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Molecular Design with Silicon Core: Toward Commercially Available Hole Transport Materials for High-Performance Planar *p*-i-*n* Perovskite Solar Cells

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Abstract

Organic hole transport layer (HTL) play very important role for realizing high performance and low-cost planar *p-i-n* perovskite solar cells (pero-SCs). In this work, we synthesized two X-shaped organic HTL materials Si-OMeTPA and SiTP-OMeTPA with silicon cores and triphenylamine (TPA) derivative branches. This molecular design strategy can substantially simplify synthetic procedure making them available for reducing device cost. Particularly for Si-OMeTPA, it can be synthesized by two steps from commercial raw materials showing a total yield of over 60%. This molecular design Si-OMeTPA possesses advantages of high thermal stability, high crystallinity with a long range ordered lamellar structure, and excellent hole mobility. The resulting HTL can also facilitate the sequent growth of high-quality perovskite films, giving a significantly enhanced photovoltaic performance with a best power conversion efficiency of 19.06%, which is one of the highest PCE among the planar *p-i-n* pero-SCs to date. In addition, the devices exhibit negligible hysteresis, good reproducibility and stability. To the best of our knowledge, this is the first example of an easily synthesized HTL materials in planar *p-i-n* pero-SCs that shows even superior performance relative to the well-known poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA) HTL.

Keywords: hole transport materials; X-shaped molecules; long range ordered lamellar structure; silicon core; planar *p-i-n* perovskite solar cell.

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1. Introduction

The planar *p-i-n* organic-metal halide perovskite solar cells (pero-SCs) with lowtemperature-processed organic/polymer hole transport layer (HTL) on ITO as bottom electrode have attracted great attention in recent years, because of its high efficiency and less hysteresis of photovoltaic performance, low cost and easy fabrication by low temperature solution-processing.¹⁻⁵ In the p-i-n pero-SCs, poly(3,4-ethylenedioxythiophene)/ poly(styrenesulfonic acid) (PEDOT:PSS) is the most commonly used organic HTL material. But the PEDOT:PSS-based *p-i-n* pero-SCs show poor long-term stability due to its acidic and hygroscopicity nature,⁶ and lower open-circuit voltage (V_{oc}) (0.90-0.95 V)⁷ due to the energy mismatch between the PEDOT:PSS HTL and the perovskite photoactive layer. Therefore, exploiting neutral and hydrophobic organic/polymer HTL that possessing matched energy levels are particularly important to fully unveil the potential of *p-i-n* pero-SCs. Although many HTL materials such as poly(3-hexylthiophene) (P3HT),⁸ poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine] (poly-TPD),⁹ polytriarylamine (PTAA),¹⁰⁻¹² 1,4'-bis(4-(diptoyl)aminostyryl)benzene (TPASB),¹³ TAPC,¹⁴ Trux-OMeTAD¹⁵ and PhNa-1T¹⁶ have been exploited to enhance the V_{oc} and power conversion efficiency (PCE) of the *p-i-n* pero-SCs. It is still needed to develop new HTL materials with easy synthesis and high reproducible photovoltaic performance.

X-shaped organic molecule HTL materials as shown in Fig. 1a, consisting of a core and four branches, have drawn particular interest in the *n-i-p* pero-SCs due to their well-defined structure, easier purification, and fine-tuned energy levels. For example, 2,2',7,7'- tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-spiro-bifluorene (Spiro-OMeTAD) and its analogues^{17, 18} as top HTLs in *n-i-p* pero-SCs demonstrated high photovoltaic performance with the highest PCE over 20%.^{19, 20} However, they usually require additive to improve their conductivities²¹ which makes the device processing complicated and results in hysteresis and poorer device stability. Besides, the spiro or fused-ring core derivatives are expensive in

considering future application. More recently, Li *et al.* reported a series of X-shaped HTL materials (such as TPP-SMeTAD or TPP-OMeTAD) using 3-D triphenylamine (TPA) moiety as branches and *p*-xylene as core, and used them in *p-i-n* pero-SCs. The resulting HTLs can efficiently enhance charge extraction and passivate surface traps of the perovskite film, realizing a PCE of over 16% for the *p-i-n* pero-SCs.²² However, the PCE of the *p-i-n* pero-SCs needs further improved and the structure-property relationships between the HTL materials and the perovskite films remain less understood.

Silicon-containing organic semiconductor materials have been known to exhibit altered properties with respect to their carbon analogues,^{23, 24} which have been reported to show promising characteristics as photoactive layer materials for thin-film transistors²⁵ and polymer solar cells.²⁶ It was demonstrated that incorporation of silicon atom in organic semiconductor materials can be used to optimize molecular orbital shapes and energies, as well as molecule packing property by rational molecule design.²⁷ However, this promising strategy for designing HTL materials of planar p-i-n pero-SCs has not been reported.

