Solution-Processed CsPbBr$_3$ Quantum Dots/Organic Semiconductor Planar Heterojunctions for High-Performance Photodetectors

Kaixuan Chen, Xuliang Zhang, Ping-An Chen, Jing Guo, Mai He, Yanqin Chen, Xincan Qiu, Yu Liu, Huajie Chen, Zebing Zeng, Xiao Wang, Jianyu Yuan, Wanli Ma, Lei Liao, Thuc-Quyen Nguyen,* and Yuanyuan Hu*

Planar heterojunctions (PHJs) are fundamental building blocks for construction of semiconductor devices. However, fabricating PHJs with solution-processable semiconductors such as organic semiconductors (OSCs) is a challenge. Herein, utilizing the orthogonal solubility and good wettability between CsPbBr$_3$ perovskite quantum dots (PQDs) and OSCs, fabrication of solution-processed PQD/OSC PHJs are reported. The phototransistors based on bilayer PQD/PDVT-10 PHJs show responsivity up to $1.64 \times 10^4$ A W$^{-1}$, specific detectivity of $3.17 \times 10^{12}$ Jones, and photosensitivity of $5.33 \times 10^6$ when illuminated by 450 nm light. Such high photodetection performance is attributed to efficient charge dissociation and transport, as well as the photogating effect in the PHJs. Furthermore, the tri-layer PDVT-10/PQD/Y6 PHJs are used to construct photodiodes working in self-powered mode, which exhibit broad range photosresponse from ultraviolet to near-infrared, with responsivity approaching $10^{-7}$ A W$^{-1}$ and detectivity over $10^6$ Jones. These results present a convenient and scalable production processes for solution-processed PHJs and show their great potential for optoelectronic applications.

1. Introduction

Planar heterojunction (PHJ) consisting of different layered semiconductors is a basic and important structure for constructing high-performance electronic and photonic devices. For instance, PHJs based on inorganic semiconductors AlGaAs/GaAs are used to construct high electron mobility transistors (HEMTs) (see Figure S1a, Supporting Information).\[1\] Compared to inorganic semiconductors, solution-processable semiconductors such as organic semiconductors (OSCs) are attractive for large-area, low-cost, and flexible/stretchable electronics, and have been widely applied in devices such as organic field-effect transistors (OFETs),\[2–4\] organic light-emitting diodes (OLEDs),\[5,6\] organic photodetectors (OPDs),\[7,8\] and organic photovoltaics (OPVs).\[9,10\] Although the solution-processability of OSCs...
brings prominent advantages to them, it also leads to challenges in fabrication of PHJ structures, because the successive deposition of the second layer may dissolve or cause damage to the first layer. Therefore, bulk heterojunctions (BHJs) where two semiconductors fully intermix with each other are more commonly seen in solution-processed OSCs (Figure S1b, Supporting Information).

Several strategies have been proposed to address this problem. For example, OSCs dissolved in orthogonal solvents that do not dissolve the first layer were employed as the second layers for fabricating PHJs. Alternatively, the first layer can be insolubilized or crosslinked to reduce the damage from the second layer. Recently, a self-assembly method was adopted to achieve monolayer molecule crystalline PHJs. These methods, although feasible for obtaining PHJs, generally place restrictions on the selection of OSCs, limiting the general applicability of them. There have also been reports of using film transfer method to construct organic PHJs, which cannot dissolve OSCs such as hexene, which provides possibilities for forming PHJs with OSCs. In particular, PQDs have good wetting with OSCs owning to the existence of surface organic ligands, which allows the deposition of them on top of OSCs, offering more freedom to the structure of PHJs. More importantly, the ion migration is greatly inhibited in PQDs, which is crucial to the operation stability of devices and to the realization of field-effect devices. All these features of PQDs render them very attractive for being combined with OSCs to construct PHJs for novel photonic and electronic devices. However, although PQDs were previously reported to form heterojunctions with thermally evaporated OSCs, the demonstration of solution-processed PQD/OSC PHJs and their applications have not been reported.

