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COMMUNICATION

## Simple Planar Perovskite Solar Cells with a Dopant-free Benzodithiophene Conjugated Polymer as Hole Transporting Material

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**Dopant-free poly[(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b;4,5-b']dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiophene)-2,6-diyl] (PBDTTT-C) polymer is used as hole transporting material (HTM) in an electron transporting material (ETM) free planar perovskites solar cells (PSCs). The devices with PBDTTT-C HTM show higher power conversion efficiency (PCE=9.95%) than the devices with P3HT HTM (PCE=6.17%) with enhanced short circuit current density ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ) and fill factor (FF) in simple device configuration (ITO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PBDTTT-C/MoO<sub>3</sub>/Ag), due to the suitable energy level, better carrier mobility and lower interfacial charge recombination.**

Organometal halide perovskites (MAPbX<sub>3</sub> or FAPbX<sub>3</sub>) based solar cells have received great attention for their remarkably high power conversion efficiency (PCE).<sup>1-3</sup> Various kinds of perovskites solar cells (PSCs) device configurations are used to optimize device performances, including mesoporous metal oxide-based PSCs, mesosuperstructured PSCs and planar heterojunction PSCs.<sup>4</sup> The PCE of PSCs based on different structures has rapidly increased from 3.8% to 20.1%.<sup>5-17</sup> Recently, planar PSCs become popular for their simple fabrication process, cost-effective and easy industrialization production. Generally, a typical planar device is composed of a n-type metal oxide (e.g. TiO<sub>2</sub>, ZnO) electron transport material

(ETM) coated on transparent conductive oxide (FTO or ITO) glass substrates, organometal halide perovskite active layer, hole transport material (HTM) and metal back electrode. In other words, it is based on the structure of ITO or FTO/ETM/perovskite/HTM/metal electrode structure.<sup>11, 13, 17</sup> The most used ETM n-type metal oxide (e.g. TiO<sub>2</sub>, ZnO) need high-temperature thermal treatment (normally over 450 °C) to crystalize, which restricts them from devices with the flexible polymer substrates. Recently, a compact layer free PSCs with 13.5% PCE has been reported.<sup>18</sup> This device configuration is a good choice for low temperature-processed low-cost PSCs.

Despite the rapid development of different types of device structures for improving PCE, the evolution of HTM is relatively limited. In particular, spiro-OMeTAD is the model material in small molecular HTM, and P3HT (Fig.1b) is the most used polymer HTM.<sup>19-22</sup> Spiro-OMeTAD were synthesized by a tedious route which made future commercialization difficult. Furthermore, it needs dopant to improve its transport performance,<sup>23</sup> which complicates the device fabrication process. PSCs employing P3HT as HTM showed moderate performances due to its low carrier mobility and the mismatch energy level. Therefore, new HTM with higher carrier mobility, good solubility for solution processing and compatible highest occupied molecular orbital (HOMO) energy level to perovskites, is needed for high performance low cost PSCs.

In this work, we found the well-known semiconducting benzodithiophene polymer, poly[(4,8-bis-(2-ethylhexyloxy)benzo[1,2-b;4,5-b']di-thiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]th-iopene)-2,6-diyl] (PBDTTT-C, Fig.1a) with good stability, high charge-carrier mobility, and a suitable HOMO energy level, is a potential HTM for PSCs. Simple planar devices were fabricated with ITO/perovskite/PBDTTT-C (or P3HT control devices)/MoO<sub>3</sub>/Ag structure (Fig 1d). The energy level diagram of materials used in the devices is shown in Fig.1c, which values are extracted from literatures.<sup>18, 24</sup> Without the inorganic ETM (e.g. TiO<sub>2</sub>, ZnO), the PSCs can be processed at only 100 °C in this work. The PSCs with PBDTTT-C HTM (ITO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PBDTTT-C/MoO<sub>3</sub>/Ag) show higher power

