

High Short-circuit Current Density via Integrating the Perovskite and Ternary Organic Bulk Heterojunction

Wei Chen,^{†,‡,#} Huiliang Sun,^{†,#} Qin Hu,^{§,⊥,#} Aleksandra B. Djurišić,^{*,‡} Thomas P. Russell,^{§,⊥} Xugang Guo^{*,†} and Zhubing He^{*,†}

[†]Department of Materials Science and Engineering, Southern University of Science and Technology, No. 1088, Xueyuan Rd., Shenzhen, 518055, Guangdong, P.R. China.

[‡]Department of Physics, The University of Hong Kong, Pokfulam, Hong Kong SAR.

[§]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States.

[⊥]Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, United States.

Corresponding Author

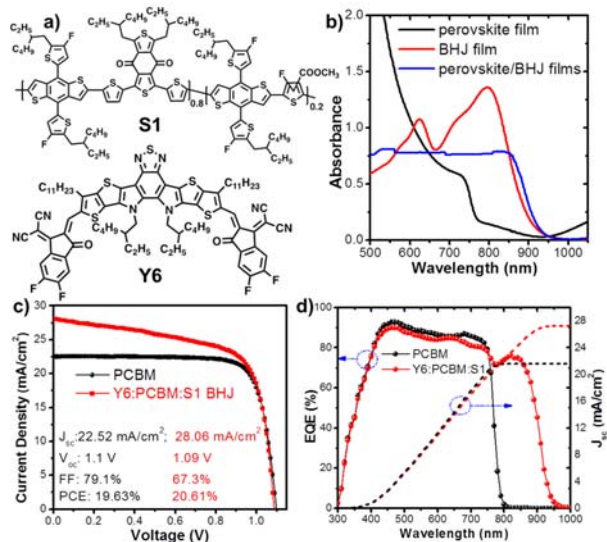
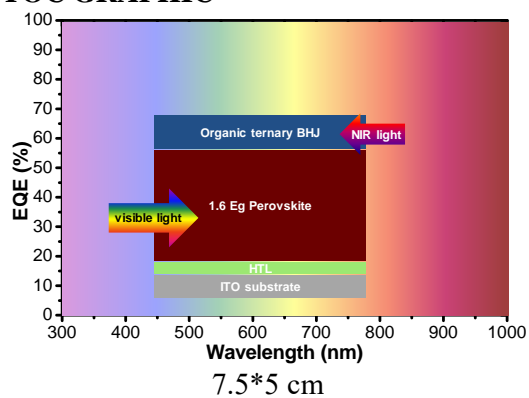
*Email: hezb@sustech.edu.cn (Z.H.)

*Email: guoxg@sustech.edu.cn (X.G.)

*Email: dalek@hku.hk (A.B.D.)

Abstract: We demonstrate a record short-circuit current density (28.06 mA/cm^2) in a single junction perovskite solar cell with a 1.6 eV bandgap absorber. We achieve this by integrating ternary organic bulk heterojunction structure into perovskite top layer to extend the photoresponse to near-infrared region.

