Dopant-free F-substituted benzodithiophene copolymer hole-transporting materials for efficient and stable perovskite solar cells

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Polymeric hole-transporting materials (HTMs) with low production cost and versatile wet processing procedures are important for efficient and stable perovskite solar cells. In this study, three F-substituted benzodithiophene copolymers were introduced in perovskite solar cells as dopant-free efficient HTMs. Among them, perovskite solar cells based on dopant-free PBDT[2F]T achieved a comparable power conversion efficiency (PCE) (17.52%) to that of the well-known p-type doped spiro-OMeTAD (~20.2%). More importantly, the solar cells with pristine PBDT[2F]T HTMs presented impressive stability in contrast to that with doped spiro-OMeTAD as the HTM in ambient atmosphere and even in high humidity. The detailed study showed that the dopant-free PBDT[2F]T HTM presents exceptional ability to extract holes from the perovskite layer, and simultaneously the capability to reduce trap-assisted recombination at the interface of perovskite/PBDT[2F]T. These findings pave the way for the development of dopant-free polymeric HTMs for the fabrication of cost-effective and stable perovskite solar cells.

Introduction

Organic–inorganic hybrid perovskite solar cells (PSCs), as one of the most promising alternative energy sources, have attracted widespread research attention due to their simplicity, low-cost and fast-growing power conversion efficiency (PCE). The PCEs of PSCs were enhanced from 3.8% in 2009 to recently a certified 25.2% which is mainly due to the great efforts on device structure optimization and new material exploration. In the state-of-the-art PSCs, the light-absorbing perovskite layer is sandwiched between an electron-transporting material (ETM) and a hole-transporting material (HTM). In particular, the HTM plays a key role in extracting and transporting photogenerated holes from the perovskite to contact electrodes as well as suppressing charge recombination. Although HTM-free PSCs have been proposed, their PCEs are far below that of HTM PSCs, suggesting the indispensability of hole-transporting materials for high-efficiency PSCs.

A wide range of HTMs, including organic and inorganic materials, have been studied recently. Among them, 2,2'-7,7'-tetrakis-(N,N'-di-p-methoxyphenylamine)-9,9'-spirobi-fluorene (spiro-OMeTAD) is the most commonly used and has been commercialized. However, due to the rather tedious procedures for the synthesis and purification of spiro-OMeTAD, its production cost is quite expensive. Moreover, to enhance its electrical conductivity and hole mobility, pristine spiro-OMeTAD requires additional dopants, such as bis(trifluoromethane) sulfonimide lithium (LiTFSI), which can adversely accelerate device degradation due to its high hygroscopicity and migration of Li⁺ into the perovskite layer.

Aiming to bypass these drawbacks, polymeric and small molecular HTMs have been well utilized in perovskite solar cells. With respect to some small molecules, dopant-free HTMs have recently been reported with a comparable PCE and stability to that of doped spiro-OMeTAD HTMs. However, polymers, have been much less explored than small molecules as HTMs in perovskite solar cells, albeit they offer excellent properties, such as cost effectiveness and thermal stability, and most of exhibit superb performances in OPVs and OLEDs. One of the best known polymeric HTMs is poly[bis(4-
phenyl)(2,4,6-trimethylphenyl)-amine] (PTAA). However, although PTAA gives a PCE up to 22.1% and shows improved stability at higher temperatures, its high cost and dopant requirement obviously limit its large-scale production and long-term stability. Simultaneously, mostly reported PCEs based on pristine polymer HTMs are at a low level, with only a few examples up to 19%, due to their limitation of hole mobility. Therefore, it is of great importance to develop dopant-free polymeric HTMs for achieving more affordable and stable PSCs.