In this work, we showcase the utilization of CsPbBr$_3$ PQDs and OSCs for fabrication of solution-processed PHJs, including bilayer PQD/OSC PHJs and tri-layer OSC/PQD/OSC PHJs by simple spin-coating method. Phototransistors based on the bilayer PQD/PDVT-10 PHJs are constructed, which exhibit high responsivity up to 1.64 $\times$ 10$^4$ A W$^{-1}$, specific detectivity of 3.17 $\times$ 10$^{12}$ Jones, and ultrahigh $I_{\text{photo}}/I_{\text{dark}}$ ratio up to 5.33 $\times$ 10$^6$. We reveal that efficient charge dissociation and transport, together with photogating effects in the PHJs contribute to the high performance of the phototransistors. Furthermore, we demonstrate photodiodes with tri-layer PHJs consisting of PDVT-10/PQD/Y6. The devices work in self-powered mode (zero bias voltage) and exhibit decent photodetection performance in broad range from ultraviolet to near-infrared (NIR). Our work demonstrates that the combination of PQDs with OSCs is an effective strategy to fabricate solution-processed PHJs, and opens opportunities for more exploration and application of such PHJs.

2. Results and Discussion

2.1. Characterization of CsPbBr$_3$ QDs and Fabrication of PQD/OSC PHJs

Figure 1a,b illustrates the crystal structure of CsPbBr$_3$ QDs and the chemical structures of PDVT-10 (p-type) and Y6 (n-type), respectively. In this work, CsPbBr$_3$ QDs were prepared using the hot-injection method, and corresponding films were obtained through spin-coating the solution at room temperature under ambient conditions. Figure 1c presents the transmission electron microscopy (TEM) image of the CsPbBr$_3$ QDs films, which shows clearly the lattice fringes of CsPbBr$_3$ QDs and their mean size of ±11.3 nm (see the inset in Figure 1c). As the CsPbBr$_3$ QDs are capped with oleic acid and oleylamine ligands, they provide good solubility in various organic solvents. Here, we use hexane...
Figure 1. Structural and physical properties of CsPbBr₃ QDs. a) Schematic structures of the CsPbBr₃ QDs. b) The chemical structure of PDVT-10 and Y6. c) TEM image of the CsPbBr₃ QDs film. d) Contact angle measurements showing the wettability of FAPbI₃ and CsPbBr₃ QDs on PDVT-10 films. e) Schematic diagrams of OSC/PQD, PQD/OSC, and OSC/PQD/OSC PHJs.

(Hex) as the solvent for CsPbBr₃ QDs as this solvent does not dissolve PDVT-10 and Y6 which are processed from CB.

In addition to orthogonal solubility, wettability is another important issue for successful fabrication of solution-processed PHJs. As mentioned above, generally MHPs can be easily deposited on top of OSCs films yet it is difficult to perform the reversed deposition. This is directly observed in Figure 1d, which shows that the contact angle between formamidinium lead iodide (FAPbI₃) and PDVT-10 is 80°, leading to strong dewetting effect during spin-coating of the former semiconductor on top of the latter one. By comparison, the small contact angle of 15° for the CsPbBr₃ QDs droplet on the PDVT-10 film indicates the excellent wettability of CsPbBr₃ QDs with OSCs, which ensures the deposition of CsPbBr₃ QDs layers on OSCs. Therefore, depending on the deposition sequence of PQDs and OSCs, there are two configurations of bilayer PHJs: PQD/OSC PHJs with the PQD film being the bottom layer and OSC/PQD PHJs with the OSC film being the bottom layer, as shown in Figure 1e, providing various device configurations. Moreover, tri-layer OSC/PQD/OSC PHJs are achievable thanks to the unique wetting properties of CsPbBr₃ QDs. It should be mentioned that while hexane does not dissolve OSCs, which ensures the successful deposition of PQDs on OSCs, CB actually partially dissolves CsPbBr₃ QDs. However, in our experiments we find that this dissolvability has little effects on the performance PQD/OSC PHJs as detailed below, probably because the spin-coating process for OSCs only lasts 20 s which is too short to result in severe dissolution of the PQDs.

