Engineering of dendritic dopant-free hole transport molecules: enabling ultrahigh fill factor in perovskite solar cells with optimized dendron construction

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Abstract

Developing dopant-free hole-transporting materials (HTMs) for high-performance perovskite solar cells (PVSCs) has been a very active research topic in recent years since HTMs play a critical role in optimizing interfacial charge carrier kinetics and in turn determining device performance. Here, a novel dendritic engineering strategy is first utilized to design HTMs with a D-A type molecular framework, and diphenylamine and/or carbazole is selected as the building block for constructing dendrons. All HTMs show good thermal stability and excellent film morphology, and the key optoelectronic properties could be fine-tuned by varying the dendron structure. Among them, MPA-Cz-BTI and MCz-Cz-BTI exhibit an improved interfacial contact with the perovskite active layer, and non-radiative recombination loss and charge transport loss can be effectively suppressed. Consequently, high power conversion efficiencies of 20.8% and 21.35% are achieved for MPA-Cz-BTI and MCz-Cz-BTI based devices, respectively, accompanied by excellent long-term storage stability. More encouragingly, ultrahigh fill factors of 85.2% and 83.5% are recorded for both devices, which are among the highest values reported to date. This work demonstrates the great potential of dendritic materials as a new type of dopant-free HTMs for high-performance PVSCs with excellent FF.

Keywords: Dendritic molecules, Hole-transporting materials, Dopant-free, Ultrahigh fill factor, Perovskite solar cells

1. Introduction

As a disruptive photovoltaic technology, perovskite solar cells (PVSCs) are gaining tremendous research interests, recently. PVSCs are generally fabricated with a sandwich structure, in which metal halide perovskite active layer is in direct contact with n-type or p-type charge transporting layers (CTLs) [1-2]. During the rapid progress of PVSCs with the power conversion efficiency (PCE) now exceeding 25% [3-5], it is well known that the CTLs can significantly affect the perovskite crystallinity, surface defect formation and interfacially related charge transport and recombination processes, which will fundamentally impact the open-circuit voltage (V_{oc}) and fill factor (FF) of the resulting photovoltaic devices [6]. According to the Shockley-Queisser (SQ) model, FF over 85% at room temperature is expected to be achieved for PVSCs assuming an ideality factor of 1.5 and a typical V_{oc} of 1.1 V [7]. However, in real cases, most of PVSCs exhibit much lower FFs even for some state-of-the-art devices which typically show FFs of around 80%, significantly lower than the SQ limit [8-11]. The major reason is likely attributed to the additional charge recombination losses which mainly originate from inefficient charge extraction, suboptimal charge transporting ability or current leakage through shunt leakage [12]. In this regard, developing high-performance CTLs is envisioned as an effective strategy to overcome the issues and finally enhance device performance.

Among CTLs, hole-transporting materials (HTMs) are highly important and are receiving a lot of attention [13-15]. Due to the intrinsic drawbacks of the conventional HTMs (e.g. Spiro-OMeTAD and PTAA) such as high synthetic cost, dopant

dependence and low reproducibility, novel efficient dopant-free HTMs are long sought to replace the conventional HTMs [16-18]. Among tremendous efforts devoted to the design of new HTMs [19-21], we recently developed a D-A type dopant-free small molecular HTM, i.e. MPA-BTTI, by integrating several molecular design principles which delivered a remarkably high PCE > 21% in *p-i-n* PVSCs despite its somewhat tedious synthetic route [19]. Importantly, it can be learned from this work that the film morphology seems to be the paramount factor contributing to the remarkable performance in PVSCs. To achieve good film morphological properties for organic semiconducting materials, several principles should be taken into consideration in molecular design such as good solubility in common solvents, high thermal stability, amorphous molecular stacking and high hydrophobicity, *etc.* Actually, polymers are usually conceived as one type of good materials for constructing dopant-free HTMs due to their promising charge-transporting capacity and intrinsically excellent film morphology [22-23]. Nevertheless, the batch-to-batch variation of polymers is the major shortcoming for future commercialization of PVSCs.

As such, dendritic molecules might be excellent alternatives for HTMs. It is known that dendritic molecules feature well-defined structures, good solution processability and superior film morphology owing to their branched structures [24], which have been widely explored in organic light-emitting diodes (OLEDs) [25-26], organic field-effect transistors (OFETs) [27] and dye-sensitized solar cells (DSSCs) [28]. As discussed above, good film morphology is highly favorable for the interfacial contact and growth of high-quality perovskite film, especially for *p-i-n* PVSCs. However, there are few

reports using dendritic HTMs for PVSCs till today and systematic study on such a new type of HTMs is missing. The potential advantages of dendritic HTMs have been overlooked in the past years [29].

