Integrated Perovskite/Bulk-Heterojunction toward Efficient Solar Cells

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ABSTRACT: We successfully demonstrated an integrated perovskite/bulk-heterojunction (BHJ) photovoltaic device for efficient light harvesting and energy conversion. Our device efficiently integrated two photovoltaic layers, namely a perovskite film and organic BHJ film, into the device. The device structure is ITO/TiO2/perovskite/BHJ/MoO3/Ag. A wide bandgap small molecule DORST-TBDT was used as donor in the BHJ film, and a power conversion efficiency (PCE) of 14.3% was achieved in the integrated device with a high short circuit current density (JSC) of 21.2 mA cm⁻². The higher JSC as compared to that of the traditional perovskite/HTL (hole transporting layer) device (19.3 mA cm⁻²) indicates that the BHJ film absorbs light and contributes to the current density of the device. Our result further suggests that the HTL in traditional perovskite solar cell, even with good light absorption capability, cannot contribute to the overall device photocurrent, unless this HTL becomes a BHJ layer (by adding electron transporting material like PC71BM).

KEYWORDS: perovskite, photovoltaic, bulk heterojunction, photoresponse, carrier recombination

Recently, hybrid metal halide perovskites, such as CH₃NH₃PbI₃ and CH₃NH₃PbI₃·CL, with three-dimensional structures, have been used as efficient light absorbers for solar cells and shown high performance due to its direct bandgap, large absorption coefficient, long exciton diffusion lengths and very high charge carrier mobility. In 2009, Miyasaka and co-workers pioneered the first photovoltaic results for CH₃NH₃PbI₃ based perovskite with power conversion efficiency (PCE) of 3.8%. In 2012, Gratzel and Park et al. used CH₃NH₃PbI₃ as a light harvester in combination with the 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) hole transport materials on mesoporous TiO₂, which led to a PCE of up to 9.7%. In the past two years, the PCE of larger than 15% has been reported by different groups as new materials and engineering process improved. The quickly increased PCE makes perovskite solar cells promising as highly efficient and cost-effective solar energy technologies. Thus, perovskite-based solar cells have been predicted as the “next big thing in photovoltaics”.

The current hybrid lead halide perovskite materials such as CH₃NH₃PbI₃ or CH₃NH₃PbI₃·CL shows an onset light response at ~800 nm due to its optical band gap of 1.55 eV, which leaves a wide spectral range in the near-infrared unused, and thus hinders the efficient harvest of photon and the further improvement of PCE. One important strategy to further enhance the photovoltaic performance of perovskite solar cells lies in full utilization of the solar light below 800 nm or broadening the light absorption to the near-infrared spectrum region. Although the photoresponse up to 1060 nm has been reached using a hybrid tin halide based perovskite as a light absorber, the efficiency was compromised by the poor Sn(II) stability and a low open circuit voltage (VOC). An alternative approach could be the combination of materials with similar absorbing spectra or complementary absorbing materials with a broad spectral coverage using the tandem cells structure. Series-connected tandem structure consisting of two or more subcells with same or complementary absorption has been considered as a promising approach to enhance photovoltaic efficiency. The advantages are to reduce the thermalization loss and to achieve broad absorption. The VOC of tandem cell equals to the sum of those of individual subcells, and the short circuit current density (JSC) is limited by the subcell that delivers the smaller JSC. In order to reach maximal power output, JSC generated by each subcell should be equal or similar to prevent the accumulation of photogenerated charges. As for parallel connected tandem devices, the coupling of J-V characteristics of the subcells results in photocurrent add-up, whereas the VOC lies in between. However, in either serial- or parallel-connected tandem structures, physical isolation of the subcells is needed, thus making device fabrication complicated. With these disadvantages in mind, interlayer free parallel tandem cells are an attractive option because such devices do not require a recombination layer and are much

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easier to manufacture. However, the materials suitable for efficient interlayer-free parallel tandem devices are very limited and successful demonstration of such devices have been scarce. However, the favorable properties of perovskite, as discussed below, make the high performance of this kind of tandem device possible.

