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As a pump for extracting carriers from the absorber to the cathode, hole transporting material (HTM) has indispensable meanings to promote the power conversion efficiencies (PCE) of perovskite solar cells (PSCs). In this context, we present two simple HTMs using a 2,2'-(1,2-phenylene) bisthiophene or a naphtha[1,2-b:4,3-b'] dithiophene as π -bridges to link two electron-donor (4',4''-dimethoxytriphenylamine): PBT and NDT. Their frontier molecular orbital energies match with that of perovskite well as is consistent to the DFT calculation results. The PCE measured under mimetic solar illumination (AM 1.5, 100 mW·cm⁻²) increases from 13.6% (PBT) to 18.8% (NDT), which surpass that of spiro-OMeTAD (18.1%) reference. The modified annulated core in NDT make it perform better in photovoltaic conversion ability than PBT. The reason for this is discussed from aspects of hole mobility, charge collection probability (Pc) and recombination kinetics.

Introduction

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Intense light-absorption, narrow exciton binding energy, high chargecarrier mobility, long diffusion length, low-cost fabrication and the skyrocketing power conversion efficiencies (PCE) based on these advantages have attracted abroad attention to organic-inorganic halide perovskite solar cells (PSCs).1 Historic breakthroughs were made since the first demonstration on a solid-state PSC in 2012 by Park's group² with long-term stability and a PCE of 9.7%, and a prominent PCE of 15.0% was demonstrated by Grätzel's group³ in 2013. The best-performing devices configuration for PSCs comprises an active perovskite layer sandwiched between an electron transporting material (ETM) and a hole transporting material (HTM), and this is also commonly used in PSCs' fabrication procedure.⁴ In addition to intrinsic opto-electronic properties of perovskite layer, as a pump for extracting carriers from the absorber to the cathode, HTM play an essential role in promoting PCEs of PSCs quickly to increase from 3.8 to a certified 22.1%.^{1a,5}

With well-matched frontier molecular orbital energies, sufficient hole mobility, simplicity and convenience in film-fabrication, and

9,9'-spirobiuorene which was abbreviated as spiro-OMeTAD stands out from the crowd, becoming one kind of commercial and the most popular HTM for efficient PSCs.⁶ For example, Snaith and coworkers⁷ showed a maximum PCE of 15.4% in 2013, based on CH₃NH₃PbI_{3-x}Cl_x deposited as thin layers with spiro-OMeTAD as the hole conductor, and a PCE as high as 19.3% was reported by Yang and his co-workers⁸ in 2014. However, complicated synthesis, difficult purification, and environmental instability seriously limit the commercial applications of spiro-OMeTAD to PSCs.⁹ In such situations, to develop low-cost and effective HTMs for PSCs is a challenging and investigation with far-reaching significates.¹⁰ Recently, lots of simple triphenylamine-based HTMs in typical donor- π -donor structure employing π -linkers such as thiophene,¹¹ carbazole,12 triazatruxene,13 3,4-ethylenedioxythiophene14 and so on have been developed for PSCs. It has been predicted by theoretical



| Fig. 1 Chemical structures of PBT, NDT and thermal ellipsoid plot of the X |
|---|
| ray single-crystal structure of NDT (probability: 50%). Atom colour code: C |
| grey; N, blue; S, yellow; O, red. |



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Fig. 2 (a) Thermogravimetric analysis of PBT and NDT at a scan rate of 10 °C/min. (b) DSC of PBT and NDT with a scan rate of 20 °C/min. (c) UPS spectrum of PBT, and NDT films on Si substrates. (d) Normalized UV-visible spectra of PBT, NDT, and spiro-OMeTAD films, at ambient temperature. (e) HOMO and LUMO energies of PBT and NDT calculated by DFT at the B3LYP/6-31G*/CPCM level and their electron density distribution of HOMO and LUMO in CH_2CI_2 . (f) Relative energy levels diagram of each component in PSCs.

calculation that HTMs with planar cores performed better in the PCEs of PSCs than HTMs with no planar cores.¹⁵ More than one thiophthene derivative¹⁶ have been reported to own higher hole mobility than spiro-OMeTAD, making them to be promising competitors and alternatives to spiro-OMeTAD.

