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Efficient Inverted Perovskite Solar Cells by Employing N-Type (D-A₁-D-A₂) Polymers as Electron Transporting Layer

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It is highly desirable to employ n-type polymers as electron transporting layers (ETLs) in inverted perovskite solar cells (PSCs) due to their good electron mobility, high hydrophobicity, and simplicity of film forming. In this research, we firstly explore the capability of three n-type donor-acceptor₁-donor-acceptor₂ (D-A₁-D-A₂) conjugated polymers (pBTT, pBTTz and pSNT) as electron transporting layers because these polymers possess electron mobility as high as 0.92, 0.46 and 4.87 cm²/Vs in n-channel organic transistors, respectively. The main structural difference among pBTT, pBTTz and pSNT is the position of sp²-nitrogen atoms (sp²-N) in the polymer main chains. Therefore, the effect of different substitution positions on the PSC performances was comprehensively studied. The as-fabricated p-i-n PSCs with pBTT, pBTTz and pSNT as ETLs showed the maximum photoconversion efficiencies (PCEs) of 12.8%, 14.4%, and 12.0%, respectively. To be highlighted, pBTTz-based device could maintain 80% of its stability after ten days due to its good hydrophobicity, which was further confirmed by a contact angle technique. More importantly, pBTTz-based device showed a neglected hysteresis.

Our study reveals that the n-type polymers can be promising candidates as ETLs to approach solution-processed highly-efficient inverted perovskite solar cells.

1. Introduction

Nowadays, inverted perovskite solar cells (p-i-n PSCs) have received more researchers' attentions, attributing to their several promising factors compared with regular perovskite solar cells (n-i-p) PSCs.^[1] (1) The p-i-n PSCs with metal oxide-free charge transporting layers (e.g. organic charge transporting layers) would simplify the fabrication of p-i-n PSCs at low temperature; (2) Organic layers provide more opportunities to fabricate flexible solar cells as well as integrate other devices into flexible substrates; and (3) The replacement of traditional TiO₂ inorganic compounds with organic electron-transporting materials in inverted p-i-n PSCs makes solution-processing large-area fabrication possible. All these advantages of p-i-n PSCs have opened a novel route toward the future commercialization and marketing of p-i-n PSCs.^[2]

From the architecture point of view, PSCs can be classified into two groups according to the arrangement of charge transporting layers: One is the n-i-p PSC, where the electron-transport layer (ETL) is deposited on indium tin oxide (ITO) prior to the perovskite layer,^[3] and the other is the p-i-n PSC, where the ETL is deposited after the perovskite layer.^[4] Although hole transporting layers were well studied and even decent efficiencies could be achieved in HTL (hole-transport layer)-free PSCs,^[5] ETL has been considered as a performance-dependent layer in PSCs.^[6] The first p-i-n PSC was fabricated by employing PCBM as an ETL and the power conversion efficiency (PCE) could reach up to 3.9 %.^[7] Few years later, the PCE has been pushed to 21%.^[8] However, the high cost of PCBM as well as its poor film-morphology stability under thermal treatment has become stumbling blocks toward its large scale fabrication.^[9] Later on, modified-PCBM compounds have been developed as alternatives of PCBM to enhance the PCE and the stability of p-i-n PSCs.^[10] However, the cost to synthesize these compounds still frustrates scientists for practical applications. Thus, searching new organic materials to replace PCBM or its derivatives is very important and highly desirable.

Currently, several types of n-type organic small molecules (e.g. azaacenes,^[11] naphthalene diimide (NDI),^[12] perylene diimide (PDI),^[13] hexaazatrinaphthylene derivatives (HATNA),^[14] coronene diimide (CDIN),^[15] benzobis(thiadiazole) (B2F)^[16] and copper phthalocyanine derivatives (F₁₆CuPc)^[17]) have been developed and employed as ETLs in p-i-n PSCs, and the PCEs based on these molecules as ETLs range from 2% to 19%. In our research, we also developed a series of novel n-type organic small molecules^[18] and some of them have been applied as promising ETLs in p-i-n PSCs with the PCE up to 18.2%.^[19] However, organic small

molecules still face several issues during device fabrication, including poor morphology control (conjugated small molecules are easy to aggregate and crystallize), uneven surface coverage while using dilute solutions, and crack formation. Thus, in order to address these issues, more and more efforts have been made to develop high-performance n-type conjugated polymers.^[20] In fact, some of n-type conjugated polymers have shown better electron mobility, higher hydrophobicity, and the simplicity of film forming compared to the n-type small molecules.^[21] Even in this case, the number of the reported PSCs using n-type polymers as ETLs is still much smaller,^[22] and the highest reported PCE based on n-type conjugated polymers is about 17 %.^[21] Thus, we believe that there is still plenty of room left for us to search new n-type conjugated polymers as ETLs for enhancing the performance of PSCs.

