

Highly Efficient p-i-n Perovskite Solar Cells Utilizing Novel Low-Temperature Solution-Processed Hole Transport Materials with Linear π -Conjugated Structure

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Alternative low-temperature solution-processed hole-transporting materials (HTMs) without dopant are critical for highly efficient perovskite solar cells (PSCs). Here, two novel small molecule HTMs with linear π -conjugated structure, 4,4'-bis(4-(di-p-toyl)aminostyryl)biphenyl (TPASBP) and 1,4'-bis(4-(di-p-toyl)aminostyryl)benzene (TPASB), are applied as hole-transporting layer (HTL) by low-temperature (sub-100 °C) solution-processed method in p-i-n PSCs. Compared with standard poly(3,4-ethylenedioxythiophene): poly(styrenesulfonic acid) (PEDOT:PSS) HTL, both TPASBP and TPASB HTLs can promote the growth of perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) film consisting of large grains and less grain boundaries. Furthermore, the hole extraction at HTL/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ interface and the hole transport in HTL are also more efficient under the conditions of using TPASBP or TPASB as HTL. Hence, the photovoltaic performance of the PSCs is dramatically enhanced, leading to the high efficiencies of 17.4% and 17.6% for the PSCs using TPASBP and TPASB as HTL, respectively, which are $\approx 40\%$ higher than that of the standard PSC using PEDOT:PSS HTL.

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1. Introduction

Organometallic trihalide perovskite materials have received a great deal of attention due to their unique properties, such as high absorption coefficient,^[1] long carrier diffusion length,^[2] facile tunable band gaps,^[3] and solution processability. For perovskite solar cells (PSCs), the power conversion efficiency (PCE) has received continued increase from 3.8% to 22.1%^[4,5] in the last few years, making them a promising kind of contenders for new generation photovoltaic technology. Since the PSCs being evolved from dye-sensitized solar cells (DSSCs),^[4] the efficient solid state mesoscopic (like solid-state DSSC),^[6] mesosuperstructured,^[7] and planar^[8,9] PSCs have been developed successively. The planar structure can also be divided into two categories: regular (n-i-p) and inverted (p-i-n).^[10] The former could be traced back to DSSC and has been extensively studied with the PCE surpassing 19%.^[11] The latter is derived from the organic solar cells and recently, the PCE of the PSCs with p-i-n structure has been pushed over 18% on the basis of high quality perovskite film.^[9,12] Moreover, the p-i-n PSCs