In present work, we introduce two simple HTMs using a 2, 2'-(1,2-phenylene)bisthiophene or a naphtha[1,2-b:4,3-b']dithiophene as π -bridges to link two electron-donor units (4',4''dimethoxytriphenylamine) which are denoted as PBT and NDT as shown in Fig. 1. Ultroviolet photoelectron spectroscopy (UPS), hole mobility and opto-electronic properties including PCE, incident photon-to-current efficiency (IPCE), photoluminescence (PL) in PSCs, charge collection probability (Pc) and recombination kinetics were found to be intensely related to the different π -bridge between the donor groups. With the annulated core of naphtha[1,2-b:4,3b']dithiophene, NDT tends to stack through strong π - π and O- π interactions and leads to excellent hole mobility and performance in PSCs.

Results and discussion

Synthesis

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Thiophene-triphenylamine based derivatives, PBT and NDT were

synthesized through straightforward Suzuki-Miyaura crosscouplings¹⁷ with high yields (for PBT, 68%; NDT, 79%) by binding the suitable donor groups (4',4''-dimethoxytriphenylamine) to a 2,2'-(1,2- phenylene)bisthiophene or a naphtha[1,2-b:4,3-b']dithiophene core (Scheme 1), which can be obtained in a simple synthetic route starting from commercial products, and the synthesis details are in the



Scheme 1. Synthetic Route for Obtaining PBT and NDT: (a) 2-(tributylstannyl)thiophene, Pd(PPh₃)Cl₂, DMF, 130 °C; (b) NBS, CHCl₃/AcOH, 0 °C to RT; (c) DDQ, BF₃OEt₂, dry CH₂Cl₂, 0 °C to RT; (d) 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-

dioxaborolan-2-yl)phenyl) aniline, Pd(PPh_3)_4, 2M K_2CO_3, THF/H_2O (10 : 1), reflux.

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| Table 1 | Electrochemical | and photoph | nysical data | of spiro-OMeTAD | PBT and NDT |
|---------|-----------------|-------------|--------------|-----------------|-------------|
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| | | - | - | | | DO | I: 10.1039/C8TA02071 |
|--------------|---------------------------------------|--------------------------|--------------------------|-----------------|---------------------------------|-------------------------------|---------------------------------|
| Compound | $E_{\text{HOMO, exp}}^{a}(\text{eV})$ | Abs _{peak} (nm) | Abs _{edge} (nm) | $E_{g}^{b}(eV)$ | $E_{\text{LUMO, exp}}^{c}$ (eV) | $E_{\rm HOMO, cal}^{d}$ (eV) | $E_{\text{LUMO, cal}}^{d}$ (eV) |
| РВТ | -5.23 | 367 | 450 | 2.76 | -2.47 | -4.69 | -1.39 |
| NDT | -5.32 | 386 | 445 | 2.79 | -2.53 | -4.72 | -1.42 |
| Spiro-OMeTAD | -5.1218 | 305, 384 | 417 | 2.97 | -2.15 | -4.16 ¹⁸ | -0.54 ¹⁸ |

^aDetermined from UPS measurements. ^bThe absorption edges of films determined the $E_{g.}$ ^c $E_{LUMO, exp} = E_{HOMO, exp} + E_{g.}$ ^dDFT-calculated energies of HOMO and LUMO at the B3LYP/6-31G*/CPCM level of theory including solvent effects (CH₂Cl₂).

supplementary information (SI). The PBT central core (3, dibrominated derivative) was prepared by Stille cross coupling¹⁸ between commercially available 1,2-dibromo-4,5-dimethoxybenzene and 2-(tributylstannyl)thiophene, followed by a bromination employing N-bromosuccinimide (NBS). The subsequent dichlorodicyano-p-benzoquinone (DDQ)/acid-mediated oxidative cyclization¹⁹ of compound 3 gives rise to the formation of the π extended NDT central core under a mild synthetic condition. All the above steps have ideal yields, and the intermediate products can be obtained by sample recrystallization without further purification. The overall yields from compound 1 to PBT and NDT are 55% and 59%, respectively, and the estimated cost are 98.1 and 78.8 \$/g for PBT and NDT, respectively, which are much lower than the purchased spiro-OMeTAD (\approx 271.4 \$/g). Molecular structure of the two new HTMs were confirmed by ¹H and ¹³C (400 MHz) nuclear magnetic resonance (NMR), and high resolution mass spectra (HRMS).