2.2. Phototransistors Based on CsPbBr₃ QDs/PDVT-10 PHJs

The bilayer and tri-layer PHJs allow us to construct various photonic and electronic devices. As an example, we first fabricated phototransistors based on the CsPbBr₃ QDs/PDVT-10 PHJs, as shown in Figure 2a. Bottom-contact electrodes (2 nm Cr/30 nm Au) were defined by photolithography on Si²⁺/SiO₂ (300 nm) substrates with a channel length of 40 μm and width of 1000 μm. Then, CsPbBr₃ QDs and PDVT-10 were deposited onto SiO₂ sequentially by spin-coating (see the Experimental Section for more details). The absorption spectra of CsPbBr₃ QDs film, PDVT-10 film, and CsPbBr₃ QDs/PDVT-10 PHJ are shown in Figure 2b. The CsPbBr₃ QDs film shows an absorption edge at a wavelength of ≈520 nm, while the PDVT-10 film shows prominent absorption in the range of 600–950 nm. The schematic diagram showing the energetic levels of the two semiconductors is illustrated in Figure 2c. CsPbBr₃ QDs exhibit a valence band maximum (VBM) of −5.87 eV, and a conduction band minimum (CBM) of −3.52 eV.[31] The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of PDVT-10 are located at −3.60 and −5.28 eV,[32] respectively. Such energy levels of CsPbBr₃ QDs and PDVT-10 lead to the formation of type I heterojunctions (straddling gap). However, different types of PHJs are available by choosing OSCs with appropriate energy levels.

Figure 2d shows the cross-section image of the device characterized by SEM, in which the CsPbBr₃ QDs/PDVT-10 PHJ...
Figure 2. Fabrication of phototransistors based on the CsPbBr$_3$ QDs/PDVT-10 PHJs. (a) Schematic device structure of the CsPbBr$_3$ QDs/PDVT-10 PHJ phototransistor. b) The absorption spectra of pristine CsPbBr$_3$ QDs film, pristine PDVT-10 film, and CsPbBr$_3$ QDs/PDVT-10 PHJs. c) Energy-level diagram of CsPbBr$_3$ QDs and PDVT-10. d) The cross-section SEM image of the device e) AFM images of CsPbBr$_3$ QDs film and CsPbBr$_3$ QDs/PDVT-10 PHJs. f) The film thickness of CsPbBr$_3$ QDs and CsPbBr$_3$ QDs/PDVT-10 PHJs.

is clearly seen. Atomic force microscopy (AFM) measurements were also performed to probe the surface morphology of the PHJs. The CsPbBr$_3$ QDs film shows a rough morphology while the deposition of PDVT-10 significantly smoothens the surface, with roughness reduced from $\approx 22.8$ to $\approx 11.2$ nm (Figure 2e). The thicknesses of CsPbBr$_3$ QDs and CsPbBr$_3$ QDs/PDVT-10 layers are $\approx 117.0$ and $\approx 141.1$ nm, respectively, as determined by AFM measurements (Figure 2f).

Next, we characterized the photoresponse performance of the devices. As shown in Figure 3a, the transfer characteristics of the device were measured in the dark and under various illumination power intensities ($\lambda = 450$ nm) from $0.01$ to $10$ mW cm$^{-2}$, with a $V_{GS}$ sweeping from $-60$ to $10$ V at a fixed $V_{DS}$ of $-60$ V. In the dark condition, the device exhibits a typical p-type transistors behavior, with off-current below $10^{-10}$ A and on-current above $10^{-5}$ A. Notably, the transistor behavior of the PHJ device indeed reflects that the CsPbBr$_3$ QDs have weak ion motion effect, which does not screen the gate electric field and so the gate modulation over the device current is realized. This is in strong contrast with MHP films, where ion motion is commonly observed and believed to cause the gate screening effect at room temperatures, resulting in dysfunction of transistors based on such bilayer PHJs.$^{[13]}$

Under illumination, the current in both the off-state and on-state increases significantly, indicating that the device has a strong light response. In comparison, the control device made of PDVT-10 alone only exhibits very weak photoresponse (Figure S2, Supporting Information). Another control device based on CsPbBr$_3$ QDs without the PDVT-10 layer does not show obvious transistor characteristics (Figure S3, Supporting Information). These results together justify the importance of using the PHJ as the core component for constructing high-performance phototransistors.