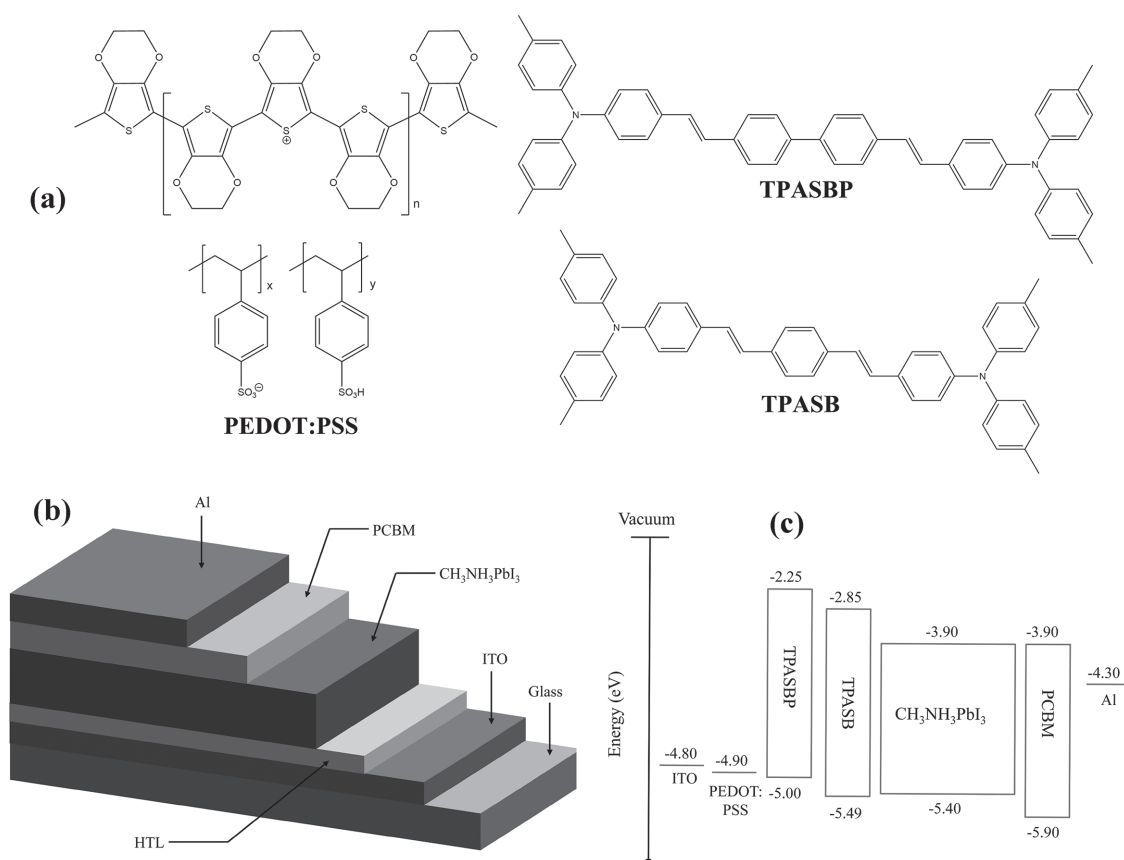


Figure 1. a) Chemical structure of PEDOT:PSS, TPASBP, and TPASB. b) Schematic device architecture of the p-i-n PSCs constructed by ITO/HTL/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Al. c) Schematic energy level diagram of each layer.

are able to be fabricated by all solution processes and at low temperature, and hence they are compatible to be applied in many fields.

In p-i-n architecture, the hole-transporting layer (HTL) functionalizes as the p-type layer for constructing the junction and plays hole-transport and hole-selective roles for efficient hole collection and reducing interface carrier recombination. Especially, the HTL affects the morphology of the perovskite layer which is fabricated on the HTL.^[9,13–15] The typically used HTL is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS).^[16] However, it is prone to degrade the devices because of its hygroscopic nature,^[17] which is specifically problematic for PSCs due to the easy decomposition of organometallic trihalide perovskite upon water exposure.^[18] Hence, exploring alternative hole-transporting materials (HTMs) is considered to be desirable for highly efficient and stable PSCs. One kind of the alternative materials is the inorganic materials including NiO_x . However, the preparation of NiO_x film usually needs high temperature ($>275^\circ\text{C}$).^[19,20] In addition, the poor wetting of the perovskite film on NiO_x also causes the formation of crystallite islands, resulting in a rough perovskite film with pinholes.^[20] Meanwhile, trap states forming at the NiO_x /perovskite interface lead to significant carrier recombination,^[19] which lowers the device performance. Recently, polymer HTMs are emerged as the HTLs for p-i-n PSCs, which enable the fabrication of low-temperature solution-processed and highly efficient PSCs. For example,

poly(*N,N'*-bis(4-butylphenyl)-*N,N'*-bis(phenyl)benzidine) (poly-TPD) and poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA) were used as HTLs in PSCs with $\text{CH}_3\text{NH}_3\text{PbI}_3$ as the absorption layer, yielding PCEs of 15.3%^[14] and 18.3%,^[9] respectively.

Here, two novel small molecular materials with linear π -conjugated structure based on a triphenylamine unit, 4,4'-bis(4-(di-*p*-tolyl)aminostyryl)biphenyl (TPASBP) and 1,4'-bis(4-(di-*p*-tolyl)aminostyryl)benzene (TPASB) (as shown in **Figure 1a**), were explored as the HTL for p-i-n PSCs to replace PEDOT:PSS. The materials are able to be dissolved in a mixture of chlorobenzene/tetrahydrofuran and form the films by spin coating on indium tin oxide (ITO)-coated substrates at 100°C , which enable the low-temperature solution-processed fabrication of the HTLs. Furthermore, perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) films formed on the as-prepared HTLs show larger grain size than these on the standard PEDOT:PSS HTL. The PSCs with the p-i-n planar architecture exhibit high efficiencies of 17.4% and 17.6% for TPASBP and TPASB HTL, respectively, which are $\approx 40\%$ higher than that based on PEDOT:PSS HTL.

2. Results and Discussion

Figure 1a presents the molecular structures of PEDOT:PSS, TPASBP, and TPASB. The synthetic routes for TPASBP and TPASB, which own a linear π -conjugated structure, are

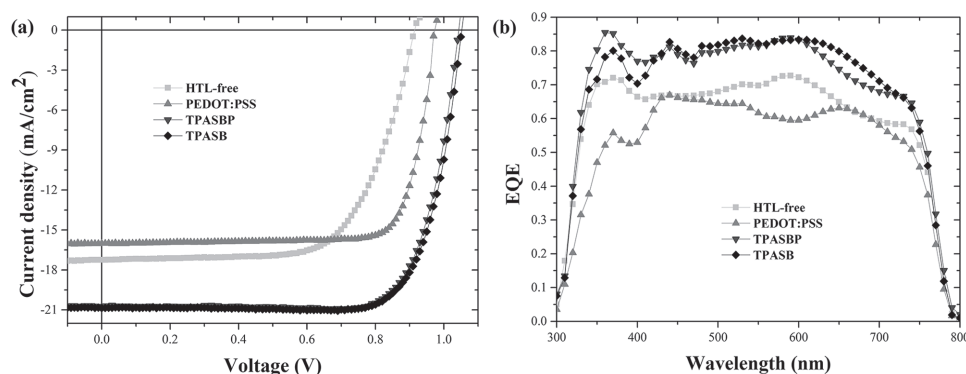


Figure 2. a) J - V characteristics of the PSCs with different HTLs under irradiation of 100 mW cm^{-2} with reverse scan (V_{OC} to J_{SC}), b) EQE spectra of the PSCs with different HTLs.