The fluorination of π-conjugated polymer backbones has been proven to be a particularly effective strategy in the design of p-type and high hole mobility polymers. A broader consensus emphasizes that F-substituted p-type polymers are prone to adopt planar backbone conformations, favorable electronic coupling patterns, and preferential polymer backbone face-on orientations with respect to the substrate, which are the essential properties for efficient polymer HTMs. Previously, Beaujuge et al. reported a set of wide-bandgap polymers composed of benzo[1,2-b:4,5-b’]dithiophene (BDT), and thienyl (2H)[T] or 3,4-difluorothiophene (2F)[T] motifs as donor materials for polymer solar cells with PCEs of more than 9.8%. These F-substituted polymers, PBDT[2F][T] and PBDT(T)[2F][T], presented many desirable merits, for example, the appropriate HOMO energy levels of 5.29 eV and LUMO energy level of 3.19 eV, high hole mobility of (9.2 ± 0.4) × 10^{-6} cm² V^{-1} s^{-1} and good film formability, and thus, may be good HTM candidates and can be examined in perovskite solar cells.

In this study, we explored the abovementioned materials as alternative HTMs for high-efficiency and stable perovskite solar cells. We used three pristine, dopant-free copolymers, PBDT[2F][T], PBDT[2H][T] and PBDT(T)[2F][T] (structures in Fig. 1a) as HTMs and fabricated n–i–p type planar PSCs. Among them, PBDT[2F][T] as an HTM delivered a decent PCE of 17.52%. Systematic studies showed that PBDT[2F][T] as an HTM exhibits excellent ability in extracting holes, simultaneously passivating surface traps, making it a good competitor of doped spiro-OMeTAD. In addition, the hydrophobic nature of PBDT[2F][T] endows the corresponding PSCs with better ambient stability (91.34% after 16 days) compared with that based on doped spiro-OMeTAD (64.87% after 16 days).

**Results and discussion**

The chemical structures and photographs of PBDT[2H][T], PBDT[2F][T] and PBDT(T)[2F][T] are shown in Fig. 1a and b, respectively, which have the typical conjugated characteristics. The energy level diagrams of these polymers and each layer in the PSCs are presented in Fig. 1c, showing energetic compatibility with CH3NH3PbI3 and Ag electrode. Fig. 1d displays the cross-sectional scanning electron microscopy (SEM) image of the cell, illustrating that the thickness of SnO2, perovskite, HTM and Ag is about 40, 400, 30 and 80 nm, respectively. Since the thickness of the HTM has a significant influence on the device performance, the thickness of the spin-coated HTM film was confirmed using a profilometer to be 30 nm (Fig. S2b and c in the ESI†).

The optical and electronic properties of the three HTMs are presented in Table S1 in the ESI, which were discussed in previous publications. The thermal properties of PBDT[2H][T], PBDT[2F][T] and PBDT(T)[2F][T] were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (shown in Fig. S1a in the ESI†). The TGA...
results indicate that PBDT[2F]T shows higher thermal stability than that of PBDT(T)[2F]T and PBDT[2H]T. The corresponding decomposition temperatures ($T_d$) (410°C, 318°C and 366°C for PBDT[2F]T, PBDT[2H]T and PBDT(T)[2F]T, respectively) and the glass transition temperature ($T_g$) (138.5°C, 131.5°C and 90.7°C for PBDT[2F]T, PBDT[2H]T and PBDT(T)[2F]T, respectively) (Fig. S1b in ESI†) obviously indicate that PBDT[2F]T has a more stable morphology than others, which will be definitely favorable for the corresponding solar cells.

Fig. 2a shows the current density–voltage ($J$–$V$) of the optimized solar cells with the three HTMs, and that with the commercialized spiro-OMeTAD, measured under AM 1.5 G irradiation at 100 mW cm$^{-2}$. The concentration was optimized with $J$–$V$ curves, as demonstrated in Fig. S3a and b in ESI,† with the related parameters summarized in Table 1 and S2.† Among them, the PSC with PBDT[2F]T HTM exhibited the best performance when spin-coated at the concentration of 8 mg mL$^{-1}$ in chlorobenzene, with a short-circuit current density ($J_{SC}$) of 22.64 mA cm$^{-2}$, open-circuit voltage ($V_{OC}$) of 1.06 V and fill factor (FF) of 72.6%, yielding an overall PCE of 17.52%. This performance is comparable with the parameters of spiro-OMeTAD-based devices ($V_{OC}$ of 1.11 V, $J_{SC}$ of 22.87 mA cm$^{-2}$, FF of 78.9%, and PCE of 20.20%) and better than the performance based on PTAA ($V_{OC}$ of 1.07 V, $J_{SC}$ of 20.49 mA cm$^{-2}$, FF of 70.85%, and PCE of 15.59%) in Fig. S3c.† By contrast, the PSCs