X-ray Crystallography

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More importantly, the single crystal X-ray structure of NDT showing an obvious annulated core has been determined (Fig. 1). Slow volatilization of a CH₂Cl₂ solution help us obtained the single crystal of NDT. Crystallographic data for NDT (CCDC 1814908): C₅₆N₂O₆S₂, space group P-1(2), triclinic, a = 11.237(2), b = 12.606(3), c = 19.298(4) Å, $\alpha = 90.32^{\circ}$, $\beta = 95.79^{\circ}$, $\gamma = 109.07^{\circ}$, U = 2568.5 (10) Å.

Thermomechanical analysis

As the thermogravimetric analysis (TGA) data (Fig. 2a) showing, NDT exhibits an excellent thermal stability and start decomposing at temperatures (T_d) at 435 °C, while the T_d for PBT is 332 °C. When PBT presents a melting temperature (T_m) of 175 °C (Fig. 2b), the differential scanning calorimetry (DSC) of NDT reveals a crystalline behavior with a T_m of 213 °C and there is no an obvious cooling crystallization temperature (T_{cr}) in the cooling progress (Fig. S1a). No melting and cooling crystallized phenomenon in the second heat/cool cycle both for PBT and NDT, too (Fig. S1).

Experimental and calculated energy levels of HTMs matching with perovskite

Determination of the highest-occupied molecular orbital (HOMO) energy levels of organic molecules by ultroviolet photoelectron spectroscopy (UPS) is a common and more reliable method.²⁰ As shown in Fig. 2c, the valance band (VB) spectra of PBT and NDT were measured with a monochromatic He I light source (21.2 eV) and

a VG Scienta R4000 analyzer. The valence band energies (Ev_B) corresponding to HOMO energy levels of PBT and NDT are estimated to be -5.23 and -5.32 eV below vacuum level, respectively (Table 1), which are coincident located between the HOMO of perovskite (CH₃NH₃PbI₃, -5.43 eV) and the valence-band maximum of Au electrode (-5.10 eV), indicating that they have appropriate energy levels to extract the hole from perovskite (CH₃NH₃PbI₃) to the Au electrode like pumps. The π -conjugation effect from annulated cores in NDT leads to its 0.09 eV lower in *E*_{HOMO} than PBT.²¹

According to the normalized UV-vis absorption spectra in Fig. 2d (Table 1), films of PBT, NDT and spiro-OMeTAD on ITO substrates show their maximum absorption wavelength (λ_{max}) at 367 nm, 386 nm and 384 nm, respectively. We can attribute the bathochromic responding in spectrum to the enhancement of the conjugation in NDT by the annulated core.²² The emission maximum of PBT, NDT and spiro-OMeTAD are located at 482 nm, 502 nm and 421 nm, respectively. The correspondent transition energy which also called energy gaps (E_g) are estimated to be 2.76, 2.79 and 2.97 eV for PBT, NDT and spiro-OMeTAD respectively, with their absorption edges are located at 450, 445 and 387 and 417 nm, respectively. Therefore, based on the experimental E_{HOMO} and E_{g} , the lowest unoccupied molecular orbitals (LUMOs) energy levels of PBT and NDT are calculated to be -2.47 and -2.53 eV (Fig. 2f), meeting requirements that to be higher than the conduction band edge of CH₃NH₃PbI₃ (-3.93 eV). We listed all the experimental and calculated values in Table 1.