Figure 3b depicts the gate voltage-dependent responsivity ($R$) of the device illuminated with various light intensities. $R$ as high as $1.64 \times 10^4$ A W$^{-1}$ can be achieved in these PHJ-based phototransistors when the illumination intensity is $0.01$ mW cm$^{-2}$. Accordingly, a high detectivity ($D^*$) of $3.17 \times 10^{12}$ Jones can be achieved. It should be noted the $D^*$ values were usually calculated by assuming that the total noise is mainly resulted from shot noise of dark current ($I_{dark}$), which may underestimate the noise level and result in overestimated $D^*$ values.$^{[14–30]}$ Considering this, we extracted the noise spectra density by performing a Fast Fourier transform (FFT) of the measured dark current, as shown in Figure S6 (Supporting Information), according to previously reported method.$^{[37]}$ Besides, the dependence of photosensitivity ($P$) on the gate voltage is displayed in Figure 3c, which shows an increasing $P$ with incident light power reaching a maximum of $5.33 \times 10^6$ at $10$ mW cm$^{-2}$. Even if the light is weak ($0.01$ mW cm$^{-2}$), $P$ still shows a peak value of $4.92 \times 10^5$, suggesting the excellent photosensitivity of the phototransistors. Figure 3d shows the values of $R$, $D^*$ and $P$ as a function of illumination density, indicating both $R$ and $D^*$ decrease with the illumination density, while $P$ increases with it. Overall, the phototransistors based on the CsPbBr$_3$ QDs/PDVT-10 PHJs exhibit remarkably high performance, and the performance parameters stand out even if we compare them with those of the phototransistors ever reported in literatures, as shown in Figure 3e.$^{[29,38–47]}$
Figure 3. a) Transfer characteristics under various illumination power intensities ($\lambda = 450$ nm) when $V_{DS}$ was fixed at $-60$ V. b) Responsivity and c) photosensitivity of CsPbBr$_3$ QDs/PDVT-10 PHJ phototransistors as a function of gate bias characterized under various illumination power intensities. d) Responsivity, detectivity, and photosensitivity values of CsPbBr$_3$ QDs/PDVT-10 PHJ transistors as a function of power intensity at $V_{GS} = 3$ V; e) responsivity, detectivity, and photosensitivity of several typical state-of-the-art phototransistors reported in literatures.

Notably, although here we demonstrate the usage of CsPbBr$_3$ QDs/PDVT-10 PHJs for constructing phototransistors, the reverse PHJs such as PDVT-10/CsPbBr$_3$ QDs are also applicable for such purposes, with slightly lower device performance (see additional data in Figure S10, Supporting Information). Moreover, this strategy of using PQD/OSC PHJs for high-performance phototransistors is not only applicable to PDVT-10 or p-type semiconductors, but also to n-type semiconductors such as N2200. In Figures S11 and S12 (Supporting Information), we show the performance of phototransistors based on CsPbBr$_3$ QDs/N2200 and N2200/CsPbBr$_3$ QDs PHJs, respectively. The PHJ devices again exhibit significantly enhanced photodetection performance compared to the control devices with N2200 or CsPbBr$_3$ QDs only as active layers. Therefore, the method of using PQD/OSC PHJs for fabricating high-performance phototransistors is effective and universal.