Conjugated small molecules and polymers have been widely used as light absorbers in bulk-heterojunction (BHJ) organic solar cells that have shown high performance.\textsuperscript{18,22−24} Intimate contact between donor and acceptor molecules in a blended film facilitates efficient charge generation, and the formation of percolation paths for electrons and holes allows for efficient charge extraction from the bulk film to metal electrodes. Recently, these conjugated organic materials have been used as HTLs in perovskite solar cells.\textsuperscript{25−30} However, it is still not clear whether absorption of HTL contributes to the photocurrent,\textsuperscript{25−27} and the working mechanism of these devices is not completely understood. Here, we successfully demonstrated an integrated perovskite/BHJ device structure based on perovskite solar cells and organic BHJ solar cells for efficient light harvesting. Because both the perovskite and the organic BHJ films can deliver photocurrent in the device after absorbing light, such a structure can be regarded as an interlayer free parallel tandem connection of two subcells. The integrated device using DOR3T-TBDT/PC\textsubscript{71}BM BHJ film, which has shown good performance in organic solar cells,\textsuperscript{19} shows a PCE of 14.3\%, coupled with a high $J_{SC}$ of 21.2 mA cm$^{-2}$. We further confirmed this efficient integrated device structure by using a low band gap polymer as donor in BHJ film and an efficiency of 12\% was achieved. The EQE data shows that the photoresponse extends to 900 nm, whereas the external quantum efficiency (EQE) data of perovskite/polymer-HTL device shown no photoreponse larger than 800 nm, suggesting that polymer HTL with good light absorption in UV−vis−NIR region will not contribute photocurrent. Our results indicate that neat small molecule or polymer HTL used in perovskite solar cells does not contribute photocurrent. By blending with PC\textsubscript{71}BM acceptor, the BHJ forms an integrated device structure with perovskite, delivering higher photocurrent and, thus, higher PCE.

The integrated perovskite/BHJ device structure is shown in Figure 1a. The perovskite layer absorbs UV−vis light and BHJ layer absorbs the light that not been fully absorbed by perovskite or near-infrared (NIR) light. The proposed charge generation and transport mechanism of this integrated device is shown in Figure 1c. The design of this kind of integrated perovskite/BHJ device are based on the following reasons: (1) the organometal halide perovskites are direct band gap materials and the exciton can be easily separated due to its weak binding energy;\textsuperscript{31} (2) the perovskite materials have ambipolar transporting properties, exhibit both high electron and hole mobility, and charge recombination loss is minimal in perovskite bulk films;\textsuperscript{32} (3) the perovskite and organic BHJs are fabricated using orthogonal solvents, allowing sequential deposition of the multilayer structures; (4) the small molecules or polymers used in BHJ film can be a useful hole transport channel, thus holes generated in the perovskite film can transport through the small molecule or polymer network and collect by MoO\textsubscript{3}/Ag anode; (5) the electron that is generated from the separated exciton at the donor−acceptor interface in the BHJ film can transport through electron acceptor materials (such as PC\textsubscript{71}BM) network to the perovskite and be collected.
by TiO2/ITO cathode due to the high electron mobility of perovskite film.

The energy diagram and the cross-sectional SEM image for the integrated perovskite/DOR3T-TBDT:PC71BM device are shown in Figure 1b and d. The photocurrent should be produced in parallel for integrated devices by both perovskite layer and BHJ layer as described above. The BHJ layer is seen to uniformly cap the perovskite layer from the SEM image, indicating that the integrated device configuration is a well-defined layer-by-layer structure. We also characterized the surface morphology using atomic force microscope (AFM) in tapping mode (5 μm × 5 μm) (Figure S1, Supporting Information). The roughness was reduced from 40 to 15 nm after spin coating a DOR3T-TBDT:PC71BM BHJ layer on perovskite.