TOC GRAPHIC



8.5*7.5 cm

Metal halide perovskite solar cells (PSCs) are one of most promising next generation photovoltaics (PV) due to the excellent optoelectronic properties and record-breaking power conversion efficiencies (PCE), close to the single-junction Shockley–Queisser (SQ) radiative efficiency limit.¹⁻² Currently, the most efficient PSCs typically use 3D perovskites with a bandgap of 1.5-1.6 eV,²⁻³ which restricts the light-harvesting range to mainly the visible-light region (300-800 nm), resulting in large solar radiation losses in the near-infrared (NIR)/infrared (IR) region. One possible approach to mitigate this is to develop low-bandgap (~ 1.2 - 1.3 eV) perovskite absorbers via composite engineering.⁴ However, the device efficiency of low bandgap perovskites is far lower than that of the commonly used perovskites which have a wider bandgap ($< 20\%$).⁴ In addition to reducing the bandgap, using a tandem configuration with other thin film PV technologies, such as crystalline silicon (c-Si) and copper indium gallium diselenide (CIGS), can extend the photoresponse to some extent.⁵⁻⁶ Nevertheless, highly complicated fabrication processes for tandem solar cells significantly increases the cost and it would likely not be compatible with large scale application. A much simpler and more feasible strategy is to integrate low bandgap semiconductors into charge transport layers (CTL) in single-junction PSCs to form a bulk-heterojunction (BHJ) structure,⁷⁻⁸ which is frequently employed in organic solar cells. In such integrated devices, BHJ layers function as absorbers of the NIR/IR light and charge transporters.⁹ However, though single-junction PSCs with low bandgap CTLs or BHJ layers demonstrate improved response of NIR light, they have not shown comparable efficiency to the first class single-junction PSCs.⁹

In this work, we show significant improvement in the NIR light response of 1.6 eV bandgap perovskite solar cells using a ternary organic BHJ structure as the electron transport layer (ETL). The champion PSC with perovskite/BHJ structure

shows a record short-circuit current density (J_{sc}) over 28 mA/cm², and a PCE of 20.6% under 100 mW/cm² AM1.5G solar irradiation. The extremely high J_{sc} is achieved due to the high photoresponse of BHJ layer in the NIR region. To the best of our knowledge, this is the first time that single-junction PSCs with 1.6 eV bandgap perovskite absorber shows a J_{sc} exceeding the corresponding SQ radiative limit.

We fabricate inverted perovskite solar cells where the PTAA is used as the hole transport layer (HTL),¹⁰ and 1.6 eV bandgap CsFAMA mixed cation perovskite as the absorber (see details in Supporting Information).¹¹ For a control device, PCBM is used as the ETL, as described previously.¹¹ For devices with BHJ ETL, two efficient organic semiconductors (molecular structures shown in **Figure 1a**), one p-type polymer, S1, and one n-type small molecule, Y6, with record high efficiencies in organic solar cells,¹²⁻¹³ are used with PCBM to form ternary BHJ layers on top of the perovskite films. As shown in the **Figure 1b**, the 1.6 eV bandgap perovskite films showed an absorption edge at ~ 775 nm which is consistent with the optical bandgap. We can find that the absorption of the BHJ film extends up to ~980 nm. As a result, combining the perovskite with the BHJ film, the absorption can cover a wide spectral range, from ~ 300 to 980 nm. We obtained a PCE of 19.63 % for the optimal control device, with a J_{sc} of 22.52 mA/cm², an open-circuit voltage (V_{oc}) of 1.1 V and fill factor (FF) of 79.1% (**Figure 1c**). The external quantum efficiency (EQE) for the control device has a similar photoresponse to the absorption spectrum of perovskites, and the integrated J_{sc} from EQE is calculated to be 21.57 mA/cm² (**Figure 1d**), where underestimation can be attributed to the spectral mismatch factor. To improve the IR photoresponse, we initially mixed Y6 (9.5 mg/ml in CF) with PCBM (1:1 weight ratio), and we achieved an optimal device PCE of 19.62 %, very similar to the PCBM control device, but with a slightly higher J_{sc} of 22.75 mA/cm² (**Figure S1**). From the