2.3. Mechanism Studies of CsPbBr$_3$ QDs/PDVT-10 PHJ Phototransistors

We inspect the factors responsible for the high photodetection performance in the CsPbBr$_3$ QDs/PDVT-10 PHJ phototransistors. We first investigated the charge transport properties in such PHJ phototransistors. The transfer characteristics of the PDVT-10 control device and CsPbBr$_3$ QDs/PDVT-10 PHJ device as a function of temperature measured in dark conditions are shown in Figure 4a,c, respectively. The similarity of the transfer curves between the PHJ device and control device implies that the current in the PHJ device is attributed to hole transport in the PDVT-10 layer. Indeed, it is found that the CsPbBr$_3$ QDs have low charge transport ability and thus can function as a dielectric with dielectric constant of about 8.4 (see Figure S4, Supporting Information). The device currents are significantly lowered as the temperature decreased, indicating hopping transport mechanism. It is observed that, compared to the control device, the mobility of the PHJ device is obviously decreased. It is also noted that the activation energy $E_a$ of the PHJs device extracted from the temperature-dependent mobilities (Figure 4b,d) according to the Arrhenius equation: $\mu = \mu_0 \exp(-E_a/kT)$ is about 7.4 meV higher than that of the control device. The lower mobility and higher $E_a$ values are possibly due to interface trapping of holes by CsPbBr$_3$ QDs.

Next, we investigated the charge dissociation process in the device by PL spectra and time-resolved PL measurements. Figure 4e shows the PL spectra (excitation wavelength of 510 nm) of the CsPbBr$_3$ QDs film and CsPbBr$_3$ QDs/PDVT-10 PHJs on glass substrates. Both samples exhibit a PL peak around 518 nm, which is consistent with the bandgap of CsPbBr$_3$ QDs. However, the PL intensity of the PHJs is significantly quenched compared to that of pristine CsPbBr$_3$ QDs. Figure 4f exhibits the time-resolved PL decay of the pristine CsPbBr$_3$ QDs and PHJ samples, from which a reduced lifetime of excitons is observed in the PHJs. These experimental results clearly demonstrate that the PHJs can boost exciton dissociation efficiency, which is important to the enhancement of detector responsivity.

Based on the experimental results shown above, we now can depict the physical processes in the PHJs phototransistors. The strong light-absorption property of CsPbBr$_3$ QDs is crucial to
the achievement of high device performance.\textsuperscript{[48]} Upon illumination ($\lambda = 450$ nm), firstly a large number of excitons are expected to be produced in CsPbBr$_3$ QDs upon light illumination. Although considerable dissociation of the excitons can happen in CsPbBr$_3$ QDs layers because of the small exciton binding energy,\textsuperscript{[49]} the above experimental results apparently show this dissociation process becomes more efficient with the existence of the PHJs. Subsequently, the dissociated holes are transferred to PDVT-10, enhancing the conductivity of PDVT-10, which can be taken as the photoconductive effect. Meanwhile, the photogenerated electrons are trapped in CsPbBr$_3$ QDs, causing a photogating effect in the device by generating an additional electric field to the PDVT-10 channel. Indeed, the coexistence of photoconductive and photo-gating effect in the system can be more clearly seen by depicting the photocurrent as a function of illumination intensity (see Figure S8, Supporting Information). This photogating effect is important for achieving the high responsivity or gain in the PHJ-based phototransistors due to the prolonged excess carrier lifetime.\textsuperscript{[41,50]} It might be argued that the photogenerated electrons can also transfer to the PDVT-10 layer because of its slightly lower LUMO level relative to the CB level of CsPbBr$_3$ QDs, and then combine with the holes in PDVT-10. However, this assumption is clearly inconsistent with the dramatically enhanced conductivity observed in Figure 3a. Possibly, the ligands provide a barrier for electron transfer from the QDs to the PDVT-10. The schematic diagram shown Figure 4g illustrates the physical processes in the PHJ-based transistors. Overall, it can be concluded that the formation of the CsPbBr$_3$ QDs/OSC PHJs is essential for the high photodetection performance of the phototransistors.