previously described by Li and co-workers.^[21] The introduction of double bonds to these new HTMs molecules could increase the conjugated structure, regulate the energy levels and improve the film-forming characteristics. Meanwhile, the flexible methylalkane could improve the solubility of these two materials at low temperature, which enables the convenient fabrication of devices with solution process. Moreover, the two small molecular materials possess higher hole mobility compared to PEDOT:PSS because of the linear π -conjugated structure, and the hole mobilities of TPASBP, TPASB, and PEDOT:PSS are 2.73×10^{-4} , 1.65×10^{-3} , and $1.86 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, indicating that TPASBP and TPASB have the potential for good HTMs. The architecture of the p-i-n PSC with ITO/HTL/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /[6,6]-phenyl-C61-butyric acid methyl ester (PCBM)/Al is schematically shown in Figure 1b and the corresponding energy levels of each layer are shown in Figure 1c. It is clear that TPASBP has a higher level of the highest occupied molecular orbital (HOMO) relative to the valence band (VB) of $\text{CH}_3\text{NH}_3\text{PbI}_3$, which can facilitate the extraction of the photogenerated holes from $\text{CH}_3\text{NH}_3\text{PbI}_3$. TPASB has a similar HOMO level to the VB of $\text{CH}_3\text{NH}_3\text{PbI}_3$, which can also effectively extract holes from $\text{CH}_3\text{NH}_3\text{PbI}_3$, as photoexcited electron-hole pairs exist as free charge carriers in $\text{CH}_3\text{NH}_3\text{PbI}_3$ due to its low exciton binding energy^[22] and thus energy drop for exciton dissociation is not necessary. Moreover, the lowest unoccupied molecular orbital energy levels of TPASBP and TPASB are higher than the conduction band (CB) of $\text{CH}_3\text{NH}_3\text{PbI}_3$, which provide good electron blocking ability. Hence, TPASBP and TPASB are able to select holes

at HTL/perovskite interface and construct the p-i-n junction with perovskite/electron transport layer (PCBM).

The photocurrent density-voltage (J - V) curves of $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based PSCs with different HTLs are shown in Figure 2a. For better comparison, HTL-free PSCs were also fabricated. The best and average photovoltaic parameters including short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), and PCE of the PSCs are extracted and listed in Table 1. The HTL-free PSCs suffer relatively poor performance with the highest PCE of 10.5%, which is due to the lack of the hole selective layer for reducing the carrier recombination.^[13] With PEDOT:PSS as the HTL, the PSC exhibits relative high performance with the highest PCE of 12.4% and an average PCE of 12.1%. On employing TPASBP or TPASB as HTL, the performance of the PSCs are significantly better compared to these without HTL or with PEDOT:PSS HTL. As can be seen from Figure 2a and Table 1, the PCEs of the PSCs based on TPASBP and TPASB are 17.4% and 17.6%, respectively. The better performance is induced by notably increased J_{SC} and V_{OC} , especially J_{SC} which is increased from 16.0 mA cm^{-2} for PEDOT:PSS HTL to more than 20 mA cm^{-2} for TPASBP or TPASB HTL. Statistical data of HTL-free, PEDOT:PSS, TPASBP, and TPASB PSCs on PCE, J_{SC} , V_{OC} , and FF can be found in Figure S1 (Supporting Information).

External quantum efficiency (EQE) spectra of the PSCs with different HTLs were shown in Figure 2b. PSC with PEDOT:PSS HTL yields even lower EQE over the whole spectrum than the HTL-free PSC, which is consistent with its lower J_{SC} . In comparison, the EQE of the PSCs with either

Table 1. The photovoltaic parameters of PSCs with different HTLs.

PSCs ^{a)}	Best values ^{b)}				Average values ^{c)}			
	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF [%]	PCE [%]	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF [%]	PCE [%]
HTL free	0.91	17.2	67	10.5	0.88	17.1	65	9.8
PEDOT:PSS	0.97	16.0	80	12.4	0.95	15.8	80	12.1
TPASBP	1.04	20.7	80	17.4	1.05	19.6	76	15.7
TPASB	1.05	20.8	80	17.6	1.02	20.3	78	16.2

^{a)}All of the solar cells were fabricated in a same batch; ^{b)}The best values were obtained from the solar cell with the highest efficiency; ^{c)}The values of HTL-free PSC and PSC with PEDOT:PSS HTL were obtained by the average of four identical cells, the values of PSCs with TPASBP and TPASB HTLs were obtained by the average of 12 identical cells.