In Figure 2a and c, we show the current density−voltage (J−V) curves of the integrated perovskite/BHJ solar cells as well as single junction perovskite solar cells using different HTLs. The detailed solar cell performance parameters are summarized in Table 1. As shown in Figure 2 and Table 1, both integrated devices show higher performance than that of the pristine single junction perovskite cell using different HTLs mainly due to the increased JSC. The reference cell with DOR3T-TBDT HTL shows JSC, VOC and fill factor (FF) of 19.3 mA cm−2, 0.98 V, and 72.9, respectively, leading to a PCE of 13.8%. The integrated perovskite/(DOR3T-TBDT:PC71BM, 1:0.8) device gives a PCE of 14.3%, with a JSC of 21.2 mA cm−2, a VOC of 0.99 V, and an FF of 67.9%. Accordingly, the improved performance mainly stems from the increased values of JSC and the maintained high VOC at the same time. Yet it is difficult to differentiate the photocurrent contribution from DOR3T-TBDT HTL or DOR3T-TBDT/PC71BM BHJ film, since its absorption overlaps with that of perovskite. Therefore, as a control, we further introduced a low bandgap polymer, PBDTT-SeDPP, as the HTL for single junction perovskite device and donor in BHJ film. The energy level of PBDTT-SeDPP based device is shown in Figure S2 (Supporting Information). The device using PBDTT-SeDPP as HTL shows a JSC of 18.1 mA cm−2, with a VOC of 0.89 V, an FF of 60.4%, and a PCE of 9.7%. The BHJ film of PBDTT-SeDPP/PC71BM with the blend ratio of 1:2 has shown PCE of 7.2% in organic solar cells.33 When using this BHJ film in the integrated device, a PCE of 12.0% was achieved, combined with a VOC of 0.94 V, a high JSC of 20.6 mA cm−2, and an FF of 62.0%. Here, the polymer in BHJ acts as the HTL for perovskite subcell, and the perovskite layer plays a role to collect electrons from the BHJs. As a result, the increased JSC was observed, compared with that of the perovskite/polymer-HTL based device. In the latter device, the HTL also absorbs light but may not contribute to current density. However, in the former one, the excitons generated in the BHJ film can be separated in the blend layer and transported to the respective electrodes efficiently. The hypothesis was further confirmed by the related EQE and

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Table 1. Device Parameters for Perovskite Solar Cells Using Different HTLs and the Integrated Perovskite/BHJ Solar Cells.

“a”The BHJ film is DOR3T-TBDT:PC71BM (1:0.8, w:w) or PBDTT-SeDPP:PC71BM (1:2, w:w). “b”The blend film using PDMS as additive.
photoresponse data discussed below. Note that the $V_{OC}$ is slightly lower for the perovskite/(PBDTT-SeDPP)-HTL device than that of integrated device. The low $V_{OC}$ may ascribe to the low conductivity of PBDTT-SeDPP than that of PBDTT-SeDPP:PC71BM BHJ film.

It is obvious that the perovskite/HTL or integrated perovskite/BHJ devices using small molecule DOR3T-TBDT as HTL or donor in BHJ have shown better performance than those of polymer PBDTT-SeDPP based devices. One important role of small molecules or polymers in these devices is hole transport as discussed above. The better performance of DOR3T-TBDT based devices than those of PBDTT-SeDPP based devices may be ascribed to the improved packing structure of the conjugated small molecule DOR3T-TBDT film, thus benefiting charge transport. It should be noted that the representative perovskite/HTL and integrated perovskite/BHJ devices show hysteresis in the $J$--$V$ curves (Figure S3, Supporting Information), which are similar to those seen in typical perovskite devices.\textsuperscript{14,34,35} The detailed data is shown in Table S1 (Supporting Information).

For comparison, we further fabricated the photovoltaic devices without a MoO$_3$ layer. However, most perovskite/HTL based photovoltaic devices resulted in a short circuit. The integrated perovskite/BHJ devices showed better resistivity than those of perovskite/HTL based devices but still were inferior in performance due to the lower $V_{OC}$ and FF (Figure S4, Supporting Information). MoO$_3$ used in the devices served as a buffer between the HTL and Ag or BHJ and Ag electrode to protect the organic films from damage caused by Ag deposition as well as a layer to build the ohmic contact for hole extraction from the HTL or BHJ to the Ag electrode.\textsuperscript{36--38}