Figure 4. Mechanism investigations in the PHJ-based phototransistors. Transfer characteristics of the a) PDVT-10 FET and c) CsPbBr$_3$ QDs/PDVT-10 FET measured from 250 to 200 K in the dark. Temperature-dependent mobilities of b) PDVT-10 and d) CsPbBr$_3$ QDs/PDVT-10 FETs. The mobilities were all extracted in the saturation regime ($V_{DS}$ = −60 V). e) PL spectra of CsPbBr$_3$ QDs and CsPbBr$_3$ QDs/PDVT-10 PHJ films. f) Time-resolved PL decays of CsPbBr$_3$ QDs and CsPbBr$_3$ QDs/PDVT-10 PHJ films. g) Schematic diagrams showing the working principle of CsPbBr$_3$ QDs/PDVT-10 PHJ phototransistors.
2.4. Photodiodes Based on PDVT-10/CsPbBr₃ QDs/Y6 PHJs

In this section, we demonstrate the solution-processed tri-layer PHJs and their applications in photodiodes. Such tri-layer PHJs not only enable favorable energy level alignment for charge dissociation/transport, but also provide more flexibility in the combination of OSCs to achieve desired photoabsorption, and thus are particularly attractive for broadband photodetector applications. Here, as an example, we show the fabrication and characterization of photodiodes using PDVT-10/CsPbBr₃ QDs/Y6 PHJs.

Figure 5a presents the device structure of the photodiode, in which the core element is the PDVT-10/CsPbBr₃ QDs/Y6 PHJ solution-deposited in sequence, as seen in the cross-section image of the device characterized by SEM (Figure 5b). The energy levels of the tri-layer PHJs are illustrated in Figure 5c, which indicates that holes and electrons are prone to transport to PDVT-10 and Y6, respectively, as desired by photodiodes. In addition, the PHJ shows a wide absorption from 350 to 900 nm (Figure 5d). Particularly, the CsPbBr₃ QDs show strong absorption to light with $\lambda < 520$ nm, and the combination of PDVT-10 and Y6 results in prominent absorption in the range of 600–900 nm.

The dark and photo $J$–$V$ characteristic of the device as a function of the input power density ($\lambda = 450$ nm) is shown in Figure 5e. The photodiode shows a typical rectifying behavior and photo-response. In the dark, the current density increases rapidly under forward biases since the energetic levels are favorable for hole injection from the indium tin oxide (ITO) anode and electron injection from the Al cathode into the active layer, as shown in Figure 5c, while a low current density is expected under reverse biases. Under 450 nm illumination, the CsPbBr₃ QDs layer can absorb photons and generate excitons that subsequently dissociate at the PDVT-10/CsPbBr₃ QDs and CsPbBr₃ QDs/Y6 interfaces, and then get collected by electrodes, leading to significant photoresponse in the device.
Notably, the device can function well at even zero bias voltage as a self-powered photodetector. The dependence of photocurrent with illumination intensity at \( V = 0 \) V is presented in Figure 5f, by which a responsivity of 0.028 A W\(^{-1}\), corresponding to EQE = 7.8% was extracted. Considering that the tri-layer PHJ has significant absorption in the range of 350–850 nm, we further investigated the photoresponse of the device to illumination with different wavelengths. Figure 5g,h shows the \( R, \) EQE, and \( D* \) of the devices as functions of the wavelength of the incident light, respectively. Again, the \( D* \) values were estimated by extracting the noise current from the noise spectra density obtained by FFT of dark current, and thus may be relatively accurate (see Figure S14, Supporting Information). These results illustrate the photodiodes possess broad range photoresponse from ultraviolet to NIR. In addition, the temporal response of a photodetector is characterized by rise and fall times of the photocurrent, which are defined as the times taken for a photodetector to reach 90% and drop to 10% of steady-state values, respectively, as indicated in Figure 5g. The device shows good stability during repeated cycles of measurements and exhibits a rise time of 43.5 ms and a fall time of 65.9 ms.