TPASBP or TPASB HTL is significantly higher than that of the PSC with PEDOT:PSS HTL over the whole spectrum from 300 to 800 nm, indicating that TPASBP and TPASB based PSCs possess overall higher photo-to-electron conversion efficiency, which is in good agreement with their higher J_{SC} .

To get an insight in the underlying mechanisms governing the different performance of the PSCs with different HTLs, the device electrical parameters were extracted from the J - V curves shown in Figure S3 (Supporting Information) and analyzed. Planar structured PSCs can be treated as a single heterojunction diode. The electric parameters of the PSCs including series resistance (R_s), and reverse saturation current (J_0) of the cells can be calculated according to the diode equation^[23,24]

$$\frac{dV}{dJ} = \frac{mK_B T}{e} (J_{SC} + J)^{-1} + R_s \quad (1)$$

$$\ln(J_{SC} + J) = \frac{e}{mK_B T} (V - J \times R_s) + \ln J_0 \quad (2)$$

where J is the current density flow through the external load, m is the ideality factor of the heterojunction, e is elementary charge, K_B and T is the Boltzmann constant and absolute temperature, respectively. The plots of dV/dJ versus $(J_{SC} + J)^{-1}$ and $\ln(J_{SC} + J)$ versus $(V - J \times R_s)$ are shown in

Figure 3a,b, respectively. All the values of m , R_s , and J_0 can be found in Table S1 (Supporting Information). According to the results of linear plot fitting, the PSCs with PEDOT:PSS, TPASBP, and TPASB HTLs exhibit smaller R_s (2.16, 2.21, and $1.98 \Omega \text{ cm}^2$, respectively) while the HTL-free PSC has a R_s of $2.43 \Omega \text{ cm}^2$, indicating the important role of the HTL in decreasing R_s . The values of J_0 for HTL-free PSC and the PSCs with PEDOT:PSS, TPASBP, and TPASB HTLs are 2.81×10^{-4} , 1.40×10^{-7} , 1.54×10^{-8} , and $6.59 \times 10^{-8} \text{ mA cm}^{-2}$, respectively. J_0 reflects the thermal emission rate of electrons from the VB to the CB which is directly related to the recombination rate.^[24] Therefore, decreased J_0 under the condition of TPASBP or TPASB HTL implies reduced recombination loss in the corresponding PSCs. Moreover, according to equation $V_{oc} = (mK_B T/e) \ln((J_{SC}/J_0) + 1)$, smaller J_0 also leads to larger V_{oc} . Hence, the PSCs with TPASBP or TPASB as HTL have larger V_{oc} compared to the PSC based on PEDOT:PSS HTL.

Dark J - V characteristics shown in Figure 3c also reveal the reduced recombination loss in TPASBP and TPASB based PSCs. It is clear that the HTL-free PSC yields a leakage current density $\approx 10^{-2} \text{ mA cm}^{-2}$ at small bias (-0.5 to 0.5 V). With PEDOT:PSS HTL, the device leakage current decreases to $\approx 10^{-3} \text{ mA cm}^{-2}$. By replacing PEDOT:PSS with TPASBP or TPASB, the leakage current is further dramatically reduced ($\approx 10^{-4} \text{ mA cm}^{-2}$). It is well known that the leakage current is determined by the shunt resistance (R_{sh}) and consequent