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conversion efficiency (9.95%) than the devices based on P3HT (6.17%). This work shows that PBDTTT-C is a promising HTM for low cost solution-processed PSCs. Proof concept device with TiO<sub>2</sub> and P3HT as ETM and HTM (configuration: FTO/c-TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT/MoO<sub>3</sub>/Ag) shows PCE around 7.52%. (Supporting information Fig. S1)

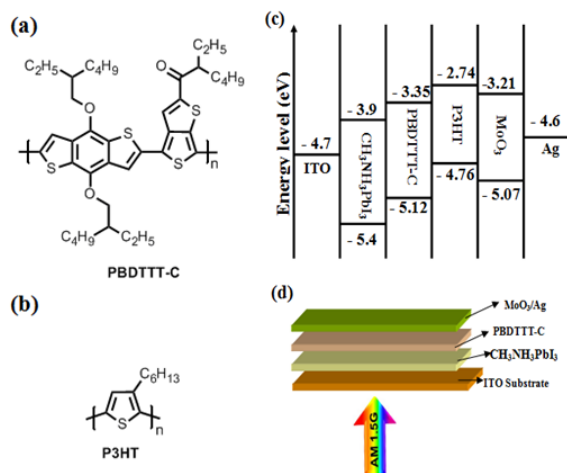


Fig. 1 (a,b) Molecular structure of PBDTTT-C and P3HT; (c) energy level diagram of the materials used in the PSCs; (d) PSCs device configuration.

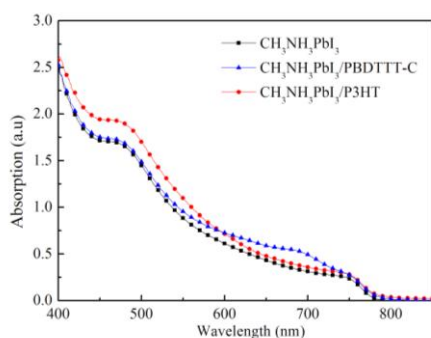


Fig. 2 UV-visible absorption spectra of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PBDTTT-C and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT thin films

Fig. 2 shows the UV-visible absorption spectra of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PBDTTT-C, and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT thin films on ITO glass. Pristine CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film shows wide absorption in 300–800 nm which is consistent with the previous report.<sup>25</sup> For CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PBDTTT-C or CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT thin film, the enhanced absorption in 690 or 450–600 nm, compared with the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> pristine film, is due to the PBDTTT-C or P3HT polymer absorption.<sup>26–27</sup>

Fig. 3(a) shows the current density–voltage ( $J$ – $V$ ) curves of the PSCs with different HTM (P3HT or PBDTTT-C) under AM 1.5G, 100 mW cm<sup>-2</sup>, with the scan rate of 0.1V s<sup>-1</sup>. The devices performance parameters of the optimized PSCs are depicted in Table 1. The photovoltaic performance of the devices with PBDTTT-C completely surpasses that of P3HT, including the open-circuit voltage ( $V_{OC}$ ), short-circuit current density ( $J_{SC}$ ), fill

factor ( $FF$ ) and  $PCE$ . For PSCs with P3HT HTM, a PCE of 6.17% was achieved with  $J_{SC}$  of 15.51 mAcm<sup>-2</sup>,  $V_{OC}$  of 0.768 V and  $FF$  of 51.59%. When PBDTTT-C was used as HTM, the PCE was increased to 9.95% with  $J_{SC}$  of 17.68 mAcm<sup>-2</sup>,  $V_{OC}$  of 0.868 V, and  $FF$  of 64.83%. Moreover, the performance of devices with different thickness of PBDTTT-C are also given in Table S1 (supporting information). With increasing film thickness, the photovoltaic performance firstly increases and reaches the optimal value at 32.11 nm (800 r/s) and then decreases. In addition, device based on PBDTTT-C HTM shows less hysteresis compared with that with P3HT HTM. (Fig. 3(a)) Meantime, the reproducibility of the PSCs based on PBDTTT-C HTM is better than the devices with P3HT HTM (Table 1).