3. Conclusion

To conclude, we have demonstrated the feasibility of fabricating solution-processed PHJs by combining OSCs with CsPbBr\(_3\) QDs. Thanks to the unique solubility and wetting properties of CsPbBr\(_3\) QDs, bilayer (PQD/OSC) and tri-layer (OSC/PQD/OSC) PHJs can be easily manufactured by solution process, ensuring the low-cost and large-scale production. Moreover, we show the promising applications of these PHJs for high-performance photodetectors. The phototransistors based on PQD/PDVT-10 PHJs exhibit a high responsivity of 1.64 × 10\(^4\) A W\(^{-1}\), detectivity approaching 3.17 × 10\(^{12}\) Jones, and a large photosensitivity over 5.33 × 10\(^7\). Detailed analysis reveals that such high phototransistor performance is ascribed to the PHJs, which lead to efficient charge generation in PQDs, charge dissociation at the heterojunction interface, charge transport in PDVT-10, and meanwhile photogating effect. Furthermore, the tri-layer PDVT-10/PQD/Y6 PHJs are fabricated and used to construct self-powered photodiodes, which exhibit broad range photoresponse due to the designed energy level alignments and combined absorption of the three component layers. These results show the possibility to combine various existing solution-processed polymers and small molecules with CsPbBr\(_3\) QDs to obtain PHJs for broadband and self-power photodetectors.

4. Experimental Section

Materials: Some of the CsPbBr\(_3\) QDs and semiconductors (PDVT-10\(^{21}\) and N2200\(^{31}\)) used in this work were synthesized according to literatures while others were purchased from companies. Chlorobenzene (99.8%, Sigma), ethanol (99%, Sinopharm), isopropyl alcohol (99%, Sinopharm), acetone (99%, Sinopharm), and hexane (99%, Sinopharm) were all used as received without further purification. The CsPbBr\(_3\) QDs were dissolved in \( n \)-hexane, and all other semiconductor materials and dopants were dissolved in chlorobenzene.

Fabrication of Phototransistors: In this work, bottom-gate, bottom-contact organic phototransistors were fabricated. Highly doped silicon wafers (0.001 Ω cm\(^{-1}\)) with 300 nm of thermally grown SiO\(_2\) were used as substrates. Standard lithography procedures were used to pattern the wafers with Au electrodes of 30 nm using 3 nm of Cr as an adhesion layer. The substrates were ultrasonically cleaned in deionized water, acetone, isopropyl alcohol each for 3 min, and blown dry by nitrogen gas, and further treated by UV–ozone in the air for 15 min. The CsPbBr\(_3\) QDs solution was spin-coated on the substrate surface at 2000 rpm for 20 s and then annealed at 100 °C for 10 min to remove the residual solvent in a nitrogen glovebox. To fabricate bilayer organic phototransistors, the OSC films were deposited on the CsPbBr\(_3\) QDs film by spin-coating at 1500 rpm for 20 s, following which the devices were annealed at 100 °C for 10 min. The channel length and the width of the fabricated devices are 40 μm and 1000 μm, respectively.

Fabrication of Photodiodes: The ITO substrates were ultrasonically cleaned in deionized water, acetone, and isopropyl alcohol each for 15 min, and blown dry by nitrogen gas, and further treated by UV–ozone in the air for 15 min. PEDOT:PSS was spin-coated on ITO under 3000 rpm for 60 s and 150 °C for 15 min in air. The PDVT-10 (5 mg mL\(^{-1}\)) films were deposited on the PEDOT:PSS film by spin-coating at 1500 rpm for 20 s, followed by annealing on hotplate at 150 °C for 5 min in glove box. Then, the CsPbBr\(_3\) QDs solution was spin-coated on the PDVT-10 films at 2000 rpm for 20 s and then annealed at 100 °C for 10 min. After that, Y6 (15 mg mL\(^{-1}\)) was spin-coated (1500 rpm for 20 s) on top of the CsPbBr\(_3\) QDs film and dried at 100 °C for 10 min. Finally, 100 nm-thick Al film was thermally evaporated on top to prepare the top electrode.