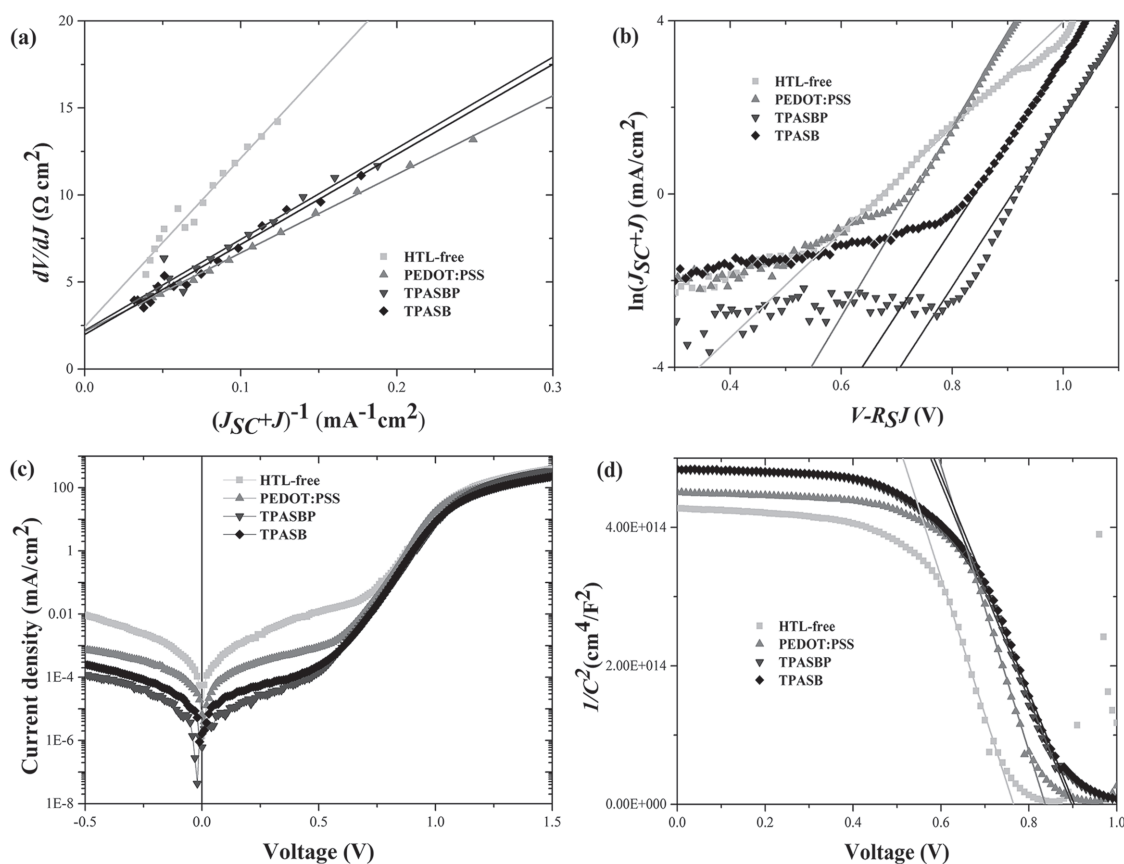


Figure 3. a) Plots of dV/dJ versus $(J_{SC} + J)^{-1}$ and the linear fitting curves, b) plots of $\ln(J_{SC} + J)$ versus $(V - R_s J)$ and the linear fitting curves, c) dark J - V characteristics of the PSCs, and d) Mott-Schottky plots of the PSCs with different HTLs.

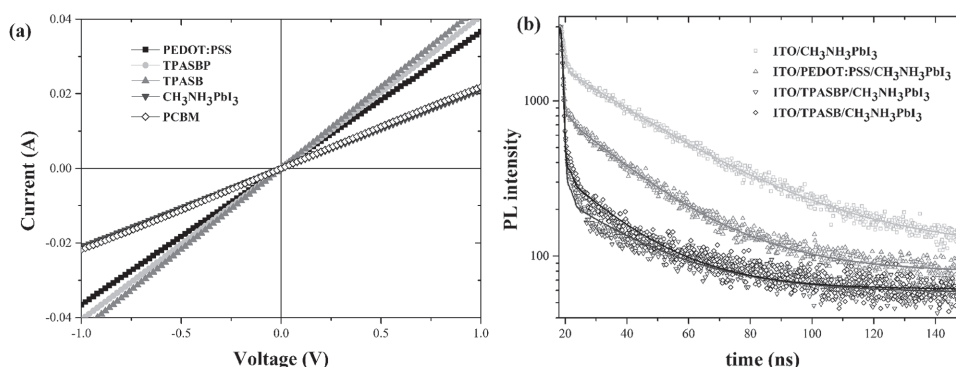


Figure 4. a) I - V characteristics of ITO/HTL or PCBM or CH₃NH₃PbI₃/Au. b) Time resolved photoluminescence (PL) decay curves of ITO/HTL/CH₃NH₃PbI₃ excited by a 485 nm diode laser. HTL utilizes PEDOT:PSS, TPASBP, and TPASB, respectively.

charge carrier recombination. Smaller leakage current indicates larger R_{sh} and lower charge carrier recombination in the device,^[25] which is in good agreement with the result of J_0 .

Apart from the resistance and carrier recombination of the different PSCs, the carrier density and junction properties are also found to be responsible for their performance difference. Mott-Schottky analysis of HTLs/CH₃NH₃PbI₃ heterojunction was carried out to illustrate the effect of different HTLs on the carrier density and junction properties in the PSCs. The Mott-Schottky plot of inverse square capacitance (C^{-2}) versus applied voltage (V) (as shown in Figure 3d) yields a straight line with its slope inversely proportional to the doping concentration. The Mott-Schottky model is described as^[26]

$$\frac{1}{C^2} = \frac{2}{e\epsilon_s N} \left(V_{bi} - V - \frac{2K_B T}{e} \right) \quad (3)$$

where ϵ_s is the dielectric constant of CH₃NH₃PbI₃, N is the doping density, V_{bi} is the built-in potential, and V is the applied bias. The doping density N of the HTL-free PSC and the PSCs with PEDOT:PSS, TPASBP, and TPASB HTL is calculated to be 2.37×10^{15} , 2.28×10^{15} , 3.02×10^{15} , and $3.00 \times 10^{15} \text{ cm}^{-3}$, respectively. Clearly, the doping density is increased under the condition of using TPASBP or TPASB as HTL, comparing with HTL-free PSC and PSC with PEDOT:PSS HTL. Due to the increase in doping density, V_{bi} is increased from 0.71 V for HTL-free PSC to 0.84 and 0.85 V for the PSCs with TPASBP and TPASB HTL, respectively, which is consistent with the increase in V_{OC} for the PSCs in Figure 2a. Larger doping density and higher V_{bi} induce stronger depleted electric field in the heterojunction and favor the charge extraction, which cause the significant enhancement of J_{SC} .