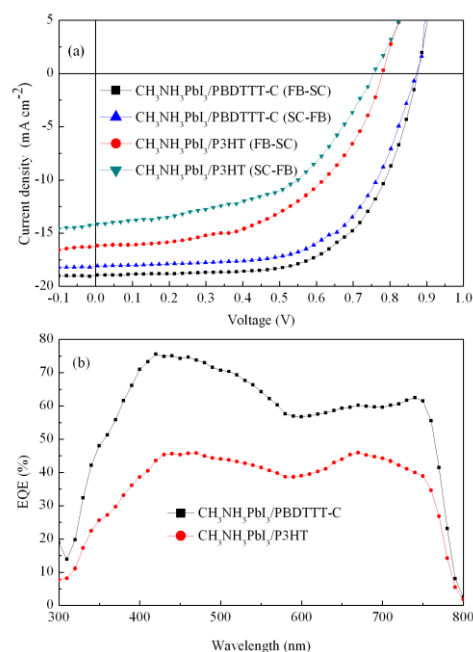


Fig. 3 (a) Forward bias to short circuit (FB-SC) and short circuit to forward bias (SC-FB) current–voltage curves measured under simulated AM 1.5G 100 mW cm<sup>-2</sup> sun light with a scan rate of 0.1 V s<sup>-1</sup>; (b) external quantum efficiency of the corresponding devices

To clarify if the PBDTTT-C or P3HT layer contribute to the PSCs photocurrent, the UV-visible absorption spectra of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PBDTTT-C and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/P3HT thin films (Fig. 2) and external quantum efficiency (EQE) of PSCs devices (Fig. 3b) were analyzed.

Table 1. Device parameters of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-based PSCs employing PBDTTT-C or P3HT HTM

HTM	$V_{OC}$ (V)	$J_{SC}$ (mAcm <sup>-2</sup> )	$FF$ (%)	$PCE$ (%)	$PCE^a$ (Average, %)	$R_s^b$ ( $\Omega$ cm <sup>2</sup> )	$R_{sh}^c$ ( $\Omega$ cm <sup>2</sup> )
PBDTTT-C	0.868	17.68	64.83	9.95	9.32 ± 0.85	9.13	6338.30
P3HT	0.768	15.51	51.59	6.17	5.47 ± 1.66	19.72	683.55

<sup>a</sup> Average PCE from 10 devices; <sup>b,c</sup> Derived from  $J$ - $V$  curves

The EQE spectra of the devices with P3HT and PBDTTT-C HTM are shown in Fig. 3b. The EQE spectra of the devices are closely consistent with the absorption spectra of the perovskite. Despite the absorption peak of P3HT and PBDTTT-C are observed at about 490 nm and 690 nm respectively in UV-vis absorption spectra, these HTM layer does not contribution to the photocurrent. Further, the similar shape of EQE spectra for all the devices indicate that light absorption of these polymers is negligible and the role of these polymers are limited to the hole transporting. The device with PBDTTT-C yields relatively higher EQE value in most of the wavelength than that with P3HT, which agrees with the higher  $J_{SC}$  of the devices with PBDTTT-C HTM obtained from  $J$ - $V$  curves.

Therefore, there must be other important factors that contribute to the much better performance of devices with PBDTTT-C HTM compared with the devices based on P3HT. When light irradiates on the devices, the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  photoactive layer will absorb photons to produce charges. Then the charges will move to the two interfaces ITO/ $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{CH}_3\text{NH}_3\text{PbI}_3$ /HTM. After that, electrons are collected by ITO, and holes directly flow to the HOMO of HTM, and then collected by Ag anode. Since the HOMO level of PBDTTT-C (-5.12 eV) is deeper than that of P3HT (-4.76 eV) and is much closer to the HOMO of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (-5.4 eV), as shown in Fig. 1c, the PBDTTT-C layer provides a better energy level matching. So holes can more easily transport to Ag anode. Simultaneously, the lowest unoccupied molecular orbital (LUMO) of PBDTTT-C (-3.35 eV), which is also deeper than that of P3HT, prevents electrons transferring from  $\text{CH}_3\text{NH}_3\text{PbI}_3$  to the Ag electrode. Therefore, devices with PBDTTT-C HTM could exhibit higher charge collection efficiencies on both electrodes than those devices based on P3HT.