Hence, we propose a novel dendritic engineering strategy to construct a series of dendritic HTMs for dopant-free PVSCs. As a proof of concept, 5-octyl-4*H*-dithieno[3,2-*c*:2',3'-*e*]azepine-4,6(5*H*)-dione (a.k.a. bithiophene imide, BTI) was selected as an acceptor unit due to its proven functionality and relatively facile synthesis [19]. Meanwhile, diphenylamine dendron, carbazole dendron and diphenylamine/carbazole hybridized dendron were used as the donor fragments to afford four D-A type dendritic HTMs, namely MPA-PA-BTI, MPA-Cz-BTI, MCz-PA-BTI and MCz-Cz-BTI (**Figure 1**). Note that diphenylamine and carbazole are adopted as the donor building blocks for dendritic engineering due to their excellent hole transporting capacity, and the peripheral methoxy groups are retained for each dendritic HTM which can act as Lewis base groups to enable passivation effect and enhance interfacial contact with perovskite layer. By varying the dendron construction mode, the number of diphenylamine units decreases accompanied by the increased carbazole number from MPA-PA-BTI to MPA-Cz-BTI and to MCz-PA-BTI and to MCz-Cz-BTI, leading to downshifted highest occupied molecular orbital (HOMO) levels and slightly reduced hole mobility. All dendritic HTMs show good thermal stability and film formation property, among them MPA-Cz-BTI and MCz-Cz-BTI exhibit better interfacial contact with the perovskite layer and the charge recombination losses (*i.e.* non-radiative recombination and charge transport losses) are effectively suppressed. As

a result, a strikingly high PCE of 21.35% is achieved for MCz-Cz-BTI based device with a very high FF of 83.5%. For MPA-Cz-BTI based device, an encouraging PCE of 20.8% along with an ultrahigh FF of 85.2% is realized which is approaching the SQ limit. Moreover, these devices based on dendritic HTMs show good long-term storage stability and operational stability. Therefore, it is believed that such dendritic engineering strategy will pave a new way toward exploring novel efficient HTMs for high-performance PVSCs with improved FF.

2. Results and discussion

2.1. Material Synthesis

The synthetic route to the dendritic HTMs is depicted in **Scheme S1**, which follows a convergent method to ensure defect-free dendrimers [24]. Starting from bis(4-methoxyphenyl)amine, Pd-catalyzed Buchwald coupling and Cu-catalyzed Ullmann coupling were carried out successively to obtain dendritic compound **2** and **5** under distinct conditions, respectively. They were then converted to corresponding boric ester **3** and **6** in high yield under Pd-catalyzed condition. With the dendrons and previously reported acceptor core BTI-Br [19] in hand, Suzuki coupling was performed to produce dendritic HTMs MPA-PA-BTI and MPA-Cz-BTI under the same conditions. Using 3,6-dimethoxy-9*H*-carbazole as the starting material, the similar procedures were conducted to give another two HTMs MCz-PA-BTI and MCz-Cz-BTI except that Cu-catalyzed coupling should be involved to yield carbazole dendron **10** in high yield rather than Pd-catalyzed coupling.

Taking MCz-Cz-BTI as the example, it should be noted that such dendritic HTMs could be obtained by relatively straightforward synthetic process with 9 steps totally and overall yields > 20%, as compared to tedious preparation of previously reported MPA-BTTI [19] (16 steps, < 3% overall yield) (**Scheme S2**). The results suggest that dendritic molecules can also be considered as a novel type of HTMs with potential low cost relative to small molecules from a synthetic point of view. The chemical structure and purity of all dendritic HTMs was well confirmed by ^1H NMR, ^{13}C NMR, MALDI-TOF mass spectrometry, and elemental analysis (EA) (see Supporting Information). They all show excellent solubility in various common solvents such as dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), toluene and chlorobenzene, *etc.*, ensuring they would form quality films by a solution process.

2.2. Optoelectronic, Charge-Transporting and Thermal Properties of dendritic HTMs

Figure 2a shows the UV-Vis absorption spectra of the dendritic HTMs in THF solution with the corresponding data summarized in **Table 1**. For pure diphenylamine dendron based MPA-PA-BTI, two distinct absorption peaks at 340 and 508 nm, assigned to the π - π^* transition and intramolecular charge transfer (ICT) absorption, respectively, are observed which is similar with previously reported MPA-BTI [19]. The slightly red-shifted peaks for MPA-PA-BTI compared to MPA-BTI can be attributed to more extended conjugation framework resulting from increasing number of phenylamine units. While for pure carbazole dendron based MCz-Cz-BTI, both the π - π^* transition peak (373 nm) and ICT absorption peak (426 nm) are blue-shifted,

