Photoinduced charge carrier transfer within the PDDTT:PbS QDs BHJ composite gave rise to the photocurrent, resulting in detectivities greater than 10<sup>12</sup> Jones (cm Hz<sup>1/2</sup>/W) over the wavelength region from 300 nm to 2000 nm under a low applied bias. Thus, our findings of the utilization of the PDDTT:PbS QDs BHJ composites and an “inverted” vertical photodiode without the incorporation of the transparent oxide electrodes provide a facile way to realize broadband PDs.

## Conflicts of interest

We declare that we have no competing financial interest and all the financial support has been acknowledged in the manuscript.

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