On the basis of the electrical parameters and Mott-Schottky analysis, it is clear that the high performance of the PSCs with either TPASBP or TPASB HTL is governed by their lowered series resistance, reduced carrier recombination and enhanced built-in potential, which promote high V_{OC} and J_{SC} in these PSCs. As the main difference in these PSCs with different HTLs is the HTL, hence, the main origins for these improvements will correlate with the properties of the HTL itself (hole transport) and/or the HTL/perovskite interface (hole selectivity).

Hence, the conductivity of the HTLs were characterized to investigate their hole transport ability. The current-voltage (I - V) characteristics of sandwich cells composed by ITO/PEDOT:PSS or TPASBP or TPASB or CH₃NH₃PbI₃ or PCBM thin film/Au were measured to calculate the conductivity of the active films and shown in Figure 4a. The direct current conductivity (σ_0) can be determined from the slope of I - V plot^[12,27]

$$I = \sigma_0 A d^{-1} V \quad (4)$$

where A is the sample area (4 mm^2) and d is the sample thickness, respectively. The thicknesses of PEDOT:PSS, TPASBP, TPASB, CH₃NH₃PbI₃, and PCBM films are ≈ 20 , ≈ 25 , ≈ 25 , ≈ 500 , and $\approx 60 \text{ nm}$, and the corresponding σ_0 are ≈ 0.0018 , ≈ 0.0025 , ≈ 0.0027 , ≈ 0.025 , and $\approx 0.0033 \text{ mS cm}^{-1}$, respectively. Therefore, it can be expected that the generated carriers from CH₃NH₃PbI₃ layer are more efficiently transported by TPASBP or TPASB than PEDOT:PSS. Furthermore, according to the σ_0 values of HTLs and PCBM, it can be speculated that the hole flux (J_h) and the electron flux (J_e) in the PSCs under the conditions of using TPASBP or TPASB as HTL are more balanced comparing with PEDOT:PSS, which can minimize the carrier recombination at HTL/CH₃NH₃PbI₃ and CH₃NH₃PbI₃/PCBM interfaces.

To confirm the hole extraction property at HTL/CH₃NH₃PbI₃ interface, time resolved photoluminescence (TRPL) decay curves of ITO/HTL/CH₃NH₃PbI₃ stacks have been measured and shown in Figure 4b. By fitting the data with two exponential decay model, the lifetime of the carriers can be obtained and the results were summarized in Table S3 (Supporting Information). ITO/CH₃NH₃PbI₃ stack exhibits an averaged PL lifetime of 29.36 ns. In ITO/PEDOT:PSS/CH₃NH₃PbI₃ stack, the averaged PL lifetime is reduced to 14.44 ns, due to the extraction of photogenerated holes from CH₃NH₃PbI₃ to PEDOT:PSS at PEDOT:PSS/CH₃NH₃PbI₃ interface. In ITO/HTL/CH₃NH₃PbI₃ stacks with TPASBP and TPASB as HTLs, the averaged PL lifetimes are 9.44 and 8.56 ns, respectively. Thus, the employment of TPASBP or TPASB as HTL is more beneficial to the hole extraction from CH₃NH₃PbI₃ to HTL.

The variation of the carrier recombination in the PSCs also correlates with the crystallinity property of the perovskite. Hence, the top-view scanning electron microscope