leading to a wider optical bandgap (E_g^{opt}) of 2.55 eV as compared to MPA-PA-BTI (2.11 eV). This might be due to the deeper HOMO level of carbazole unit than that of diphenylamine unit as reported in the literature [30]. As for the hybrid MPA-Cz-BTI and MCz-PA-BTI, three continuous peaks, ascribed to the mixture of π - π^* transition and multiple ICT absorption, are observed owing to the existence of both diphenylamine and carbazole dendrons. Note that the ICT absorbance of MCz-Cz-BTI is much stronger than other three HTMs which may be ascribed to more planar structure of carbazole unit than phenylamine unit and the resultant better conjugation degree and stronger oscillator strength. This could be confirmed by simulation of absorption spectra using time dependent density functional theory (TD-DFT) method as shown in **Figure S2**. The ICT absorption of MCz-Cz-BTI is indeed stronger than other three HTMs. As expected, with the decreasing diphenylamine number in the dendron, the E_g^{opt} is gradually enlarged from 2.11 eV (MPA-PA-BTI), to 2.28 eV (MPA-Cz-BTI), and 2.31 eV (MCz-PA-BTI), and then to 2.55 eV (MCz-Cz-BTI). It should be noted that although such dendritic HTMs show absorption in the visible region, the small thickness of HTMs in inverted PVSCs could ensure that the majority of the photons are reaching the perovskite active layer. Specifically, the transmittance of all dendritic HTMs could be maintained above 70% in the range of 450-650 nm with the highest value (>80%) for MCz-Cz-BTI (**Figure S1**), which should be beneficial for the enhancement of short-circuit current (J_{sc}) in PVSCs.

To explore the electrochemical properties of these dendritic HTMs, cyclic voltammetry (CV) was performed (**Figure 2b**) with the relevant data included in **Table**

1. Upon the cathodic scan, only one reversible reduction peak for each HTM was detected with similar onset potential values. Hence, with ferrocene/ferrocenium redox couple as the reference, the lowest unoccupied molecular orbital (LUMO) levels of dendritic HTMs are calculated to be in a small range from -3.02 to -3.19 eV. This is understandable because LUMO levels are typically determined by acceptor moiety in such D-A type molecules [19]. However, during the anodic scan, multiple oxidation events appear with the onset potential shifting to more positive values from MPA-PA-BTI to MCz-Cz-BTI, resulting in gradually downshifted HOMO levels from -4.80 eV for MPA-PA-BTI, to -4.92 eV for MPA-Cz-BTI, to -5.25 eV for MCz-PA-BTI, and then to -5.32 eV for MCz-Cz-BTI. This is attributed to the incorporation of more carbazole units with deeper HOMO levels for the corresponding HTMs. The HOMO levels of HTMs are closely correlated with the efficiency of hole extraction from perovskite layer and the HTM with a better matched HOMO level with perovskite (*ca.* 5.4 eV) should yield a higher V_{oc} in the device performance.

To gain more insight into the electronic properties of such dendritic HTMs, density functional theory (DFT) calculations were performed at the B3LYP/6-31G* level using the Gaussian 09 software package. As shown in **Figure 1**, the LUMOs are completely localized on acceptor core fragment and the neighboring phenyl moiety for all dendritic HTMs, whereas the HOMOs are mainly contributed by inner diphenylamine units and outer carbazole units for MPA-PA-BTI and MCz-Cz-BTI, respectively, but delocalized evenly on the whole dendrons for both MPA-Cz-BTI and MCz-PA-BTI. Additionally, with the decreasing diphenylamine number, the HOMO levels reduce from -4.29 eV

(MPA-PA-BTI) to -4.82 eV (MCz-Cz-BTI), which is in good agreement with the CV results, suggesting an easier oxidizability of diphenylamine unit than that of carbazole unit. On the other hand, although the acceptor unit BTI has good structural planarity, the linkages between BTI and donor dendrons feature twisted dihedral angle of $\sim 20^\circ$ for all HTMs and the dendrons themselves all possess 3D branched configuration especially for phenylamine based dendrons due to their more flexible structure than carbazole unit (see **Figure S3**). The distinct chemical topological structure of the HTMs may play a critical role in determining stacking mode in thin films and consequent interfacial interactions as will be discussed later.

Based on space charge-limited current (SCLC) method, the hole mobilities ($\mu_{h,SCLC}$) of neat HTM films are found to be 2.03×10^{-4} , 1.82×10^{-4} , 1.57×10^{-4} , and 1.16×10^{-4} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for MPA-PA-BTI, MPA-Cz-BTI, MCz-PA-BTI, and MCz-Cz-BTI, respectively (**Table 1** and **Figure 2c**). The decreasing $\mu_{h,SCLC}$ tendency from MPA-PA-BTI to MCz-Cz-BTI is likely attributed to reduced phenylamine number in the dendrons since the phenylamine unit usually exhibits superior hole-transporting ability than the carbazole unit [30]. Despite this, all dendritic HTMs show nearly one order of magnitude higher $\mu_{h,SCLC}$ than our previously reported MPA-BTI ($3.99 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) [12a], suggesting this dendritic engineering strategy should be favorable for further improving the hole-transporting capacity of HTMs.