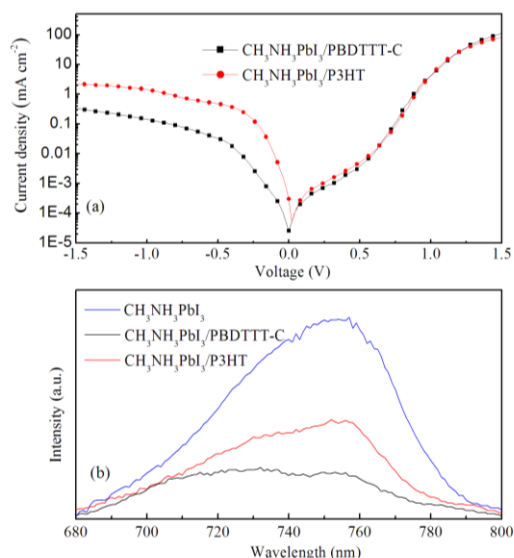


Fig. 4 (a) Dark current density–voltage characteristics of the devices using PBDTTT-C or P3HT as HTM; (b) PL intensity of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ ,  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PBDTTT-C}$  and  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{P3HT}$  thin films (the excitation wavelength: 600 nm).

Subsequently, the interfacial charge recombination is an important energy loss mechanism in solar cells,<sup>28</sup> and this may significantly affects the  $J_{SC}$ . For this reason, we measured the dark  $J$ - $V$  characteristics (Fig.4a) and the photoluminescence (PL) (Fig.4b). As shown in Fig.4a, the devices with PBDTTT-C has a lower dark current density in contrast to devices with P3HT, which indicates that the back charge recombination for device based on PBDTTT-C is suppressed much more effectively. In other words, using PBDTTT-C as HTM could effectively suppress the possibility of charges recombining before they reach the electrode. This could contribute to the high  $J_{SC}$  value. As shown in Fig.4b, the PL peak of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  is at 758 nm, which is consistent with the previous report.<sup>29</sup> The PL of  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PBDTTT-C}$  film is quenched more effectively than  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{P3HT}$  film, which could mean that the interfacial charge recombination in  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PBDTTT-C}$  based devices is lower than  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{P3HT}$  based devices. Further work utilizing time-resolved photoluminescence measurements to analyze charge extraction is under way.

The origin of  $V_{OC}$  in PSCs is partly related to the difference between the LUMO level of perovskite and the HOMO of HTM.<sup>30</sup> From Fig.1c, it can be easily find that the PBDTTT-C has a HOMO energy level of -5.12 eV which is deeper than that of P3HT (-4.76 eV), resulting in higher  $V_{OC}$  of devices based on PBDTTT-C. What is more, the greatly reduced bimolecular recombination plays a significant role on improving the  $V_{OC}$ .<sup>31</sup> The lower dark current of devices with PBDTTT-C as HTM illustrated in Fig.4 (a) may indicate the less bimolecular recombination which is good for higher  $V_{OC}$ .