In this study, we are interested in some recently reported n-type donor-acceptor₁-donor acceptor₂ (D-A₁-D-A₂) conjugated polymers (namely, pBTT, pBTTz and pSNT, **Figure 1**).^[23] We employed them (pBTT, pBTTz and pSNT) as ETLs in PSCs and investigated the effect of substitution position of sp²-N atoms on the PSC performances. There are two reasons to choose these polymers: (1) These polymers are naphthalene-diimide (NDI)-based n-type polymers (pBTT, pBTTz and pSNT) with field-effect electron mobilities up to 0.92, 0.46 and 4.87 cm²/Vs, respectively, which should be promising candidates as ETLs in PSCs; and (2) NDI-based polymers have been demonstrated to show a great record of high photovoltaic performances in the field of organic solar cells,^[20c,22a] which made us believe that they should also have a good performance in PSCs. We successfully fabricated p-i-n PSCs with pBTT, pBTTz and pSNT as ETLs and the maximum PCEs delivered by these polymers were 12.8%, 14.4%, and 12.0 %, respectively. Although introducing sp²-N atoms into the donor thiophene units of pBTT produced pBTTz with a slightly declined electron mobility, the PCE of PSCs was still significantly improved. On the other hand, pSNT with two additional sp²-N atoms and very high electron mobility showed a poorer PSC performance. In addition, we found that the electron-rich sulfur atoms have a strong impact on the passivating of the under-coordinated Pb-atoms, as reflected by the current density-voltage (J-V) hysteresis curves of the pBTTz-based devices. More importantly, due to the hydrophobic nature of polymers, pBTTz-based devices retained 80% of its stability after ten days. It is worthy to point that, to the best of our knowledge, this study is the first demonstration of the effect of sp²-N position in polymer main chain (pBTT) on the properties of (D-A₁-D-A₂) n-type polymers as ETLs in PSCs.

2. Results and discussion

Three n-type polymers (pBTT, pBTTz and pSNT, **Figure 1**) were synthesized according to the reported methods.^[23] It is well-known that inserting electron-withdrawing groups (EWG, such as F, Cl and CN) into the main chains of conjugated polymer strengthens n-type characters, which is beneficial for the efficient electron injection and transport. In this study, we introduced sp^2 -N atoms to the n-type polymers since it is seldom studied in the field of PSCs. Strating from pBTT composed of the NDI and thiophene-benzothiadiazole-thiophene moiety, the replacement of the electron-donating thiophene rings with the thiazole units gave pBTTz, while the incorporation of the diazole unit into the electron-accepting benzothiadiazole moiety produced pSNT (**Figure 1**). As a result, these three polymers are a class of n-type polymers suitable for the investigation of the sp^2 -N effect on the PSC performances.

Figure 2 shows the structures of pBTT, pBTTz and pSNT-based p-i-n PSCs. The configuration of the as-fabricated PSCs is built as ITO/PEDOT:PSS/ $CH_3NH_3PbI_{3-x}Cl_x$ /ETLs/Ag, where poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) acts as an HTL for extracting the holes from the perovskite layer and blocking electron transfer to the anode, $CH_3NH_3PbI_{3-x}Cl_x$ perovskite layer functions as a light absorbing material, and n-type polymers are employed as ETLs for facilitating the electron transfer to the cathode and blocking the hole transport to the anode. The corresponding energy level diagram is depicted in **Figure 3**, in which the lowest unoccupied molecular orbital (LUMO) of pBTTz matched well with the conduction band of the perovskite layer by comparing with pBTT. Thus, electrons can readily transfer from the perovskite layer to the cathode through the pBTTz layer. In addition, the highest occupied molecular orbital (HOMO) of pBTTz is deeper than the valence band of the perovskite layer, which supports the efficient blocking of holes toward the cathode. Compared with pBTTz, the HOMO and LUMO of pBTT suggest the less efficient electron transfer and hole blocking from the perovskite layer to the cathode. Regrettably, the HOMO of pSNT is approximately similar to the valence band of the perovskite layer, which could result in a negligible hole blocking effect and thus deteriorate the photovoltaic parameters of the as-fabricated PSCs. The light photons can be absorbed by the perovskite active materials, where excitons are generated and dissociated to electrons and holes that can further diffuse through the perovskite material to the carrier-transport layeres. Eventually, holes pass through PEDOT:PSS and are collected by the ITO electrode, while electrons pass through the ETL and are collected by the Ag electrode.