To evaluate the thermal properties of dendritic HTMs, the thermogravimetric analysis (TGA) and the differential scanning calorimetry (DSC) were conducted with the corresponding curves shown in **Figure S4** and **Figure 2d**, respectively. All HTMs

display good thermal stability with a decomposition temperature (T_d , corresponding to a 5% weight loss) higher than 400 °C along with a gradual increment from MPA-PA-BTI to MCz-Cz-BTI. This may arise from more rigid carbazole unit compared to the relatively flexible diphenylamine unit, leading to an improved thermal stability for the dendritic HTM with more carbazole unit. Similarly, all dendritic HTMs exhibit much higher glass transition temperatures (T_g) above 120 °C than that (86 °C) of previously reported MPA-BTI [19], indicating that the dendritic modification can indeed enhance thermal stability of these small molecules. The higher thermal stability can endow such dendritic HTMs with good tolerance to annealing process during device fabrication, ensuring improved film morphology stability.

2.3. Film Morphological Properties of Dendritic HTMs

It is known that apart from transmittance, energy level alignment and hole mobility, film morphology plays a more critical role in determining the device performance of PVSCs [19,31]. Hence, atomic force microscopy (AFM) was first utilized to examine the surface morphology of dendritic HTMs (**Figure 3a**). Apparently, highly smooth and homogeneous surface could be obtained for all dendritic HTMs with the minimum root-mean-square roughness (R_q) of merely 0.30 nm for MPA-Cz-BTI and the maximum R_q of 0.35 nm for MPA-PA-BTI, showing much improved film surface compared to the previously reported MPA-BTI ($R_q = 0.96$ nm) [19]. This is attributed to the enhanced dendritic HTM thermal stability which is beneficial to thermal annealing at high temperature (~100-110 °C). Furthermore, two-dimensional grazing-incidence wide-angle X-ray scattering (2D-GIWAXS) was performed to investigate the molecular

stacking in dendritic HTM thin films. As exhibited in **Figure S5**, no obvious diffraction peaks are observed for all HTMs either along the out-of-plane direction or in-plane direction, indicating an amorphous nature of these dendritic materials. It is reasonable that branching structure of dendritic molecules is prone to weaken molecular ordering and inhibit crystallization, resulting in amorphous film morphology [26,32].

To probe the hydrophobicity of film surface, the contact angle measurements were carried out as shown in **Figure 3b**. Encouragingly, compared to the contact angle (59.1°) for the MPA-BTI [19], much larger angles of $> 80^\circ$ are observed for all dendritic HTMs which indicates that high-quality perovskite films with larger grains may form upon such hydrophobic dendritic HTMs (*vide infra*). Empirically, such superior film morphological characters (e.g. smooth and hydrophobic surface, amorphous and densely stacked bulk film as well as intrinsic high thermal stability) should enable efficient interfacial contact and subsequently enhance charge extraction and reduce recombination losses in the devices, contributing to high FF [17,19,31].

2.4. Photovoltaic Performance

Benefiting from the matched HOMO energy level, decent hole mobility, high thermal stability and good film morphological property, these dendritic molecules were applied as HTMs to explore their potentials in PVSCs with the device structure shown in **Figure 4a**. The HTM films were deposited on ITO glass substrates by spin coating their toluene solutions without any dopants. Triple cations (Cs, FA, and MA) perovskites were employed as the active layers (see more experimental details in Supporting Information). From the cross-section SEM image of a typical inverted

device with dendritic HTM (**Figure 4c**), it can be observed that the perovskite films were compact and dense with a thickness of ~ 460 nm, while the HTM layer cannot be clearly distinguished owing to the very low thickness of the organic layer.

The J - V curves of the optimal PVSCs with distinct HTMs were plotted in **Figure 4d**. The MPA-PA-BTI based device achieves a J_{sc} of 22.15 mA cm^{-2} , V_{oc} of 0.99 V , and FF of 79.4% , leading to a PCE of 17.41% under a reverse scan. The performance is dramatically improved to a PCE of 20.81% when using MPA-Cz-BTI as HTM, with a J_{sc} of 22.84 mA cm^{-2} , V_{oc} of 1.07 V , and ultrahigh FF of 85.2% (**Table 2**). The improved J_{sc} and V_{oc} for MPA-Cz-BTI based device as compared to MPA-PA-BTI based one might be attributed to its better transmission and deeper HOMO level. Comparable efficiency (PCE of 20.09% with good FF of 82.1%) can be achieved for the device based on MCz-PA-BTI, and the MCz-Cz-BTI based device delivered the best performance, yielding a J_{sc} of 23.24 mA cm^{-2} , V_{oc} of 1.1 V , FF of 83.5% , and PCE of 21.35% . The higher V_{oc} for the MCz-Cz-BTI based devices compared to the other three HTMs is likely due to the deeper HOMO level of MCz-Cz-BTI, which results in more favorable energy alignment with perovskite layers (**Figure 4b**). The significantly high FFs achieved by both MPA-Cz-BTI and MCz-Cz-BTI based devices could be attributed to the very low series resistance and large shunt resistance (**Table 3**), which might stem from the excellent film morphology and the resultant improved hole extraction ability of both HTMs, and the devices' extremely low shunt leakage [12a,23]. The statistical distributions of the photovoltaic parameters of PVSCs with different HTMs are presented in **Figure 4e** and **4f**. The MCz-Cz-BTI based devices deliver an averaged

PCE of 20.3%, significantly higher than other three HTMs based devices. The PVSCs with MPA-Cz-BTI HTM show the best averaged FF of ~83%, which is slightly higher than the second best ones with MCz-Cz-BTI HTM (averaged FF of 81.6%). The results demonstrate that these dendritic HTMs hold great potential for realizing highly efficient PVSCs with substantial FF (>83%), which is among the best reported values in the literatures [6,33,34-36].