Last but not least, the difference in the  $FF$  can be understand from three aspects. Firstly, according to Burschka et al.<sup>32</sup> who demonstrates that the carrier mobility of an organic semiconductor is important for achieving a high photovoltaic performance of the device, the holes can be more easily transported using PBDTTT-C as HTM because the hole mobility of PBDTTT-C ( $2.4 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ )<sup>26</sup> is higher than that of P3HT ( $5.1 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ).<sup>33</sup> Secondly, the PBDTTT-C film between Ag anode and perovskite layer provides a better energy level matching due to well-aligned HOMO of PBDTTT-C with the HOMO of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$ . Thirdly, the series resistance ( $R_s$ ) and shunt resistance ( $R_{sh}$ ) have a great influence on the  $FF$ . The higher  $R_{sh}$  and the lower  $R_s$  enabled a larger  $FF$ .<sup>34</sup> As shown in Table 1, the  $R_s$  value of PBDTTT-C based devices is lower than that with P3HT, meanwhile the  $R_{sh}$  value is higher. What is more, the surface morphology also affects the devices performances. In Fig. 5, the surface of bare perovskite was rough (RMS=10.7 nm). PBDTTT-C coated perovskite film had root mean square (RMS) value of 4.35 nm, whereas P3HT based film show RMS value of 4.68 nm. After modified with HTM polymer, the perovskite surface became smooth. All these aspects could lead to the higher  $FF$  of devices based on PBDTTT-C.

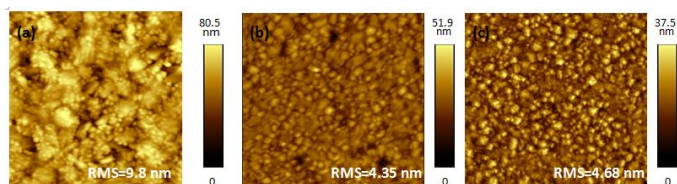


Fig.5 AFM surface morphology (5  $\mu\text{m} \times 5 \mu\text{m}$ ) of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  thin film (a);  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PBDTTT-C}$  thin film (b);  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{P3HT}$  thin film (c)

In conclusion, the dopant-free PBDTTT-C HTM was introduced to a simple planar  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite solar cells which did not contain ETM. Due to compatible HOMO energy level, relative high hole mobility and good surface morphology, the low temperature processed PBDTTT-C HTM based ETM free PSCs device shows a substantial increase in  $PCE$ ,  $J_{SC}$ ,  $V_{OC}$  and  $FF$ , compared with the reference device based on P3HT.

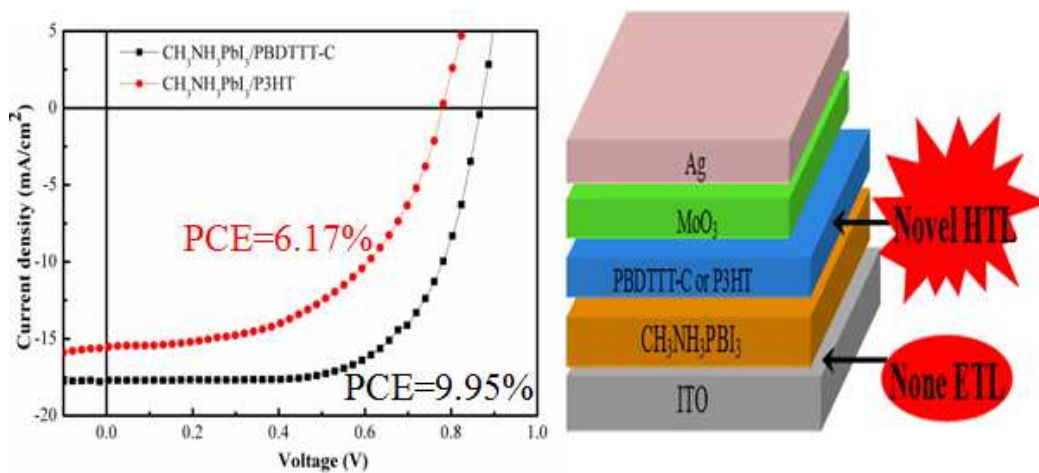
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## Graphical Abstract



Compact layer free perovskite solar cell devices with PCE up to 9.95% are demonstrated employing a new hole-transport material - PBDTTT-C.