The as-prepared perovskite films have been characterized by several tools. As shown in Figure S1, the crystallinity of the perovskite layer was investigated by XRD. Three characteristic peaks could be found at 14.2° , 28.5° and 31.9° , which can be assigned to the (110),

(220) and (310) planes of the perovskite crystal. Scanning electron micrograph (SEM) (Figure S2) indicated that the as-prepared perovskite layer consists of large grains without any pin holes. UV-visible absorption spectroscopy indicated that the optical band gap of the as-prepared perovskite layer is ~1.58 eV because the optical absorption onset of this layer was observed at 785 nm as shown in Figure (S3 a). **To further verify the band gap value, Tauc plot has been drawn with extracted band gap as shown in Figure (S3 b).** The as-prepared perovskite layer also displayed strong photoluminescence under excitation at 532 nm, indicating the high purity of the as-prepared perovskite layer. However, this photoluminescence was gradually quenched when the ETLs were deposited on it. The order of quenching was pSNT<pBTT<PCBM<pBTTz (**Figure 4**). Surprisingly, pBTTz has a more efficient quenching effect than the common ETL material PCBM. To further investigate the lifetime of the perovskite/pBTTz and perovskite/PCBM referenced to the bare perovskite, time-resolved photoluminescence (TRPL) measurements were carried out as shown in **Figure 5**. After fitting the resultant TRPL curves and employing the exponential decay equation (1) for the bare perovskite layer, exponential decay equation (2) was applied to the perovskite/pBTTz bilayer and perovskite/PCBM bilayer, as showing below.

$$Y = Y_0 + A_1 e^{-x/\tau_1} \quad (1)$$

$$Y = Y_0 + A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2} \quad (2)$$

where A is the amplitude and τ in nano second (ns) is the lifetime of the exciton. All calculated data from **Figure 5** are summarized in Table 1. The results confirm that the electron transfer from the perovskite layer to pBTTz was more efficient than that from the perovskite to PCBM. All these results indicate that these n-type polymers are promising candidates as ETLs in p-i-n PSCs.

The surfaces of pBTT, pBTTz, and pSNT on the perovskite layers were studied through atomic force microscopy (AFM). As shown in Figure S4, the AFM images of pBTT, pBTTz and pSNT suggested that the roughness parameters (RMS) of the grains are 18.0, 18.8 and 17.8 nm, respectively. As shown in **Figure 6**, the dark current-voltage (I-V) curves of pBTT, pBTTz, pSNT and PCBM-based devices were consistent with the previous results, in which the pBTTz-based device showed smaller dark currents. This result implies that the pBTTz-based devices have less current leakage.