The photocurrent hysteresis behaviors for the optimal devices with four dendritic HTMs are then probed. As shown from the J - V curves under forward and reverse scan in **Figure 4i-l**, the devices show negligible differences under different scan directions. Moreover, the best performing devices with distinct HTMs are further held at maximum power point (MPP) voltages to record the stabilized power output. As shown in **Figure 4g**, the stabilized PCE of 17.3%, 20.8%, 21.2% and 19.9% are obtained for the corresponding devices based on MPA-PA-BTI, MPA-Cz-BTI, MCz-Cz-BTI and MCz-PA-BTI, respectively. The J_{sc} values from the J - V characteristics are further verified by integrating the external quantum efficiency (EQE) spectra (**Figure 4h**), showing a good consistency.

2.5. Morphology and Optoelectronic Properties of Perovskite films on HTMs

As shown in **Figure S6**, the SEM images for perovskite films on four distinct HTMs exhibit no notable differences. All perovskites show uniform morphology with similar grain sizes. UV-Vis absorption spectra of the corresponding perovskite films were then characterized, which exhibited no apparent variation among the four samples (**Figure S7**). Since the UV-Vis spectrum is not sensitive enough to measure the absorption in

the sub-bandgap region, photothermal deflection spectroscopy (PDS) was then adopted which allows the detection of sub-bandgap features of a semiconductor. By fitting the exponential drop in absorption at the band edge, we can extract the energetic disorder parameter, known as Urbach energy (E_u) [37], which is given by $\alpha = A * \exp\left(\frac{E-E_C}{E_u}\right)$, where α is the absorption coefficient of perovskites, E is the photon energy, and E_C and A are material constants, respectively [38]. As shown in **Figure 5a**, we can estimate the energetic disorder by fitting the Urbach energy to the band edge. It is revealed that a low Urbach energy of 31.9 ± 0.4 meV is achieved for the perovskite coated on MPA-Cz-BTI, which is slightly lower than the values of the perovskites on MCz-Cz-BTI (32.3 ± 0.3 meV) and MCz-PA-BTI (33.5 ± 0.5 meV), and significantly lower than that on MPA-PA-BTI (39.0 ± 0.5 meV) (see the inset of **Figure 5a**). The PDS results suggest a higher level of electronic order in the perovskite films on MPA-Cz-BTI and MCz-Cz-BTI compared to others, which is likely to reduce non-radiative recombination losses and contribute to the ultrahigh FF of both HTMs based devices. On the other hand, from the XRD patterns, it can be observed that the intensities of (110) diffraction peak at 2θ of 14.2° for the perovskite films on MPA-Cz-BTI and MCz-Cz-BTI are obviously stronger than other two samples (**Figure S8**). This indicates a better crystallinity of perovskite films deposited on MPA-Cz-BTI and MCz-Cz-BTI, which is also responsible for the higher FF and improved PCE of devices based on both HTMs [19].

2.6. Interfacial Analysis and Investigation on High FF

It is known that defects in grain boundaries and interfaces are detrimental to device performance since they can form trap states to inhibit charge transport and lead to

severe charge recombination. Hence, designing HTMs with passivation functionality toward perovskite layer is an effective way to enhance interfacial contact and reduce interfacial defects [19,39]. For our dendritic HTMs, the carbonyl groups in acceptor fragment together with the peripheral methoxy groups on the dendrons can act as chemical passivators due to their Lewis base character which are able to form coordination interactions with Pb^{2+} ion defects [19,40]. To confirm this, Fourier transform infrared spectroscopy (FTIR) was first performed to study the intermolecular interactions in powders as shown in **Figure S9**. It can be observed that the characteristic peaks for stretching vibration of carbonyl groups located at $\sim 1650\text{ cm}^{-1}$ for all HTMs slightly shift to higher wavenumber after blending with PbI_2 , indicative of weak interaction between carbonyl group and Pb^{2+} ion. For more direct proofs, X-ray photoelectron spectroscopy (XPS) was conducted as displayed in **Figure S10** and **Figure S11**. Compared to pure perovskite film, pronounced left shifts for Pb 4f core level peak are observed in all dendritic HTMs, suggesting certain intermolecular interactions between Pb^{2+} ion and HTMs, which likely arise from either carbonyl groups or methoxy groups. Interestingly, the larger degree of peak shifts for MPA-Cz-BTI/perovskite and MCz-Cz-BTI/perovskite indicates that more strengthened passivation effect can contribute to optimized interfacial contact and hence the higher FF. Such passivation effect could be confirmed by detecting O 1s peak variation in XPS spectra (**Figure S11**). Apparently, for pure HTM films, the O signals exhibit one main peak at $\sim 533.5\text{ eV}$ along with a shoulder peak at $\sim 531.7\text{ eV}$ which could be ascribed to the O atom in methoxy group (C-O) and that in carbonyl group (C=O), respectively.