<table>
<thead>
<tr>
<th>HTM $^a$</th>
<th>$V_{OC}$ [V]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
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<tr>
<td>Spiro-OMeTAD (doped)</td>
<td>1.11</td>
<td>22.87</td>
<td>78.90</td>
<td>20.20</td>
</tr>
<tr>
<td>PBDT[2F]T</td>
<td>1.06</td>
<td>22.64</td>
<td>72.60</td>
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<tr>
<td>PBDT(T)[2F]T</td>
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<td>16.59</td>
<td>67.95</td>
<td>11.63</td>
</tr>
<tr>
<td>PBDT[2H]T</td>
<td>1.05</td>
<td>20.89</td>
<td>64.67</td>
<td>14.24</td>
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$a$ Numbers are average values of forward scan data, measured from over 18 devices (values are from the best performing devices).

Fig. 2 (a) $J$–$V$ curves and (b) IPCE spectra of the PSCs based on different dopant-free HTMs. (c) Stabilized PCEs at the maximum power point voltage for different HTMs. (d) Steady-state photocurrent measurements at maximum power point (0.93, 0.87, 0.71 and 0.87 V) within 80 s for the spiro-OMeTAD, PBDT[2F]T, PBDT[2H]T and PBDT(T)[2F]T based devices, respectively.
based on PBDT[T][2F] and PBDT[2H]T HTMs give lower PCEs of 14.24% (1.05 V, 20.89 mA cm⁻², and 64.67%) and 11.64% (1.03 V, 16.59 mA cm⁻², 67.95%), respectively. The best efficiency of the cell is highly related to the excellent hole mobility of PBDT[2H]T, which is 4 times higher than that of PBDT[2H]T. ¹⁷

The incident photon-to-current conversion efficiency (IPCE) measurements of devices based on these polymeric HTMs are shown in Fig. 2b. The three devices display a prominent absorption band in the 300–800 nm regions, agreeing well with the absorption range of CH₃NH₃PbI₃. Moreover, the IPCE of the PBDT[2F]T-based device is higher than that of the other two HTM-based devices. The corresponding integrated Jsc was determined to be 21.7, 20.66 and 15.7 mA cm⁻² for the solar cells based on the three HTMs, matching well with the data from the J–V curves. The reproducibility of the corresponding PSCs was characterized by 2 devices for each material, and the statistic distribution is displayed in Fig. 2c. The average PCEs of the PBDT[2F]T, PBDT[2H]T and PBDT[T][2F] based devices are 16.55 ± 0.69%, 10.25 ± 1.3% and 13.5 ± 0.72%, respectively. The smallest standard deviation of the cell efficiency with PBDT[2F]T manifests its outstanding and stable performance as an HTM.

To further confirm the device performance, steady-state photocurrent measurement at maximum power point (0.93, 0.87, 0.71 and 0.87 V) within 80 s was carried out (Fig. 2d). The current densities were stabilized at 21.02, 19.74, 16.10, 15.52 mA cm⁻² and the PCEs were stabilized at 19.54%, 17.37%, 14.14% and 11.17%, for the spiro-OMeTAD, PBDT[2F]T, PBDT[2H]T and PBDT[T][2F]T based devices, respectively (Table S3 in the ESI†). The smaller standard deviation of the PCE for the devices with spiro-OMeTAD, PBDT[2F]T, PBDT[2H]T and PBDT[T][2F]T manifests its outstanding and stable performance as an HTM.