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Fig. 3 (a) Current (*J*)–voltage (V) curves of the solar cells with PBT, NDT, and spiro-OMeTAD under 1 sun (AM 1.5, 100 mW·cm⁻²) with a scan rate of 20 mV/s⁻¹. (b) Incident photon-to-electron conversion efficiency (IPCE) for the PSCs in (a). (c) The statistics of PCE distribution for devices with HTMs of PBT, NDT, and spiro-OMeTAD under ambient conditions. 30 devices were fabricated for each tests. (d) A cross-sectional SEM image of a full cell of NDT (the perovskite absorber is around 600 nm). (e) Continuous wave (CW) photoluminescence (PL) spectra, excitation at 600 nm. (f) Time-resolved PL spectra for the pristine perovskite (PVSK) film and perovskite/HTM bilayer, excitation at 445 nm and monitored at 765 nm.

| Table 2 Photovoltaic parameters of the PSCs based on three HTMs and HTMs' hole mobilities | | | | | | | | | |
|---|------------------------|--|-------------------------------------|---|-----------|---------------------------------------|------------|--|--|
| Compound | V _{oc} (V) | V _{OCavg} ^a (V) | $J_{\rm SC}$ (mA·cm ⁻²) | $J_{\rm SCavg}{}^a$ (mA·cm ⁻²) | FF (%) | FF _{avg} ^a (%) | PCE (%) | PCE _{avg} ^a (%) | Hole mobility ^b (cm ² /V/s) |
| PBT | 1.06 | 0.97 | 16.53 | 14.83 | 63 | 57 | 13.56 | 11.03 | $9.736	imes10^{-4}$ |
| NDT | 1.11 | 1.05 | 23.47 | 21.52 | 74 | 70 | 18.78 | 16.25 | $5.101	imes10^{-3}$ |
| Spiro-OMeTAD | 1.09 | 1.04 | 22.21 | 20.35 | 73 | 68 | 18.05 | 16.13 | $4.243\times10^{\text{-3}}$ |

^aAverage V_{OC}, J_{SC}, FF and PCE obtained from 30 identical devices of each HTM under the same condition. ^bHole mobility was calculated by the SCLCs method using the Mott-Gurney law.

Density functional theory (DFT) calculations were employed to evaluate the HOMOs and LUMOs of the two new HTMs in theory aspect. As shown in Fig. 2e, the orbital density in the HOMOs of PBT (-4.69 eV) and NDT (-4.72 eV) are delocalized in the whole molecule, whereas the orbital density of the LUMOs of PBT (-1.39 eV) and NDT (-1.42 eV) are mainly localized on the bridge groups. Similar donor- π -donor structure of PBT and NDT leads to their similar orbital density, which is agrees with the similarity of photophysical and electrochemical properties.

Photovoltaic conversion

Devices in the configuration of ITO/SnO₂/CH₃NH₃PbI₃/HTM/Au as shown in Fig. 3d were fabricated to investigate the performance of PSCs employing PBT and NDT as HTM which was measured under 1 sun irradiation, when devices with spiro-OMeTAD were fabricated

as the reference. Fig. 3a displays the current density-voltage (*J*-V) curves (forward: from -0.2 to 1.2 V) of the PSCs prepared with PBT, NDT and spiro-OMeTAD as HTMs. The corresponding photovoltaic parameters of devices are listed in Table 2. It can be observed that NDT based device has the best performance with a power conversion efficiency (PCE) above 18.7%, a short-circuit currents (*J*_{SC}) of 23.47 mA·cm⁻², an open-circuit voltage (V_{oc}) of 1.11 V, and a fill factor (FF) of 74%, which are all slightly higher than that of reference (spiro-OMeTAD with a PCE of 18.1%), indicating that NDT can act as a promising HTM for PSCs. PBT based PSCs show a PCE of 13.6% under the same conditions. The statistical data of the PSCs based on 30 uniform devices with each HTM are shown in Fig. 4c, and the average PCE values of the PSCs employing PBT, NDT and spiro-OMeTAD as HTMs are 11.03%, 16.25%, and 16.13%, respectively. Average values of *J*sc, FF, and Voc in Figure 3c are also listed in

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Table 2. As shown in Fig. S2, *J*-V curves of the devices were measured by different voltage scan directions (forward and reverse) with a 20 mV/s⁻¹ scan rate. Although they all have relatively large hysteresis, hysteresis of the devices based on NDT is the smallest among these three kinds of PSCs, indicating the least trap states in NDT based devices.^{1d, 23} It can be seen that the open-circuit voltages of devices based on different HTMs are quite similar while the performance of the devices employing NDT as HTM improved remarkably due to the increased *J*_{SC} and FF.