To fully elucidate the potential of pBTT, pBTTz and pSNT, PSCs with pBTT, pBTTz and pSNT as the ETLs were fabricated. In order to optimize the film thickness of the ETLs, different concentrations of the polymers (3, 5 and 8 mg/ml in *o*-dichlorobenzene (DCB)) were applied. For example, it was revealed that the concentration of the pBTT solution played a critical role in the PSC performances. Among the current density-voltage (J-V) curves of the as-fabricated devices based on pBTT (3, 5 and 8 mg/ml in DCB) as ETLs, the highest PCE of 12.8% with the Voc of 0.88 V, Jsc of 22.51 mA/cm² and FF of 64.4 % was achieved if the concentration of 5 mg/ml was used. When the concentration of pBTT decreased to 3 mg/ml, the corresponding PCE declined to 10.7%. This declination was ascribed to the uncoverage of the surface, which led to the decrease in the Jsc and FF. In contrast, increasing the concentration of pBTT to 8 mg/ml dramatically dropped the PCE to 8.9% associated with the decrease in the Jsc and FF due to the increase in the series resistance as shown in Figure S5(a). Embedding the sp²-N into the donor (thiophene) unit of pBTT resulted in a new polymer pBTTz with a significantly modified energy levels (deeper HOMO and LUMO). The corresponding HOMO and LUMO levels are shown in **Figure 3**. The highest PCE of the device based on pBTTz was 14.4 % with the Voc of 0.91 V, Jsc of 21.95 mA/cm² and FF of 72.3%. This improvement was induced by the HOMO and LUMO of pBTTz well-matched with the valence and conduction bands of the perovskite layer, respectively, leading to an enhancement of both Voc and FF, and accordingly, a higher PCE resulted. The optimum concentration of pBTTz in DCB was 5 mg/ml. By decreasing or increasing the concentration, the PCEs decreased as shown in **Figure 7**. **For further verification of the measured Jsc of champion pBTTz-based PSC, external quantum effcieincy (EQE) plot was investigated as shown in Figure 8 and the calculated Jsc was 21.5 mA/cm², which is well matched with measured Jsc.** Embedding sp²-N atoms into the electron-accepting benzothiadiazole of pBTT through the addition of a fused ring with two sp²-N atoms produced another new polymer pSNT. The electron mobility of this polymer significantly increased, and the LUMO became slightly deeper and much closer to the conduction band of the perovskite layer. However, the HOMO also became shallower and it is very close to the valence band of the perovskite layer. This change resulted in a decrease of FF, then a deterioration of the PCE. The highest PCE achieved was 12% with the concentration of 5 mg/ml. By changing the concentration of pSNT to 3 or 8 mg/ml in DCB, the PCEs became poorer as shown in Figure S6(a). To explore the reliability of our solar cells, 36 devices based on each polymer as ETLs have been prepared and tested. The distributions of the PCEs are shown in Figure S5(b), **Figure 9** and Figure S6(b) for pBTT, pBTTz and pSNT, respectively.

All photovoltaic parameters of the experiments are summarized in Table S1. The thermal annealing effect on the performances of the pBTTz-based devices was investigated by heat treatment of the devices at 80, 90 and 100 °C after spin-coating of pBTTz. The PCEs gradually increased from 12.8% to 14.4% by increasing the temperature from 80 °C to 100 °C as shown in **Figure 10** and Table S2. In addition, the pBTTz-based devices showed negligible hysteresis effects as shown in **Figure 11** and Table S3. We attribute this result to the well-matched HOMO and LUMO of pBTTz with the conduction and valence bands of the perovskite, respectively. Moreover, the sulfur atoms have successfully passivated the under-coordinated Pb atoms. This passivation reduced the charge accumulation, therefore reducing the hysteresis.

Furthermore, the dewettability of each polymer was measured and compared with that of PCBM. Interestingly, the contact angles of these polymers were higher than that of PCBM as shown in Figure S7. This result reflects the hydrophobic nature of these n-type polymers. Finally, the stability of the PSCs based on both pBTTz and PCBM was evaluated. After ten days of testing, the pBTTz-based device still retained 80% of its original PCE, which is higher than that of the PCBM-based device with a stability retention of 73 % **as shown in Figure 12. Each cell was tested in ambient air first, and then kept in controlled humidity condition in dry box.** All these results strongly suggest that our polymers are suitable candidates to replace PCBM as effective ETLs in future p-i-n PSCs.

3. Conclusion

For the first time, the effect of the sp^2 -N substitution position in the main chains of polymers on the photovoltaic properties of PSCs has been investigated. Inverted perovskite solar cells based on pBTT, pBTTz or pSNT as ETLs have been successfully fabricated. Our research indicates that PSCs based on pBTTz (possessing the sp^2 -N atoms at the thiophene units) delivered the highest PCE of 14.4% with a negligible hysteresis. Moreover, the device based on pBTTz retained 80% of its original PCE even after ten days. On the other hand, pSNT with two additional sp^2 -N atoms at the electron-accepting benzothiadiazole unit showed a poor efficiency due to its inappropriate HOMO level that was very close to the valence band of the perovskite layer.

4. Experimental Section

Materials: All polymers are prepared according to the reported precedures.^[23] PEDOT:PSS, Clevios™ P VP Al 4038, Heraeus. Lead iodide (PbI₂), Sigma Aldrich , 99.999%, anhydrous, beads. Lead chloride (PbCl₂), Sigma Aldrich, 99.999 %, anhydrous, beads. Methylammnium iodide (CH₃NH₃I), DYESOL. Dimethylsulfoxide (DMSO) 99.9 %, anhydrous. γ -Butyrolactone (GBL), Sigma Aldrich, *ReagentPlus*®, $\geq 99\%$. Toluene, Sigma Aldrich, 99.8%, anhydrouys.