After coating on the perovskite film, a new peak at ~ 530.3 eV could be obviously observed for MPA-Cz-BTI, MCz-PA-BTI and MCz-Cz-BTI, which could be attributed to O atom in carbonyl group interacted with Pb^{2+} ion as reported in the previous work [41]. Coincidentally, the intensity of the new peak follows the sequence of MPA-Cz-BTI > MCz-Cz-BTI > MCz-PA-BTI, indicating that more passivation effect could be offered by MPA-Cz-BTI and MCz-Cz-BTI which is in good consistent with the results for Pb peak shifts. However, for MPA-PA-BTI, the peak at ~ 530.0 eV could not be detected, instead a new peak at ~ 531.0 eV could be observed which can be tentatively attributed to O atom in methoxy group interacted with Pb^{2+} ion. We speculate that the distinct chemical topological structure of such dendritic HTMs will remarkably affect their stacking mode in solid state and consequent interfacial interactions. As depicted in **Figure S3**, the more branched dendrons (e.g. for MPA-PA-BTI and MCz-PA-BTI) may endow BTI core with more effective encapsulation effect which will in reverse inhibit the interactions between carbonyl groups and Pb^{2+} ions at the interfaces. This may be the reason for varied passivation effect imposed by different dendritic HTMs although they feature the same number of passivation groups.

We measured the steady and time-resolved photoluminescence (PL) of the perovskite films on different HTMs to explore the possible charge transport dynamics. We observe a significant PL quenching of the perovskite film on MPA-PA-BTI as compared to that on ITO substrate, while the PL quenching is not pronounced for the perovskite films on MPA-Cz-BTI and MCz-Cz-BTI (**Figure S12**). The PL quenching of the perovskite films on HTMs indicates either faster charge transfer from perovskite to HTM or more

serious charge recombination losses at the perovskite/HTMs interfaces. Thus, from the steady PL results, it is hard to conclude which process dominates the PL quenching. We therefore investigated the PL decay dynamics, and the time-resolved PL spectra (**Figure 5b**) of all samples show bi-exponential decay with a fast (τ_1) part and a slow (τ_2) one. Bi-exponential equation is employed to fit the PL decay [42], and the corresponding fitting data are summarized at **Table S1**. Previous reports suggest that the fast initial decay mainly originates from the charge extraction from perovskite to the transport layers, and the second slow decay is related with the interface recombination losses [19,43]. It is observed that the τ_1 of perovskite films coated on all HTMs is significantly shorter compared with that of pure perovskite film, indicative of a sufficient charge transfer from perovskite to HTMs. The τ_2 for the perovskites on four HTMs are calculated to be 107.2 ns (for MPA-PA-BTI), 273.9 ns (for MPA-Cz-BTI), 253.1 ns (for MCz-Cz-BTI) and 252.8 ns (for MCz-PA-BTI), respectively. More than twice reduction of τ_2 for perovskite on MPA-PA-BTI than other three mainly indicates a larger recombination loss at MPA-PA-BTI/perovskite interface, which is consistent with the lowest FF and PCE of the corresponding device. Moreover, the highest τ_2 for MPA-Cz-BTI/perovskite is also in good agreement with the best FF obtained in the device. We further analyzed the trap density of states (t-DOS) of the devices with different HTMs via capacity-frequency measurements [44]. It is clear that the devices based on MPA-Cz-BTI and MCz-Cz-BTI have apparently low t-DOS over the band 1 and band 2 trap depth regions (0.28 to 0.53 eV), while the highest t-DOS of the device based on MPA-PA-BTI is observed in this region (**Figure 5c**). The density of shallower

trap states (0.28 to 0.41 eV) of the MCz-Cz-BTI based device is more than two orders of magnitude lower than that of MPA-PA-BTI based device. Previous reports have demonstrated that the shallow traps are mainly located at the interfaces and/or grain boundaries [44,45]. Thus, these results indicate that significant suppression of interfacial trap states might account for the high FF and enhanced PCE of the MPA-Cz-BTI and MCz-Cz-BTI based devices. The reduced trap state density might result from the suppression of non-radiative recombination as well as the decrease of charge transport losses at the perovskite/HTM interfaces [6].