EQE spectrum, we can see obvious photoresponse in the region from 800-980 nm, a result of the absorption of Y6 in the NIR region. However, the overall improvement in the J_{sc} is negligible due to the large losses between 550 and 760 nm (**Figure S1**). The inefficient charge separation and transfer between Y6 and PCBM may contribute to large losses of photogenerated charges from Y6. To address this problem, we introduce a p-type polymer S1 into the BHJ structure, making a ternary system to provide an efficient driving force for charge separation and hole transport.¹² The optimal J_{sc} exceeds 28 mA/cm² with a PCE of 20.61% for the Y6:PCBM:S1 (weight ratio: 1:1:0.5) ternary system (**Figure 1c**), significantly outperforming the PCBM control device (**Figure 1c,d** and **Figure S2**). As shown in the EQE spectra in **Figure 1d**, a maximum EQE response of 76% at 820 nm, and an average EQE over 50 % between 770 and 950 nm were obtained for perovskite/ternary BHJ devices, and a J_{sc} of 27.19 mA/cm² was determined from the EQE (the screenshot of EQE measurement is shown in **Figure S3**). We can calculate that the perovskite/BHJ structure contributes additional 5.65 mA/cm² photocurrent density to the PSCs as compared with the control device. The high charge separation efficiency and very low energy losses in the Y6:S1 system may contribute to the record high EQE for the perovskite/ternary BHJ system.¹² It is obvious that the FF for the perovskite/BHJ device is lower than that of the PCBM control device (**Figure S2**), possibly due to large recombination losses at the perovskite/BHJ interface. Optimization of the composition of the BHJ system is expected to further improve the PCE and is currently being investigated.

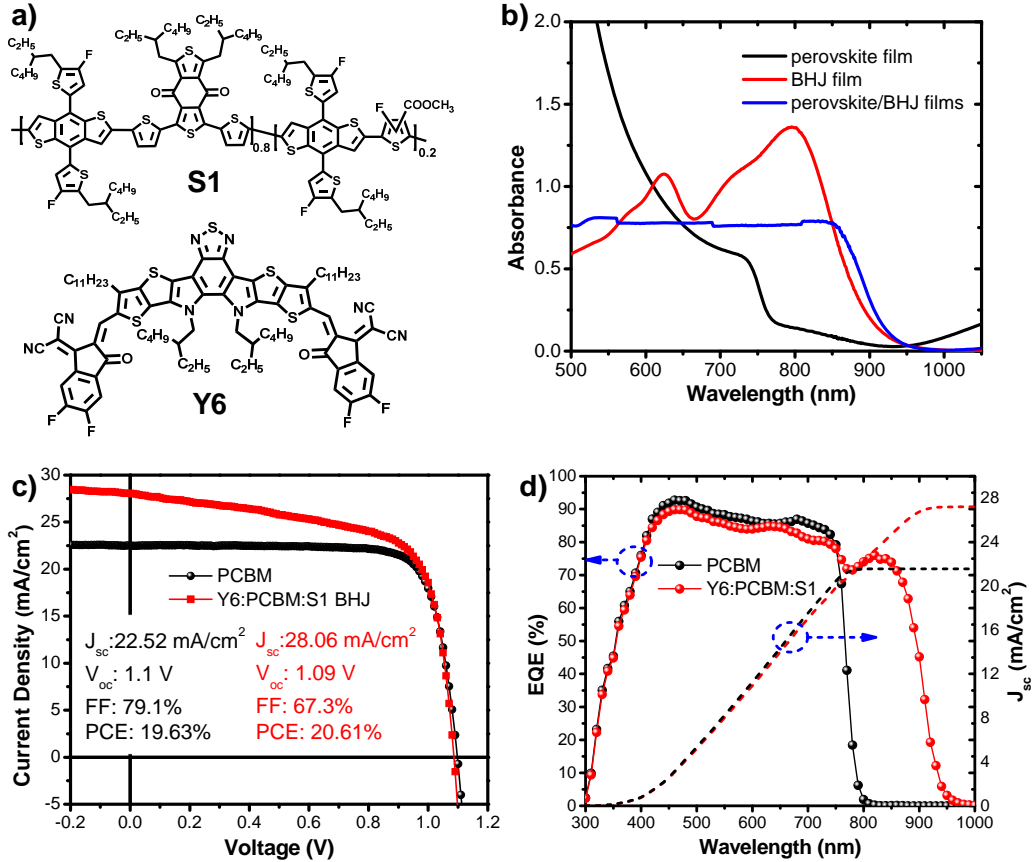


Figure 1. a) Chemical structure of materials in the bulk heterojunction (BHJ) films; b) Absorption spectra of the different layers; c) J-V characteristics of optimal inverted PSC with PCBM and BHJ ETL. The aperture area of the device is 7.5 mm², calibrated by an optical mask; d) External quantum efficiency (EQE) spectra for the devices shown in (a). The integrated short-circuit current density from EQE are 21.57 and 27.19 mA/cm², respectively.