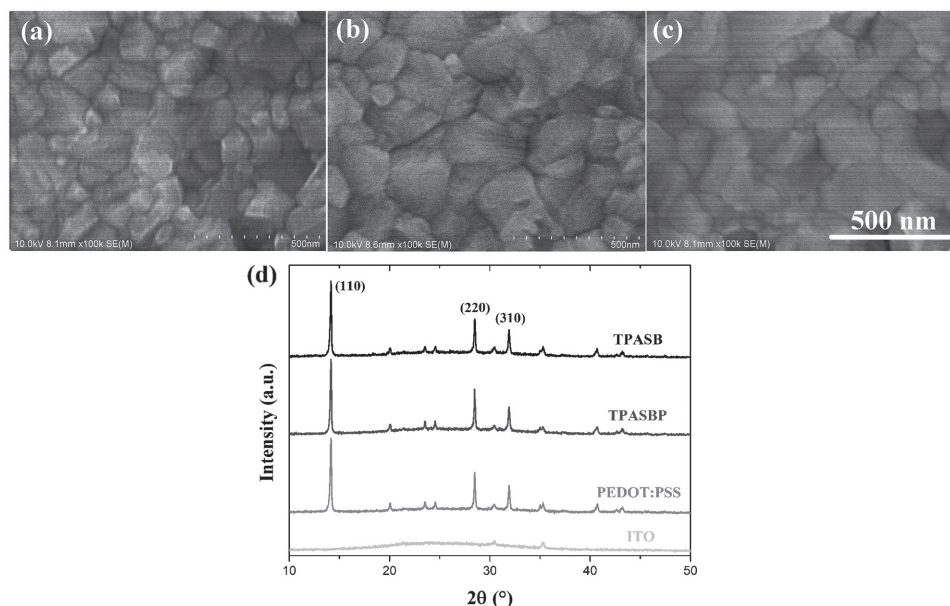


Figure 5. Top-view SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films prepared on a) PEDOT:PSS, b) TPASBP, and c) TPASB. d) XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films fabricated on PEDOT:PSS, TPASBP, and TPASB.

(SEM) images and X-ray diffraction (XRD) spectroscopy of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films on different HTLs were measured. SEM images shown in **Figure 5a–c** reveal an interesting phenomena that the grain size of the perovskite film on TPASBP or TPASB is larger than that on PEDOT:PSS. It has been reported that the grain boundaries is correlated to the trap density in the PSCs, and the much less grain boundaries result in a lower trap density.^[9] As the recombination of the PSCs is evidenced to be governed by the trap states,^[25] the larger grain size of the perovskite film based on TPASBP or TPASB indicates less recombination. Hence, we can conclude that large grain of the perovskite film on TPASBP or TPASB facilitates decreased carrier recombination and loss.

XRD patterns also reveal the better crystallinity of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film fabricated on TPASBP or TPASB than that on PEDOT:PSS. The XRD spectra in **Figure 5d** present intense diffraction peaks at 14.15° , 28.48° , and 31.92° in all the samples, corresponding to (110), (220), and (310) crystal planes of $\text{CH}_3\text{NH}_3\text{PbI}_3$,^[28] respectively. The full width at half maximum varies with different HTLs (shown in Table S2, Supporting Information), which is narrower for $\text{CH}_3\text{NH}_3\text{PbI}_3$ film fabricated on TPASBP or TPASB, indicating better film crystallinity and larger grain size of $\text{CH}_3\text{NH}_3\text{PbI}_3$ fabricated on these new HTLs than that fabricated on PEDOT:PSS HTL. This result is in accordance with the SEM images, again revealing that TPASBP and TPASB favor the growth of large grain $\text{CH}_3\text{NH}_3\text{PbI}_3$ films.

3. Conclusion

In conclusion, a remarkable enhancement ($\approx 40\%$ in device efficiency) of p-i-n planar PSCs is demonstrated by introducing new small molecule hole-transporting materials (TPASBP and TPASB) with linear π -conjugated structure as low-temperature solution-processed HTLs. The new HTLs

possess high conductivity without any doping and superior hole extraction ability from the perovskite. Moreover, they promote the growth of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film with large grain size. These advantages of the new HTLs enable the corresponding PSCs yield less carrier losses than the standard PSCs with PEDOT:PSS as the HTL, leading to their superior performance. This work highlights the great potential of TPASBP and TPASB as HTLs in PSCs, which also provides an efficient way to improve the device performance of the p-i-n PSCs.

Supporting Information

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

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- [1] C. C. Stoumpos, C. D. Malliakas, M. G. Kanatzidis, *Inorg. Chem.* **2013**, 52, 9019.
- [2] a) S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, H. J. Snaith, *Science* **2013**, 342, 341; b) G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar, T. C. Sum, *Science* **2013**, 342, 344.