Device fabrication: After etching ITO glass slides to the desired patterns, all slides were cleaned by DI-water, acetone and isopropanol in an ultrasonic bath. Our device fabrication was started by spin-cast of PEDOT:PSS as the HTL on ITO at 6000 rpm for 60 s, followed by heat treatment at 140 °C for 15 minutes. Immediately, all slides were transferred to a glovebox for spin coating of perovskite solution. The perovskite solution was prepared by mixing of 1.26 M PbI₂, 0.14 M PbCl₂ and 1.35 M CH₃NH₃I in a mixed solvent of DMSO:GBL (3:7 v,v) at 70 °C for 12 hr. The spin coating technique was processed at two steps. The first step was at 1000 rpm for 20 s, and the second step was at 4000 rpm, after 40 s of starting, 0.65 ml of toluene dripped on the substrate. Then, the perovskite substrate was transferred onto a hot plate and thermally treated by a mixed solvent vapor annealing at 100 °C for 20 min.^[24] The ETL polymers were dissolved in *o*-dichlorobenzene (DCB) with different concentrations (3, 5 and 8 mg/ml). Each polymer solution was spin-casted at 2000 rpm for 60 s and immediately heat-treated at 100 °C for 10 minutes. The final step of fabrication was completed by evaporation of 100 nm of Ag electrode.

Characterization: The perovskite layer was investigated by powder XRD equipped with CuK α radiation ($\lambda = 0.15418$ nm operated at 40 kV and 30 mA). The surface morphology of perovskite film was investigated by SEM (JEOL, JSM 6360 at 5 KV). AFM measurements were carried out by Atomic Force Microscope, Asylum Research, Cypher S. The thickness of each layer was measured by Alpha-Step D-600 Stylus Profiler (KLA-Tencor Corporation). The optical properties of the perovskite layer were characterized by UV-visible spectroscopy (UV-Vis-NIR, Lambda 900, Perkin Elmer). The PL characteristics were measured by Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies). TRPL was measured by PicoHarp 300, PicoQuant. Contact angle of each ETL was measured by contact angle equipment, DataPhysics, OCA 15 Pro. The current density-voltage (J-V) curves of solar cells were measured using Keithley 2400 source meter under a simulated AM1.5 illumination (100 mW/cm²) by a Xenon-lamp-based solar simulator (Abet Technologies, USA). The light intensity was calibrated using a Si-reference cell certified by the National Renewable Energy Laboratory.

Supporting Information

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

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References

- [1] T. Liu, K. Chen, Q. Hu, R. Zhu, Q. Gong, *Adv. Energy Mater.* **2016**, 6, 1600457
- [2] a) O. Malinkiewicz, A. Yella, Y. H. Lee, G. M. Espallargas, M. Grätzel, M. K. Nazeeruddin, H. J. Bolink, *Nat. Photon.* **2013**, 8, 128; b) H. Choi, C. K. Mai, H. B. Kim, J. Jeong, S. Song, G. C. Bazan, J. Y. Kim, A. J. Heeger, *Nat. Commun.* **2015**, 6, 7348.
- [3] J. Y. Seo, R. Uchida, H. S. Kim, Y. Saygili, J. Luo, C. Moore, J. Kerrod, A. Wagstaff, M. Eklund, R. McIntyre, N. Pellet, S. M. Zakeeruddin, A. Hagfeldt, M. Grätzel, *Adv. Funct. Mater.* **2018**, 28, 1705763.
- [4] A. E. Shalan, T. Oshikiri, S. Narra, M. M. Elshanawany, K. Ueno, H. P. Wu, K. Nakamura, X. Shi, E. W. G. Diau, H. Misawa, *ACS Appl. Mater. Interfaces* **2016**, 8, 33592.
- [5] a) F. Liu, Q. Li and Z. Li, *Asian J. Org. Chem.* [10.1002/ajoc.201800398](https://doi.org/10.1002/ajoc.201800398); b) W. Q. Wu, Q. Wang, Y. Fang, Y. Shao, S. Tang, Y. Deng, H. Lu, Y. Liu, T. Li, Z. Yang, A. Gruverman, J. Huang, *Nat. Commun.* **2018**, 9, 1625; c) Y. Zhang, X. Hu, L. Chen, Z. Huang, Q. Fu, Y. Liu, L. Zhang, Y. Chen, *Org. Electron.* **2016**, 30, 281.
- [6] S. Sun, T. Salim, N. Mathews, M. Duchamp, C. Boothroyd, G. Xing, T. C. Sum, Y. M. Lam, *Energy Environ. Sci.* **2014**, 7, 399.
- [7] J. Jeng, Y. Chiang, M. Lee, S. Peng, T. Guo, P. Chen, T. Wen, *Adv. Mater.* **2013**, 25, 3727.
- [8] D. Luo, W. Yang, Z. Wang, A. Sadhanala, Q. Hu, R. Su, R. Shivanna, G. F. Trindade, J. F. Watts, Z. Xu, T. Liu, K. Chen, F. Ye, P. Wu, L. Zhao, J. Wu, Y. Tu, Y. Zhang, X. Yang, W. Zhang, R. H. Friend, Q. Gong, H. J. Snaith, R. Zhu, *Science* **2018**, 360, 1442.