In summary, we have achieved a record high J_{sc} (28.06 mA/cm²) in single junction PSCs with 1.6 eV bandgap of the perovskite layer by integrating the perovskite with S1:Y6:PCBM ternary BHJ layer to significantly extend the NIR photoresponse up to 980 nm. Our results demonstrate the perovskite/organic BHJ system has huge potential of breaking the single-junction SQ efficiency limits.

ASSOCIATED CONTENT

Supporting Information:

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/XXXXXX.

Materials, experimental details, and additional characterization

AUTHOR INFORMATION

Corresponding authors

*Email: hezb@sustech.edu.cn (Z.H.)

*Email: guoxg@sustech.edu.cn (X.G.)

*Email: dalek@hku.hk (A.B.D.)

Author Contributions

#W.C., H.S. and Q.H. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Yusoff, A. R.; Nazeeruddin, M. K. Organohalide Lead Perovskites for Photovoltaic Applications. *J. Phys. Chem. Lett.* **2016**, *7*, 851-866.
- (2) Jiang, Q., et al. Surface passivation of perovskite film for efficient solar cells. *Nat. Photonics* **2019**, *13*, 460-466.
- (3) Luo, D., et al. Enhanced photovoltage for inverted planar heterojunction perovskite solar cells. *Science* **2018**, *360*, 1442-1446.
- (4) Jiang, T., et al. Power Conversion Efficiency Enhancement of Low-Bandgap Mixed Pb–Sn Perovskite Solar Cells by Improved Interfacial Charge Transfer. *ACS Energy Lett.* **2019**, *4*, 1784-1790.
- (5) Bush, K. A., et al. Minimizing Current and Voltage Losses to Reach 25% Efficient Monolithic Two-Terminal Perovskite–Silicon Tandem Solar Cells. *ACS Energy Lett.* **2018**, *3*, 2173-2180.

- (6) Guchhait, A., et al. Over 20% Efficient CIGS–Perovskite Tandem Solar Cells. *ACS Energy Lett.* **2017**, *2*, 807-812.
- (7) Dong, S., et al. Unraveling the High Open Circuit Voltage and High Performance of Integrated Perovskite/Organic Bulk-Heterojunction Solar Cells. *Nano Lett.* **2017**, *17*, 5140-5147.
- (8) Kim, J., et al. High-Performance Integrated Perovskite and Organic Solar Cells with Enhanced Fill Factors and Near-Infrared Harvesting. *Adv. Mater.* **2016**, *28*, 3159-3165.
- (9) Liu, Y.; Chen, Y. Integrated Perovskite/Bulk-Heterojunction Organic Solar Cells. *Adv. Mater.* **2019**, 1805843.
- (10) Stolterfoht, M., et al. Visualization and suppression of interfacial recombination for high-efficiency large-area pin perovskite solar cells. *Nat. Energy* **2018**, *3*, 847-854.
- (11) Chen, W., et al. Alkali Chlorides for the Suppression of the Interfacial Recombination in Inverted Planar Perovskite Solar Cells. *Adv. Engery Mater.* **2019**, *9*, 1803872.
- (12) Sun, H., et al. A monothiophene unit incorporating both fluoro and ester substitution enabling high-performance donor polymers for non-fullerene solar cells with 16.4% efficiency. *Energ Environ. Sci.* **2019**, 10.1039/c1039ee01890e.
- (13) Yuan, J., et al. Single-Junction Organic Solar Cell with over 15% Efficiency Using Fused-Ring Acceptor with Electron-Deficient Core. *Joule* **2019**, *3*, 1140-1151.