Furthermore, the V_{oc} of the PVSCs as a function of illumination intensity was characterized to decouple the charge transport losses from the non-radiative recombination losses (**Figure 5d**). Since the J_{sc} is linearly related with the light intensity, the graph shows that the dependence of V_{oc} follows the Shockley equation. The ideality factor (n_{ID}) can be calculated by fitting the V_{oc} vs $\log J_{sc}$ plot for all devices with distinct HTM (1.55, 1.27, 1.34 and 1.39 for MPA-PA-BTI, MPA-Cz-BTI, MCz-Cz-BTI and MCz-PA-BTI, respectively). These different n_{ID} values suggest a distinct recombination kinetics for the devices with four different HTMs. Moreover, the FF response of devices with MPA-Cz-BTI and MCz-Cz-BTI stand almost consistent over the test region (**Figure 5e**), indicating small charge extraction limitation of the devices with these two HTMs. This is in contrast to the devices with other two HTMs which show a strong dependence on light intensity, suggesting there is strong charge extraction limitation of these devices [46]. Detailed analysis of high FF was performed according to the FF approximation equation developed by M. Green [7]: $FF_{max} =$

$\frac{v_{oc}-\ln(v_{oc}+0.72)}{v_{oc}+1}$, where the v_{oc} can be determined by the equation $v_{oc} = \frac{qV_{oc}}{n_{ID}k_B T}$. We are able to calculate the maximum FF of the corresponding devices with different HTMs that could be reached if no additional charge transport losses occur (**Figure 5f**). The corresponding SQ limit and experimental FF values are also added for comparison. It is clear that the FF loss can be decoupled into two components: non-radiative loss and charge transport loss [6,47]. It can be observed that MPA-Cz-BTI and MCz-Cz-BTI exhibit slightly less non-radiative loss compared to MPA-PA-BTI and MCz-PA-BTI. Strikingly, the MPA-Cz-BTI demonstrates very small charge transport loss as compared with others. The results indicate that the ultrahigh FF of the MPA-Cz-BTI and MCz-Cz-BTI based devices are mainly due to the significantly reduced charge transport loss which is essentially enabled by the superior film-forming property of dendritic HTMs and the resultant excellent interfacial contact. Overall, it could be concluded that our dendritic HTMs show great potential in realizing highly efficient PVSCs (> 20%) with ultrahigh FF (>83%) (**Figure S13**).

2.7. Device Stability

The long-term storage stability of the devices with different HTMs was firstly monitored, and it was found the MCz-Cz-BTI based device demonstrates an extended lifetime (**Figure 5g**). After 1400 h storage in inert environment, 95% of the initial PCE can be maintained for the MCz-Cz-BTI HTM based cell. On the contrary, the MPA-PA-BTI based device showed much faster degradation, retaining only 70% of the original value. The other two HTMs based devices demonstrated similar degradation but slightly quicker as compared to the MCz-Cz-BTI based one. The operational

stability for the most stable MCz-Cz-BTI based device (encapsulated) was monitored using MPP tracking method under illumination with the light intensity equivalent to AM 1.5 G (**Figure 5h**). The aging test was performed with a relative humidity of ~55-60% and without temperature control. After ~900 h, the PCE of the device dropped to 80% of the initial value, delivering a T_{80} of 900 h, which is among the top levels as compared to previous reports for organic HTM based *p-i-n* PVSCs [19,33,48,49]. The respective long-term storage and operational stability of these devices suggest the novel dendritic molecules are highly promising dopant-free HTMs for PVSCs.

3. Conclusions

In summary, a series of D-A type dendritic molecules were developed via relatively facile synthetic routes and explored as dopant-free HTMs in inverted PVSCs. Based on different building block (diphenylamine or carbazole unit) for dendrons, it was found that with the decreasing number of diphenylamine units in the dendron, the HOMO levels of dendritic HTMs are gradually downshifted accompanied by slightly reduced hole mobility. Despite this, all dendritic HTMs show good thermal stability and superior film morphology, among which MPA-Cz-BTI and MCz-Cz-BTI exhibit better interfacial contact with perovskite layer. As a consequent, remarkably high PCE of 20.8% and 21.35% were achieved for MPA-Cz-BTI and MCz-Cz-BTI based devices, respectively, which also show good long-term storage stability. More encouragingly, ultrahigh FF values of 85.2% and 83.5% were recorded for both devices which are among the highest reported values in the literatures. As confirmed by a sequence of characterizations, the realization of such ultrahigh FFs is likely due to the reduced non-

radiative recombination losses, enhanced hole extraction, and especially suppressed charge transport losses in the devices which in essence are mainly contributed by excellent film morphological properties of MPA-Cz-BTI and MCz-Cz-BTI and subsequent efficient interfacial contact with perovskite layer. This work highlights the great potential of dendritic HTMs as a new type of dopant-free HTMs for high-performance PVSCs with enhanced FF.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgements

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Supporting information

The supporting information is available online at <http://chem.scichina.com>

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Figure 1. Chemical structures for novel dendritic HTMs along with the corresponding HOMO and LUMO profiles calculated with DFT method.