- [9] A. F. Eftaiha, J. P. Sun, I. G. Hilland, G. C. Welch, *J. Mater. Chem. A* **2014**, 2, 1201; b) Y. He, H. Y. Chen, J. Hou, Y. Li, *J. Am. Chem. Soc.* **2010**, 132, 1377; c) A. Anctil, C. W. Babbitt, R. P. Raffaele, B. J. Landi, *Environ. Sci. Technol.* **2011**, 45, 2353.
- [10] R. S. Torrientes, J. Pascual, I. G. Benito, S. Collavini, I. Kosta, R. T. Zaera, N. Martin, J. L. Delgado, *ChemSusChem* **2017**, 10, 2023.
- [11] a) F. Wu, W. Gao, H. Yu, L. Zhu, L. Li, C. Yang, *J. Mater. Chem. A* **2018**, 6, 4443; b) Z. Jia, T. Jiu, Y. Li, Y. Li, *Mater. Chem. Front.* **2017**, 1, 2261.
- [12] a) S. K. Jung, J. H. Heo, D. W. Lee, S. C. Lee, S. H. Lee, W. Yoon, H. Yun, S. H. Im, J. H. Kim, O. P. Kwon, *Adv. Funct. Mater.* **2018**, 28, 1800346; b) J. H. Heo, S. C. Lee, S. K. Jung, O. P. Kwon, S. H. Im, *J. Mater. Chem. A* **2017**, 5, 20615.
- [13] a) M. Cheng, Y. Li, P. Liu, F. Zhang, A. Hajian, H. Wang, J. Li, L. Wang, L. Kloo, X. Yang, L. Sun, *Sol. RRL* **2017**, 1, 1700046; b) E. Castro, T. J. Sisto, E. L. Romero, F. Liu, S. R. Peurifoy, J. Wang, X. Zhu, C. Nuckolls, L. Echegoyen, *Angew. Chem. Int. Ed.* **2017**, 56, 14648; c) J. L. Wu, W. K. Huang, Y. C. Chang, B. C. Tsai, Y. C. Hsiao, C. Y. Chang, C. T. Chen, C. T. Chen, *J. Mater. Chem. A* **2017**, 5, 12811; d) J. Miaoa, Z. Hua, M. Liua, M. U. Alib, O. Gotoa, W. Luc, T. Yangc, Y. Liangc, H. Meng, *Org. Electron.* **2018**, 52, 200.
- [14] D. Zhao, Z. Zhu, M. Y. Kuo, C. C. Chueh, A. K. Y. Jen, *Angew. Chem. Int. Ed.* **2016**, 55, 1.
- [15] Z. Zhu, J. Q. Xu, C. C. Chueh, H. Liu, Z. Li, X. Li, H. Chen, A. K. Y. Jen, *Adv. Mater.* **2016**, 28, 10786.
- [16] L. Zhu, C. Song, X. Li, Y. C. Wang, W. Zhang, X. Sun, W. Zhang, J. Fang, *J. Mater. Chem. C* **2017**, 5, 10777.
- [17] F. Jin, C. Liu, F. Hou, Q. Song, Z. Su, B. Chu, P. Cheng, H. Zhao, W. Li, *Sol. Energy Mater. Sol. Cells* **2016**, 157, 510.
- [18] a) Z. Wang, P. Gu, G. Liu, H. Yao, Y. Wu, Y. Li, G. Rakesh, J. Zhu, H. Fu, Q. Zhang, *Chem Comm.* **2017**, 53, 7772; b) P. Gu, Z. Wang, G. Liu, H. Yao, Z. Wang, Y. Li, J. Zhu, S. Li, Q. Zhang, *Chem. Mater.* **2017**, 29, 4172; c) J. Li, S. Chen, Z. Wang, Q. Zhang, *Chem. Rec.* **2016**, 16, 1518; d) J. Wu, X. Rui, G. Long, W. Chen, Q. Yan, Q. Zhang, *Angew. Chem. Int. Ed.* **2015**, 54, 7354; e) C. Wang, P. Gu, B. Hu, Q. Zhang, *J. Mater. Chem. C* **2015**, 3, 10055; f) Y. Wu, Z. Yin, J. Xiao, Y. Liu, F. Wei, K. Tan, C. Kloc, L. Huang, Q. Yan, F. Hu, H. Zhang, Q. Zhang, *ACS Appl. Mater. Interfaces* **2012**, 4, 1883; g) G. Li, Y. Wu, J. Gao, J. Li, Y. Zhao, Q. Zhang, *Chem. Asian J.* **2013**, 8, 1574; h) G. Li, H. M. Duong, Z. Zhang, J. Xiao, L. Liu, Y. Zhao, H. Zhang, F. Huo, S. Li, J. Ma, F. Wudl, Q. Zhang, *Chem. Comm.* **2012**, 48, 5974; i) C.