To gain more insight into the origin of the differences between the HTMs, the surface morphology and roughness of the perovskite film w/o HTMs were studied by SEM and atomic-force microscopy (AFM). The SEM image of the bare perovskite film demonstrates a uniform surface with a crystal size in the range of 400–600 nm (Fig. 3a). After coating with the HTMs the grain boundaries of the perovskite became invisible and the surface roughness was reduced (Fig. 3c, e, and g). The root mean squares (RMS) of the PBDT[T][2F] T-coated film (14.08 nm) is larger than that of PBDT[2H]T (12.38 nm) and PBDT[2F]T (11.76 nm), respectively. This difference is caused by the enhanced crystallization tendency of PBDT[T][2F]T in comparison with PBDT[2H]T and PBDT[2F]T due to the introduction of F atoms and thienyl branches, respectively.

Further, the polymer chain packing of the three HTMs was investigated by grazing-incidence wide-angle X-ray scattering (GIWAXS), as illustrated in Fig. 4. The PBDT[2F]T and PBDT[T][2F]T films exhibited (010) scattering signals in the out-of-plane (OOP) direction, while no obvious signal could be observed in the PBDT[2H]T film, suggesting their better π–π stacking as well as the higher crystallinity. Specifically, the signals of PBDT[2F]T are the strongest, demonstrating the prominently favorable face-on orientation of the polymer chains.¹⁴,⁴₀,⁴¹ Hence, although the obtained hole mobility of PBDT[2F]T is lower than that of PBDT[T][2F]T, PBDT[2F]T favors effective hole transportation in the vertical direction, resulting in a higher FF and PCE (Fig. 2a).

The hole extraction properties of the three HTMs were studied with steady-state and time-resolved photoluminescence (PL and TRPL) spectra of FTO/perovskite/HTMs. The PL peaks at 770 nm originated from CH₃NH₃PbI₃, which were prominently undetectable, suggesting the excellent hole-extracting capability of the dopant-free PBDT[2F]T. ⁴² On the other hand, the emission lifetime of the different HTMs coated on perovskite/glass was fitted by a two-exponential decay model from the TRPL spectra (Fig. 5b). The fast decay time, τ₁, stands for the trap-assisted recombination and equals 2.29, 2.38, 2.97 and 3.18 ns for the devices with spiro-OMeTAD, PBDT[2F]T, PBDT[2H]T and PBDT[T][2F]T, respectively (Table S3 in the ESI†). Therefore, the smaller τ₁ of the device with PBDT[2F]T demonstrates a reduction in the trap-assisted recombination.

The charge transfer properties of the three HTMs were further confirmed with electrical impedance spectroscopy (EIS) measurements on the corresponding PSCs under illumination. The Nyquist plots in Fig. 5c show a semi-circle in the high frequency region, corresponding to the transfer resistance (Rq). The smaller Rq of PBDT[2F]T (147 Ω) than that of PBDT[T][2F]T (204 Ω) and PBDT[2H]T (281 Ω) based devices also indicates the efficient charge transfer process at the perovskite/PBDT[2F]T interface.

Fig. 5d shows the relationship between Voc and light intensity with the three HTMs. According to the formula: Voc = nqT ln(I/q) + C, in which C is a constant, k represents the Boltzmann constant, T is absolute temperature, and q is the elementary charge, n is an ideal factor related to intramolecular recombination. ⁴³,⁴⁴ The ideal factors n were determined to be ~1.25, 1.29, and 1.54 for PBDT[2F]T, PBDT[T][2F]T and PBDT[2H]T, respectively. It has been suggested that a smaller ideal factor means less trap-assisted recombination involved in the device operation. ⁴⁵ Therefore, the trap-assisted recombination in the perovskite/PBDT[2F]T HTM was largely suppressed compared with that in the other two cells.