EQE curves of the optimized integrated perovskite/BHJ device as well as single junction perovskite devices using small molecule or low band gap polymer as HTLs under monochromatic light are shown in Figure 2b and d. The UV--vis--NIR spectra of different HTLs as well as the related BHJ films on glass/TiO$_2$/perovskite substrate were also included for comparison. Both small molecule and polymer have strong light absorption,\textsuperscript{19,33} confirming the possibility of its additional contribution for light harvesting. As shown in Figure 2b, both single junction devices using DOR3T-TBDT as HTL and integrated device show photocurrent response from 300 to 800 nm, which is consistent with their UV--vis--NIR spectra, a characteristic absorption band of perovskite film. As for the single junction device, a V-shaped valley was observed between 520 to 740 nm, which might be due to the light filtering of DOR3T-TBDT HTL. For the integrated device, the range between 520 to 740 nm flattened and the V-shaped valley disappeared, indicating the efficient photoresponse of DOR3T-TBDT:PC$_{71}$BM BHJ film, thus improving the photocurrent. Figure 2d shows UV--vis--NIR spectra of PBDTT-SeDPP or PBDTT-SeDPP:PC$_{71}$BM blend film on glass/TiO$_2$/perovskite substrate. In addition to the characteristic absorption band of perovskite, absorption band was further extended to 900 nm, which is attributed to absorption of PBDTT-SeDPP.\textsuperscript{33} As a reference, single junction perovskite solar cell using neat polymer as HTL was fabricated too. As shown in Figure 2d, in spite of similar absorption band in the NIR range, the photovoltaic device using PBDTT-SeDPP as HTL exhibited

![Figure 3](https://example.com/fig3.png)

**Figure 3.** Photoresponse of the perovskite devices using small molecule or polymer as HTL and integrated perovskite/BHJ devices under the pulse light (10 kHz) illumination of a 620 nm red LED or a 850 nm NIR LED. (a) and (b) Perovskite/HTL and perovskite/BHJ based devices at 620 nm light pulse illumination; (c) integrated perovskite/PBDTT-SeDPP:PC$_{71}$BM device at 620 and 850 nm light pulse illumination; (d) perovskite/PBDTT-SeDPP and integrated perovskite/PBDTT-SeDPP:PC$_{71}$BM devices at 850 nm light pulse illumination.
the onset EQE at $\sim$800 nm, consistent with the band gap of CH$_3$NH$_3$PbI$_3$X$_2$Cl$_x$. The result indicates that the low band gap polymer HTL has no contribution to photocurrent. At meantime, the integrated device using this low band gap polymer as donor in BHJ film shows improved photoresponse from 500 to 800 nm, and more importantly, a notable EQE response up to 900 nm. This confirms that the polymer BHJ film absorbs light and contributes to $J_{SC}$.

To further investigate the contribution of BHJ to the photocurrent of the integrated device, we carried out photoresponse measurements for our photovoltaic cells. Using rectangle pulse light to excite the photovoltaic cells, Figure 3 gives the response of the devices using different HTLs and the integrated perovskite/BHJ devices. The light pulse from monocolor LEDs has a rising and decay edge $\sim$100 ns, which is much shorter than the delay time we observed from the devices (see the Supporting Information for measurement details). The devices are illuminated with a mono color light pulse at either 620 or 850 nm. The 620 nm light mainly excites the perovskite layer, while the low bandgap polymer absorbs light at 850 nm.

As shown in Figure 3a and b, transient photocurrent signal under 620 nm light pulse exhibits a quick increase of the current density of the devices, associated with charge collection, and quick kinetics are observed for the perovskite solar cells using small molecule or polymer as HTL. On the other hand, the device current density of the devices increases slowly for the integrated device, indicative of slow charge collection. It is clear that after the light is switched off there is still a substantial amount of charges in the devices. We can see that the photocurrent decays slower for the integrated devices than that of single junction devices. On the one hand, the presence of PC$_{71}$BM may slow down charge collection due to the lower charge mobility in BHJ film. On the other hand, the photogenerated charges in BHJ are supposed to travel longer distance to reach the electrodes. So, the photocurrent decay of perovskite/DOR3T-TBDT:PC$_{71}$BM device is significantly longer than that of the reference perovskite cell using DOR3T-TBDT as HTL because the strong absorption of DOR3T-TBDT:PC$_{71}$BM blend film at 620 nm can be efficiently converted into free charges. Similarly, the integrated devices need longer time to reach the equilibrium state, as indicated at the initial stage of the photocurrent response shown in Figure 3a and b. Yet in the integrated perovskite/polymer-BHJ device, the photoresponse delay is not significant because the light absorption of the polymer at 620 nm is weak.