Wang, J. Wang, P. Li, J. Gao, S. Tan, W. Xiong, B. Hu, P. S. Lee, Y. Zhao, Q. Zhang, *Chem Asian J.* **2014**, 9, 779.

[19] a) N. Wang, K. Zhao, T. Ding, W. Liu, A. S. Ahmed, Z. Wang, M. Tian, X. Sun, Q. Zhang, *Adv. Energy Mater.* **2017**, 7, 1700522; b) P. Gu, N. Wang, A. Wu, Z. Wang, M. Tian, Z. Fu, X. Sun, Q. Zhang, *Chem. Asian J.* **2016**, 11, 2135; c) P. Gu, N. Wang, C. Wang, Y. Zhou, G. Long, M. Tian, W. Chen, X. Sun, M. G. Kanatzidis, Q. Zhang, *J. Mater. Chem. A* **2017**, 5, 7339; d) D. B. Shaikh, A. A. Said, R. S. Bhosale, W. Chen, S. V. Bhosale, A. L. Puyad, S. V. Bhosale, Q. Zhang, *Asian J. Org. Chem.* 10.1002/ajoc.201800385; e) P. Gu, N. Wang, A. Wu, Z. Wang, M. Tian, Z. Fu, X. W. Sun, Q. Zhang, *Chem. Asian J.*, **2016**, **11**, 2135.

[20] a) W. Wang, J. Yuan, G. Shi, X. Zhu, S. Shi, Z. Liu, L. Han, H. Q. Wang, W. Ma, *ACS Appl. Mater. Interfaces* **2015**, 7, 3994; b) Z. Zhu, C. C. Chueh, G. Zhang, F. Huang, H. Yan, A. K. Y. Jen, *ChemSusChem* **2016**, 9, 2586; c) W. Chen, Q. Zhang, *J. Mater. Chem. C* **2017**, 5, 1275.

[21] H. I. Kim, M. J. Kim, K. Choi, C. Lim, Y. H. Kim, S. K. Kwon, T. Park, *Adv. Energy Mater.* **2018**, 8, 1702872.

[22] a) T. Jia, C. Sun, R. Xu, Z. Chen, Q. Yin, Y. Jin, H. L. Yip, F. Huang, Y. Cao, *ACS Appl. Mater. Interfaces* **2017**, 9, 36070; b) S. Shao, Z. Chen, H. H. Fang, G. H. ten Brink, D. Bartesaghi, S. Adjokatse, L. J. A. Koster, B. J. Kooi, A. Facchetti, M. A. Loi, *J. Mater. Chem. A* **2016**, 4, 2419; c) C. Sun, Z. Wu, H. L. Yip, H. Zhang, X. F. Jiang, Q. Xue, Z. Hu, Z. Hu, Y. Shen, M. Wang, F. Huang, Y. Cao, *Adv. Energy Mater.* **2016**, 6, 1501534.

[23] Y. Wang, T. Hasegawa, H. Matsumoto, T. Mori, T. Michinobu, *Adv. Mater.* **2018**, 30, 1707164.