Further, the space-charge-limited current (SCLC) based on the device structure of ITO/PEDOT:PSS/perovskite/HTM/Au in dark was measured to evaluate the density of trap states at the perovskite/polymer interface (Fig. S4†). The density of trap states (nᵣ) was calculated from the relation of V_TFL = enᵣd²/2εɵn, where ε₀ is the dielectric constant in vacuum, nᵣ is the trap state density, V_TFL is the threshold voltage for linear conduction, and d is the film thickness.
where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon$ is the relative dielectric constant, $V_{TFL}$ is the onset voltage of the trap-filled limit region, $e$ is the elemental charge, and $d$ is the thickness of the film.\textsuperscript{47,48} Also, the determined $n_t$ for the devices based on PBDT[2F]T, PBDT[T][2F]T and PBDT[2H]T is $1.19 \times 10^{16}$, $1.25 \times 10^{16}$ and $1.66 \times 10^{16}$ cm$^{-3}$, respectively. Together with the result in Fig. 5d, this confirms the lower trap-state density at the perovskite/PBDT[2F]T interface.

Fig. 4  (a–c) 2D GIWAXS profiles of PBDT[2F]T, PBDT(T)[2F]T and PBDT[2H]T on silicon substrates. (d and e) Out-of-plane (OOP) and in-plane (IP) line-cut profiles of the 2D GIWAXS spectra.

Fig. 5  (a) Steady-state and (b) time-resolved PL decay of bare perovskite and perovskite with HTMs on FTO/glass, excited at 450 nm. (c) EIS of the PSCs under illumination. (d) $V_{OC}$ vs. light intensity for PSCs with different HTMs.
The stability of the unencapsulated PSCs with dopant-free PBDT[2F]T and doped spiro-OMeTAD was monitored using J–V curves. As shown in Fig. 6a, the PBDT[2F]T-based PSC maintained 91.34% of its original PCE after 16 days storage in ambient environment with a relative humidity of around 30% at 30 °C. In contrast, only 64.87% of the initial value of the spiro-OMeTAD-based cell was retained under the same conditions. In addition, the unencapsulated PSCs with PBDT[2F]T also presented high humidity (24°C 70%) stability (24°C 65% @ 100 h), compared with the PSCs with spiro-OMeTAD (24°C 20% @ 90 h) (Fig. S5 in the ESI†). The water contact angle on the PBDT[2F]T and doped spiro-OMeTAD film was 110° and 71.8°, respectively, as shown in the inset of Fig. 6a, further confirming the moisture resistivity of PBDT[2F]T. Thus, it is concluded that the hydrophobic nature of PBDT[2F]T is beneficial for preventing moisture attacking the perovskite film, thereby leading to improved ambient stability. In addition, a negligible hysteresis effect was observed, as indicated by the almost identical J–V curves under forward and reverse scans for the PBDT[2F]T-based perovskite solar cell (Fig. 6b).

Conclusions

In summary, we explored a series of dopant-free polymeric HTMs, PBDT[2F]T, PBDT[2H]T and PBDT(T)[2F]T, which were utilized to fabricate high-performance PSCs. The best perovskite solar cell with PBDT[2F]T HTM showed a decent efficiency of 17.52%, which was higher than that of the devices based on the other two polymers, and comparable with that of the cells with doped spiro-OMeTAD. This enhanced photovoltaic performance is mainly attributed to the introduction of PBDT [2F]T HTM with higher hole mobility, favorable orientation and better morphology, furtherly resulting in an efficient hole-extraction process, as well as the reduced trap-assisted recombination at the perovskite/PBDT[2F]T interfaces. Moreover, due to the hydrophobic nature of PBDT[2F]T, the PSCs exhibited excellent long-term stability, even in a high humidity environment, presenting its great practical potential as a cost-effective, dopant-free HTM for stable PSCs.

Author contributions

X. K. conducted the material characterization and device fabrications. S. L. synthesized the materials. X. W., C. C. and J. L. G. contributed the optimization of the solar cell devices. X. K., Y. J., and J. W. G. wrote the manuscript. All authors discussed the results and commented on the manuscript. J. W. G. directed the research.

Conflicts of interest

There are no conflicts to declare.

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