Figure 2. (a) UV-vis absorption spectra of dendritic HTMs in THF solution (10^{-5} mol L^{-1}). (b) Cyclic voltammograms of dendritic HTMs measured in CH_2Cl_2 solution using the ferrocene/ferrocenium redox couple (Fc/Fc^+) as the reference. (c) DSC curves of dendritic HTMs during the second heating scan. (d) The corresponding $J^{1/2}$ - V curves for the hole-only devices based on the pure films of dendritic HTMs.

Figure 3. (a) AFM height (the first row) and phase images (the second row) of dendritic HTMs after thermal annealing. (b) Water contact angles on different dendritic HTM films.

Figure 4. (a) Device architecture of the inverted planar perovskite solar cell with dendritic molecules as HTLs. (b) Energy level alignments of the HTMs with perovskite and ETLs. (c) Cross-sectional SEM image of a typical device with dendritic HTM. The scale bar: 1 μm . (d) Current density-voltage ($J-V$) curves of the PSCs with different dendritic HTMs under AM 1.5 G 1 sun illuminations. (e) and (f) Statistics of the FF and PCE values for the PVSCs with different dendritic HTMs. (g) The stable PCE for the optimal PSCs with different HTMs. (h) External quantum efficiency (EQE) spectra and the corresponding integrated J_{sc} curves for the optimal PSCs with different HTMs. (i)-(l) $J-V$ curves for the optimal PSCs with different HTMs under reverse and forward scan.

Figure 5. (a) Photothermal deflection spectroscopy (PDS) spectra of the perovskite films deposited on different HTMs coated ITO glass substrates. The inset shows the calculated mean Urbach energies for these samples. (b) Time-resolved PL spectra for the perovskite films at different interfaces. (c) Trap density of states (t-DOS) spectra for the PVSCs with different HTMs. The vertical dashed lines define trap bands with different trap energy depths: shallow trap states (band 1, ~0.26 to ~0.41 eV) and deep trap states (band 2 and band 3, > 0.41 eV). (d) V_{oc} as function of J_{sc} under various light intensities for the PVSCs with different HTMs. The ideality factor (n_{ID}) can be calculated via slope of the V_{oc} versus $\text{Log}(J_{sc})$ plots. (e) FF as function of the light intensity. (f) Plots of the SQ-limit FF, calculated maximum FF and the experimental FF for four HTMs based PVSCs. We can then decouple the FF limitation of devices into non-radiative losses (blue area) and charge transport losses (yellow area). (g) Long-term stability test of PVSCs with different HTMs. (h) Operational stability test for the best performed device based on MCz-Cz-BTI.

Table 1. Optical, electrochemical, thermal, and charge transport properties of dendritic HTMs.

	$\lambda_{\text{abs,sol}}$ (nm) ^a	E_g^{opt} (eV) ^b	HOMO (eV) ^c	LUMO (eV) ^d	T_d (°C)	T_g (°C)	μ_h (cm ² V ⁻¹ s ⁻¹)
MPA-PA-BTI	340, 508	2.11	-4.80	-3.02	422	120	2.03×10 ⁻⁴
MPA-Cz-BTI	373, 418, 472	2.28	-4.92	-3.16	433	170	1.82×10 ⁻⁴
MCz-PA-BTI	332, 371, 473	2.31	-5.25	-3.10	442	130	1.57×10 ⁻⁴
MCz-Cz-BTI	373, 426	2.55	-5.32	-3.19	453	222	1.16×10 ⁻⁴

^a Measured in THF solution with a concentration of 10⁻⁵ mol/L. ^b Estimated from the absorption edge using the equation: $E_g^{\text{opt}} = 1243 / \lambda_{\text{onset}}$ (eV). ^c $E_{\text{HOMO}} = -5.1 - (E_{\text{ox}} - E_{1/2}(\text{Fc}/\text{Fc}^+))$. ^d $E_{\text{LUMO}} = -5.1 - (E_{\text{red}} - E_{1/2}(\text{Fc}/\text{Fc}^+))$.

Table 2. Photovoltaic performance parameters of inverted PVSCs with dendritic HTMs.

HTMs	Scan direction	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	R_s (Ω)	R_{sh} (K Ω)
MPA-PA-BTI	forward scan	0.98	22.20 (21.30) ^a	79.8	17.37		
	reverse scan	0.99	22.15	79.4	17.41	2.6	3.7
MPA-Cz-BTI	forward scan	1.07	22.84 (21.92) ^a	84.9	20.80		
	reverse scan	1.07	22.84	85.2	20.81	1.9	12.3
MCz-PA-BTI	forward scan	1.07	22.61 (21.74) ^a	82.9	20.03		
	reverse scan	1.08	22.66	82.1	20.09	1.8	5.8
MCz-Cz-BTI	forward scan	1.10	23.23 (22.36) ^a	83.3	21.29		
	reverse scan	1.10	23.24	83.5	21.35	1.9	4.9

^a The J_{sc} integrated from EQE spectrum.

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