Device Characterization: The UV–vis–NIR absorption spectra of solution samples were carried out with UV-3600PLUS (SHIMADZU), and the film morphologies were characterized by Park XE-7 AFM. The cross-section SEM images were characterized by a Zeiss 500 with the extra high tension of 10 kV. TEM measurements were performed by a Tecnai G2 F20 S-Twin system operated at 200 kV. The electrical current of the devices was measured by an Agilent B2912A source meter with a probe station located in glove box. The temperature measurements of field-effect transistors were done in a Lakeshore TTPX probe station.

Steady-state PL spectra were measured using the same confocal microscope but with 510 nm continuous-wave laser as the excitation. TRPL experiments were performed using a confocal microscope (WITec, alpha-300) as the collect device, and the emission signal was reflected into a streak camera (C10910, Hamamatsu) by Ag mirrors. The laser beam was focused on to the sample with a spot diameter of ≈3 μm from the top by an objective lens (50X, Zeiss, 0.75 NA), while PL emission was collected by the same objective lens.

Evaluation of Photodetector Performance: Generally, three important figure-of-merits were characterized to quantitatively evaluate the performance of photodetectors: responsivity (\( R \)), specific detectivity (\( D* \)), and photosensitivity (\( P \)). \( R \) is used to identify the capability of photoelectric conversion of photodetectors, which can be expressed as \( R = \frac{I_{light} - I_{dark}}{S} \), where \( I_{light} \) and \( I_{dark} \) represent the current under illumination and in dark conditions, respectively. \( P_{opt} \) is the incident light power intensity, and \( S \) is the effective active area of the device. EQE is correlated with \( R \) by equation: \( EQE = \frac{R}{S} \cdot \frac{hc}{\lambda} \), where \( \lambda \) is the wavelength of incident light. The EQE spectra were obtained by the Enli Technology EQE measurement system with a chopper of 210 Hz. \( D* \) represents the ability of a photodetector to detect weak light signal; the higher the specific detectivity, the stronger the ability of the device to detect low-intensity light. \( D* \) values were estimated by the formula: \( D* = \frac{\lambda}{S} \sqrt{\frac{P_{opt}}{\lambda_{iso}}} \), where \( \lambda_{iso} \) is the noise current, \( \Delta \lambda \) is the bandwidth (assumed to be 1 Hz in this work). \( P \) provides valuable information on how well the device functions as a photodetector and is defined as the signal-to-noise ratio: \( P = \frac{I_{light}}{\lambda_{iso}} \).

Statistical Analysis: All experiments were performed at least twice to confirm the reproducibility of the results. The device performance data shown in the figures are representative data of devices with optimal performance instead of the average values of a number of devices. All directly measured data are presented without pre-processing, and the extracted performance parameters were obtained as described above. The statistic-
cal data shown in the inset of Figure 1c were obtained by collecting the size of 50 CsPbBr$_3$ QDs shown in the SEM image. Statistical analysis was performed using a software of OriginPro, version 2018c.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

K.C. and X.Z. contributed equally to this work. K.C. fabricated devices and characterized device performance, and performed morphology/structure characterizations. X.Z., J.Y., and W.M. provided help with synthesis of CsPbBr$_3$ QDs and performed part of the material characterizations. P.-A.C., J.G., Y.C., X.Q., and Y.L. provided help with device characterizations. Y.L. performed AFM characterizations. H.C. synthesized PDVT-10 and N2200 semiconductors. Z.Z. helped with absorption measurements. K.C. and X.Z. contributed equally to this work. K.C. fabricated devices and characterized device performance, and performed morphology/structure characterizations. X.Z., J.Y., and W.M. provided help with synthesis of CsPbBr$_3$ QDs and performed part of the material characterizations. P.-A.C., J.G., Y.C., X.Q., and Y.L. provided help with device characterizations. Y.L. performed AFM characterizations. H.C. synthesized PDVT-10 and N2200 semiconductors. Z.Z. helped with absorption measurements. M.H., X.W., and L.L. provided help with PL and TRPL measurements. T.-Q.N. and Y.H. conceived the idea and supervised the project. K.C., T.-Q.N., and Y.H. wrote the manuscript. All the authors revised and approved the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

CsPbBr$_3$ quantum dots, organic semiconductors, photodetectors, planar heterojunctions

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