- [3] F. Hao, C. C. Stoumpos, R. P. Chang, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2014**, *136*, 8094.
- [4] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050.
- [5] a) M. Liu, M. B. Johnston, H. J. Snaith, *Nature* **2013**, *501*, 395; b) J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, M. Grätzel, *Nature* **2013**, *499*, 316; c) N. Ahn, D.-Y. Son, I.-H. Jang, S. M. Kang, M. Choi, N.-G. Park, *J. Am. Chem. Soc.* **2015**, *137*, 8696; d) Best Research-Cell Efficiencies provided by the National Renewable Energy Laboratory (NREL), http://www.nrel.gov/ncpv/images/efficiency_chart.jpg, accessed May 2016.
- [6] J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C.-S. Lim, J. A. Chang, Y. H. Lee, H.-j. Kim, A. Sarkar, M. K. Nazeeruddin, *Nat. Photonics* **2013**, *7*, 486.
- [7] J. M. Ball, M. M. Lee, A. Hey, H. J. Snaith, *Energy Environ. Sci.* **2013**, *6*, 1739.
- [8] D. Liu, T. L. Kelly, *Nat. Photonics* **2014**, *8*, 133.
- [9] C. Bi, Q. Wang, Y. Shao, Y. Yuan, Z. Xiao, J. Huang, *Nat. Commun.* **2015**, *6*, 7747.
- [10] C. Zuo, H. J. Bolink, H. Han, J. Huang, D. Cahen, L. Ding, *Adv. Sci.* **2016**, DOI: 10.1002/advs.201500324.
- [11] H. Zhou, Q. Chen, G. Li, S. Luo, T.-b. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, Y. Yang, *Science* **2014**, *345*, 542.
- [12] J. H. Heo, H. J. Han, D. Kim, T. K. Ahn, S. H. Im, *Energy Environ. Sci.* **2015**, *8*, 1602.
- [13] Q. Xue, G. Chen, M. Liu, J. Xiao, Z. Chen, Z. Hu, X. F. Jiang, B. Zhang, F. Huang, W. Yang, *Adv. Energy Mater.* **2015**, *6*, 3.
- [14] D. Zhao, M. Sexton, H. Y. Park, G. Baure, J. C. Nino, F. So, *Adv. Energy Mater.* **2015**, *5*, 1401855.
- [15] C. Zuo, L. Ding, *Small* **2015**, *11*, 5528.
- [16] L. Meng, J. You, T.-F. Guo, Y. Yang, *Acc. Chem. Res.* **2015**, *49*, 155.
- [17] M. Jørgensen, K. Norrman, F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 686.
- [18] J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. Van Schilfgaarde, A. Walsh, *Nano Lett.* **2014**, *14*, 2584.
- [19] J. R. Manders, S. W. Tsang, M. J. Hartel, T. H. Lai, S. Chen, C. M. Amb, J. R. Reynolds, F. So, *Adv. Funct. Mater.* **2013**, *23*, 2993.
- [20] a) Z. Zhu, Y. Bai, T. Zhang, Z. Liu, X. Long, Z. Wei, Z. Wang, L. Zhang, J. Wang, F. Yan, S. Yang, *Angew. Chem.* **2014**, *53*, 12571; b) J. Y. Jeng, K. C. Chen, T. Y. Chiang, P. Y. Lin, T. D. Tsai, Y. C. Chang, T. F. Guo, P. Chen, T. C. Wen, Y. J. Hsu, *Adv. Mater.* **2014**, *26*, 4107.
- [21] a) J. Wang, S. Wang, X. Li, L. Zhu, Q. Meng, Y. Xiao, D. Li, *Chem. Commun.* **2014**, *50*, 5829; b) L. Zhu, J. Xiao, J. Shi, J. Wang, S. Lv, Y. Xu, Y. Luo, Y. Xiao, S. Wang, Q. Meng, X. Li, D. Li, *Nano Res.* **2014**, *8*, 1116; c) W. Z. Gao, X. G. Li, S. R. Wang, *Appl. Mech. Mater.* **2012**, *161*, 121.
- [22] S. Qing, O. Yuhei, C. Jin, T. Syota, K. Kenji, O. Takuya, O. Naoya, Y. Kenji, K. Kenji, T. Taro, *Phys. Chem. Chem. Phys.* **2014**, *16*, 19984.
- [23] J. Shi, J. Dong, S. Lv, Y. Xu, L. Zhu, J. Xiao, X. Xu, H. Wu, D. Li, Y. Luo, *Appl. Phys. Lett.* **2014**, *104*, 063901.
- [24] J. You, Y. Yang, Z. Hong, T. B. Song, L. Meng, Y. Liu, C. Jiang, H. Zhou, W. H. Chang, G. Li, *Appl. Phys. Lett.* **2014**, *105*, 183902.
- [25] G. J. A. H. Wetzelaer, S. Max, S. A. Miquel, M. Cristina, Á. Jorge, H. J. Bolink, *Adv. Mater.* **2015**, *27*, 1837.
- [26] a) W. A. Laban, L. Etgar, *Energy Environ. Sci.* **2013**, *6*, 3249; b) J. Shi, H. Wei, S. Lv, X. Xu, H. Wu, Y. Luo, D. Li, Q. Meng, *ChemPhysChem* **2015**, *16*, 842; c) D. Song, P. Cui, T. Wang, D. Wei, M. Li, F. Cao, X. Yue, P. Fu, Y. Li, Y. He, *J. Phys. Chem. C* **2015**, *119*, 22812.
- [27] J. Obrzut, *Phys. Rev. B: Condens. Matter* **2009**, *80*, 195211.
- [28] a) Q. Xue, Z. Hu, J. Liu, J. Lin, C. Sun, Z. Chen, C. Duan, J. Wang, C. Liao, W. M. Lau, *J. Mater. Chem. A* **2014**, *2*, 19598; d) N.-G. Park, *J. Phys. Chem. Lett.* **2013**, *4*, 2423.

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