The integrated perovskite/polymer-BHJ device responds to both red and NIR light. Figure 3c shows that photoresponse of integrated perovskite/(PBDTT-SeDPP:PC$_{71}$BM) device is different with respect to different wavelength excitation. There is no photoresponse for the perovskite film when using 850 nm bias light pulse due to the onset absorption of perovskite is about 800 nm. When the low band gap polymer based device was illuminated with 850 nm bias light pulse, as shown in Figure 4d, we can see clearly that there is little photoresponse for the perovskite device using neat polymer film as HTL, whereas the integrated device shown obviously photoresponse. This is strong support that the small molecule or polymer HTL used in perovskite solar cells does not contribute photocurrent, whereas the integrated perovskite/BHJ solar cells have better light harvesting and contribute photocurrent.

To check the reproducibility of performance, photovoltaic parameters are compared using histograms obtained from 100
integrated perovskite/BHJ devices using DOR3T-TBDT/PC71BM as organic BHJ film shown in Figure 4. As can be seen from the results, the devices performed extremely well. The average PCE is 12.8%. As shown in Figure 3c, more than 80% of the integrated cells show PCE above 12%, whereas more than 40% show PCE above 13% under 1 sun conditions, indicating good reproducibility. The $V_{OC}$ values were highly reproducible and in excess of 0.95 V, and the average $J_{SC}$ was nearly 20.0 mA cm$^{-2}$. The PCE data obtained from the integrated devices shows a low standard deviation, which indicates that reproducible photovoltaic performance can be obtained for the device using integrated device structure. Both the reproducibility of the device fabrication procedure and the excellent PCEs are highly encouraging. Clearly, our results indicate that the integrated perovskite/BHJ devices are very efficient for the production of high-performance solar cells.

In order to understand losses due to the carrier recombination in the integrated perovskite/BHJ device, light intensity dependence of $J$–$V$ characteristics of the device using DOR3T-TBDT as donor in BHJ film have been measured under different incident light intensities ranging from 2.6 to 100 mW cm$^{-2}$ (from 0.026 to 1 sun). The $J$–$V$ curves are shown in Figure 5a. Figure 5b shows a linear relation of photocurrent on light intensity in a double logarithmic scale with a slope of 0.96, indicating no substantial space charge build-up in the integrated device and charge carrier losses in the absorber bulk are dominated by monomolecular recombination via defects and bimolecular recombination is a rather minor loss.\(^{39}\) Figure 5c gives $V_{OC}$ as a function of the logarithm of light intensity. We can see that $V_{OC}$ increases monotonically with light intensity, implying that trap-assisted Shockley–Read–Hall recombination is present.\(^{40}\) Figure 5d shows the FF as a function of illumination intensity for the integrated device. The increased FF of 73.1% was measured at 0.06 suns, indicating reduced recombination due to the decrease of free charge carrier concentration under low intensity of light irradiation. The results indicate that the perovskite and BHJ films are connected effectively due to the excellent ambipolar charge transport properties of perovskite.

In summary, we have developed and demonstrated an integrated perovskite/BHJ photovoltaic device by employing the perovskite and organic BHJ films as the planar layer for efficient light harvesting. The integrated device using DOR3T-TBDT/PC71BM as the BHJ layer shows a high efficiency of 14.3%. We have succeeded in harvesting energy in the NIR region by using a low bandgap polymer as donor in BHJ film and an efficiency of 12.0% was achieved. Notably, our integrated devices exhibit a photoresponse spanning the whole visible and infrared spectrum (up to 900 nm). In addition, our results indicate that the small molecule or polymer HTL used in perovskite solar cells does not contribute to the photocurrent generated by the device. That means the exciton formed in the HTL may not be separated in the perovskite/HTL interface or be collected by the electrode, which is not the same mechanism like the donor/acceptor interface in the organic solar cells. At the same time, we find a new way to harvest more light to make perovskite based solar cells more efficient. Higher photocurrent density and PCE would be expected by further device optimization to minimize the charge recombination and maximize the light harvesting capacity. Our findings open up new opportunities to efficiently harvest more solar light (from UV–vis to IR) for the fabrication of solution processed photovoltaic cells with high...
PCE that matches or even exceeds those of today’s best thin film photovoltaic devices.

**REFERENCES**