The solar cells' incident photon-to-current efficiency (IPCE) spectra which are fabricated with PBT, NDT and spiro-OMeTAD are also compared with each other in Fig. 4b. The integrated photocurrent densities of PBT, NDT and spiro-OMeTAD were shown to be 22.66, 21.34 and 16.77 mA·cm⁻², respectively, which are well consistent with the measured photocurrent density (Table 2). In a broad spectral scope from 400 to 750 nm, IPCE of NDT and spiro-OMeTAD based devices exceed 75%, and reach to a maximum 85% (600 nm). Conversely, the device employing PBT as HTM showed a rather poor IPCE (65%). Thus, the enhancement in J_{SC} and FF of NDT can be attribute to the better optical absorption.²⁴

Photoluminescence (PL) and time-resolved photoluminescence (TRPL) DOI: 10.1039/C8TA02071J

To further explore the advantage of the modified annulated core in NDT on carriers' transfer at the perovskite/NDT interface, we measured the continuous wave (CW) photoluminescence (PL, Fig. 4e) and time-resolved photoluminescence (TRPL, Fig. 4f) with the device structure ITO/perovskite/HTM/Au. It is noted that the bilayer of perovskite/NDT show an estimate dramatic quenching value of 90% when the quenching value of perovskite/HTM bilayer film are estimate 80% and 65% for spiro-OMeTAD and PBT. The comparison of the TRPL decay at 770 nm between the bilayers and the bare perovskite deposited on glass is showed in Fig. 4f. The estimated PL decay time τ_e values are 15.3 ns for pure perovskite, 6.1 ns for perovskite/NDT, respectively. The PL and TRPL results demonstrate that the modified annulated core of NDT is beneficial to hole transfer which may promote the PCE of PSCs directly.

Hole mobility analysis

The hole-transport ability of PBT, NDT and spiro-OMeTAD was



Fig. 4 (a) *J*-*V* curves obtained from the hole-only ITO/PEDOT:PSS/HTM (PBT, NDT, spiro-OMeTAD)/Au device. (b) Crystal packing diagrams of the single crystals of NDT: $\pi \cdots \pi$ distance of 3.34 Å, $O \cdots \pi$ distance of 3.56 Å. (c) Charge collection probability *VS*. internal voltage on a log-log scale for PSCs (with PBT and NDT). (d) *J*_{SC} of PSCs (with PBT and NDT) *VS*. light intensity on a log-log scale. (e) *V*_{OC} of PSCs (with PBT and NDT) *VS*. light intensity on a log-log scale. (e) *V*_{OC} of PSCs (with PBT and NDT) *VS*. light intensity on a log-log scale.

measured by space-charge-limited current (SCLC) technique (Fig. 3a) with the device structure ITO/PEDOT:PSS/HTM/Au, and the hole mobility was calculated using the Mott-Gurney law.^{1d, 25} Detailed introduction to Mott-Gurney law and the hole-only devices' fabrication are in the supporting information. For PBT, NDT and spiro-OMeTAD, the thickness are 190, 210 and 230 nm respectively, which are measured by the step profiler. The hole mobility values of

different HTMs are summarized in Table 2, and the NDT film exhibits a hole mobility of $4.9 \times 10-3 \text{ cm}^{2} \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ which is much higher than PBT's $9.8 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ when spiro-OMeTAD exhibits a hole mobility of $4.2 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. The higher hole mobility of NDT can be attributed to its intrinsic crystal structures and layer-by-layer stacking geometry.²⁶ From two adjacent crystal cells of NDT, two π - π stacking with distances of 3.34 Å between two NDT molecules in

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one cell and two $O-\pi$ interactions with distances of 3.56 Å between two close cells are measured (Fig. 3b). This indicates that the annulated core is beneficial to NDT's intermolecular interactions leading to a higher hole mobility, and predicts NDT could be a kind of effective HTM for high efficient PSCs with the matching frontier molecular orbital energy.