[24] a) F. H. Isikgor, B. Li, H. Zhu, Q. Xu, J. Ouyang, *J. Mater. Chem. A* **2016**, 4, 12543; b) X. Sun, C. Zhang, J. Chang, H. Yang, H. Xi, G. Lu, D. Chen, Z. Lin, X. Lu, J. Zhang, Y. Hao, *Nano Energy* **2016**, 28, 417.

Figure 1. Structures of the three n- type polymers: pBTT, pBTTz and pSNT.

Figure 2. Device architecture of inverted PSCs fabricated in this work.

Figure 3. Energy levels diagram of each layer used in this work.

Figure 4. PL characteristic of bare perovskite, perovskite/PCBM bilayer, perovskite/pBTT bilayer, perovskite/pBTTz bilayer and perovskite/pSNT bilayer.

Figure 5. TRPL of bare perovskite, perovskite/pBTTz bilayer and perovskite/PCBM bilayer.

Figure 6. I-V curves of pBTT, pBTTz, pSNT and PCBM-based devices under dark conditions.

Figure 7. J-V curves of PSCs with different concentrations of pBTTz as ETLs.

Figure 8. EQE of champion pBTTz-based perovskite solar cell

Figure 9. Distribution of pBTTz-based PSCs efficiency.

Figure 10. J-V curves of pBTTz-based devices with different heat treatment temperature.

Figure 11. J-V hysteresis curves of pBTTz-based devices.

Figure 12. Stability test diagram of pBTTz-based device and PCBM-based device.

Table 1. TRPL calculated amplitudes A_1 , A_2 and lifetimes τ_1 , τ_2 from **Figure 5**

	A_1	τ_1 (ns)	A_2	τ_2 (ns)
Bare perovskite	9590	220.98	-----	----
Perovskite/pBTTz	10446	1.77	6798	22.61
Perovskite/PCBM	16904	3.96	42219	40.04

The **sp²-nitrogen positions** in the n-type (D-A₁-D-A₂) conjugated polymers have a significant impact on the photovoltaic properties of inverted perovskite solar cells when they are used as an electron transport layer. pBTTz with the HOMO and LUMO levels well-matched with the valence and conduction bands of the perovskite layer, respectively, shows the excellent photoconversion efficiency and high stability.

Keyword. organic transporting layers, n-type polymers, inverted perovskite solar cells, stability of devices

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Efficient Inverted Perovskite Solar Cells by Employing N-Type (D-A₁-D-A₂) Polymers as Electron Transporting Layer

Supporting Information

**Efficient Inverted Perovskite Solar Cells by Employing N-Type (D-A₁-D-A₂)
Polymers as Electron Transporting Layer**

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Figure S1. XRD of the perovskite layer.

Figure S2. SEM of the perovskite layer.

Figure S3. a) UV-visible spectroscopy of the perovskite layer, b) Tauc plot of perovskite layer and extracted band gap

Figure S4. AFM images of (a) pBTT, (b) pBTTz and (c) pSNT.

Figure S5. (a) J-V curves of PSCs with different concentrations of pBTT as ETLs. (b) Distribution of PSCs efficiency.

Figure S6. (a) J-V curves of PSCs with different concentrations of pSNT as ETLs. (b) Distribution of PSCs efficiency.

Figure S7. Contact angle of the surface of (a) PCBM, (b) pBTT, (c) pBTTz and (d) pSNT.

Table S1. Effect of polymer concentrations on photovoltaic parameters of devices.

Polymer-based devices	Concentration (mg/1 ml DCB)	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)
pBTT	3	0.88	21.2	57.4	10.7
	5	0.88	22.5	64.4	12.8
	8	0.89	18.5	54	8.9
pBTTz	3	0.90	20.60	60.4	11.2
	5	0.91	21.95	72.3	14.4
	8	0.90	20.75	54.6	10.2
pSNT	3	0.88	18.1	56.2	9
	5	0.88	20.5	66.5	12
	8	0.90	18.6	53.1	8.9

Table S2. Effect of heat treatment on the photovoltaic parameters of pBTTz- based devices.

Polymer-based devices	Heat treatment temperature (°C)	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)
pBTTz	80	0.93	20.6	66.8	12.8
	90	0.93	21.1	69.3	13.6
	100	0.91	21.95	72.3	14.4

Table S3. Photovoltaic parameters of pBTTz-based devices under reverse and forward scan.

Polymer-based devices	Scan direction	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)
pBTTz	Reverse Scan	0.91	21.95	72.3	14.4
	Forward Scan	0.90	21.88	71.4	14.0