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Charge collection probability (Pc) and recombination kinetics

Only the higher hole mobility of NDT actually can't give an absolute explanation for the better photovoltaic conversion ability than PBT. Thus, under illumination at 100 mW/cm⁻², we examined charge collection probability (Pc) versus internal voltage (Vint)²⁴ of devices (Fig. 4c) based on NDT and PBT where

$$Pc = J_{ph}/J_{ph,sat}$$
(1)

$$V_{int} = V_{bi} - V_{applied} \tag{2}$$

in which the photocurrent density $J_{\rm ph} = J_{\rm L} - J_{\rm D}$ ($J_{\rm L}$ and $J_{\rm D}$ are the current density under illumination and in the dark), the built-in potential (V_{bi}) is the voltage when $J_L = J_D$, and the V_{applied} is the applied voltage.²⁷ The saturated photocurrent $(J_{ph,sat})$ is the J_{ph} value when J_{ph} saturates at high V_{int} (2 V).^{5a} V_{bi} for NDT and PBT based devices are 1.18 and 1.20 V, respectively. The values with no obvious difference in V_{bi} can be attribute to the similarity in HOMO levels of two HTMs. As shown in Fig. 4c, better charge extraction ability of NDT can be judged because of the NDT's Pc increases from PBT's 93.2% to 97.5% at short-circuit condition.

Study the recombination kinetics in HTMs of devices based on different HTMs by measuring Jsc and Voc with respect to gradually varied light intensities (from 100 to 1 mW/cm⁻²) on a log-log scale can give us another viewpoint to compare charge extraction or transfer ability of NDT and PBT.²⁸ The dependence of J_{SC} upon illumination intensity (I) follows the power law which is generally expressed as

$$J_{\rm SC} \propto I^{\alpha}$$
 (3)

where $\alpha = 1$ for both PBT and NDT based PSCs, as shown in Fig. 4d, indicating that, at short-circuit condition, almost all holes are swept out before recombination.5a, 27a

As all carriers would recombine in the PSCs at open-circuit conditions, charge recombination near open-circuit is usually researched to reveal the recombination mechanism.^{27a, 29} To the function of Voc versus light intensity on a log-log scale, the slopes for PBT and NDT based PSCs (Fig. 4e) are 1.9 and 1.6 kT/e (k is the Boltzmann constant, T is temperature in Kelvin, and e is the elementary charge), respectively. The slope values are higher than kT/e, implying the Voc is dependent on light intensity tightly and the recombination includes not only a bimolecular recombination mode but also a monomolecular mode which is defined as Shockley-Read-Hall (SRH) through a trap state.³⁰ The slope is much greater than that of NDT-based PSCs, indicating that the monomolecular recombination mode is dominant for PBT-based PSCs at open circuit. This result also demonstrates less trap states exist in the interface of NDT and the perovskite film which is related to the higher V_{OC} and smaller hysteresis in NDT-based PSCs (Fig. 3a).^{5a}

Conclusions

We demonstrated two new hole transporting materials in donor. constitution, PBT and NDT, Dusing1032/C87,202(97,21 donor phenylene) bisthiophene or a naphtha[1,2-b:4,3-b'] dithiophene as π bridges to link two electron-rich triphenylamine units (4',4"dimethoxytriphenylamine). They have similar matching frontier molecular orbital energies to perovskite layer which conforms to DFT calculation results well. The annulated core of NDT make it perform better in thermal properties, hole mobility and photovoltaic conversion in PSCs than PBT. The PCE which was measured under simulated solar illumination (AM 1.5, 100 mW·cm⁻²) increases from 13.6% (PBT) to a marvelous 18.8% (NDT), a value which is superior to the 18.1% of spiro-OMeTAD. Charge collection probability (Pc) of PBT and NDT, and their recombination kinetics by measuring Jsc and Voc at various light intensities were also compared to demonstrate that the optimization of π -bridge in HTMs is beneficial to the performance of PSCs by improving charge extraction and holetransport within the device.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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