In this work, two X-shaped small molecule HTMs, named SiTP-OMeTPA and Si-OMeTPA (see Fig. 1), were developed and used in planar *p-i-n* pero-SCs. In the molecules, two silicon-based derivatives (tetraphenylsilane or silicon atom) are employed as the cores, and TPA with methoxyl end group are used as the four branches. This molecular design strategy can substantially reduce the expensive synthetic procedure and improve the overall yields. In particular, chosing silicon atom as core for Si-OMeTPA plays an important role in simplifying synthetic procedure with a straightforward two-steps synthesis from commercial raw materials. In addition, silicon atom core can stabilize electronic properties of the molecules due to the high bond interaction between low-lying σ^* orbital of silicon atom and the π^* orbital of neighboring conjugated moiety.²⁸ As a result, Si-OMeTPA exhibits high crystallinity, excellent thermal stability, as well as appropriate energy levels to transfer holes. The *p-i-n* planar pero-SCs with the Si-OMeTPA HTL, showed a high PCE of 19.06% with Journal of Materials Chemistry A Accepted Manuscript

negligible hysteresis and excellent device stability. To our best knowledge, 19.06% is one of the highest PCE among the planar p-i-n pero-SCs to date.

2. Results and discussion

2.1 Synthesis and Physicochemical Properties



Fig. 1 (a) A schematic illustration of X-shaped molecule and their advantages. (b) Molecular structures and corresponding DFT-calculated electronic structures of (a) SiTP-OMeTPA and (c) Si-OMeTPA.

The synthetic routes of SiTP-OMeTPA and Si-OMeTPA are shown in Scheme S1 and S2 respectively, and the detailed synthetic processes are described in the Experimental section. Molecular structures of the two molecules were characterized by ¹H and ¹³C NMR spectra and MALDI-TOF mass spectrometry, as shown in Fig. S1-S6 in Electronic supplementary information (ESI). Briefly, tetrakis(4-bromophenyl)silane was synthesized by the reaction of SiCl₄ and 1,4-dibromobenzene with a 83.2% yield. Then it was coupled with two different arylamines (OMeTPA-BPIN and bis-OMeAm) through Suzuki coupling or Buchwald-Hartwig reaction, giving the target SiTP-OMeTPA and Si-OMeTPA with yields of 70.2% and 72.6%, respectively. It is worth noting that Si-OMeTPA can be synthesized by only two steps with a total yield over 60%. Meanwhile, the two materials are readily soluble in common organic solvent such as chlorobenzene (CB) and chloroform but insoluble in water and N,N-dimethylformamide (DMF). From this point of view, SiTP-OMeTPA and Si-OMeTPA are

suitable to be used as the HTL of *p-i-n* pero-SCs. It is worth mentioning that we also roughly estimate the synthesis cost of 1-g Si-OMeTPA and SiTP-OMeTPA according to the cost model that is described by Pablo *et al.*²⁹ and Osedach *et al.*³⁰. As shown in Table S2 and Table S3 in ESI, the estimated synthesis cost of Si-OMeTPA and SiTP-OMeTPA are ca. 29.57 \$/g and 35.1 \$/g, respectively, which are much cheaper than that of PTAA (423.3 \$/g).

Density functional theory (DFT) calculations were performed to further investigate the electronic structures of the two silicon based HTL materials. As shown in Fig. 1b and 1c, the electron density of Si-OMeTPA is more fully delocalized within the whole molecule than that of SiTP-OMeTPA owing to the higher bond interaction between low-lying σ^* orbital of the silicon atom and π^* orbital of the conjugated TPA moeity. Moreover, the incorporation of silicon atom in the center of SiTP-OMeTPA and Si-OMeTPA can also stabilize their electronic properties, as evidenced from the strong reversibility of redox peaks in the electrochemical cyclic voltammetry test (Fig. S7 in ESI).

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Fig. 2 (a) DSC thermograms of SiTP-OMeTPA and Si-OMeTPA at a heating rate of 10 $^{\circ}$ C/min in N₂. (b) Normalized absorption spectra of SiTP-OMeTPA and Si-OMeTPA films

with or without thermal annealing. (c) XRD patterns of Si-OMeTPA films and (d) *J-V* characteristics of the hole-only devices with the structure of ITO/PEDOT:PSS/SiTP-OMeTPA or Si-OMeTPA/Au. ^a Thermal annealed HTL at 150 °C for 30 min. ^b HTL doped with 3 wt% F4-TCNQ then thermal annealed at 150 °C for 30 min.

Both silicon based materials exhibit good thermal stability, with the decomposition temperatures of 435 °C for SiTP-OMeTPA and 426 °C for Si-OMeTPA, at 5% weight loss (Fig. S8 in ESI). Meanwhile, differential scanning calorimetry (DSC) thermograms (see Fig. 2a) reveal that SiTP-OMeTPA is amorphous in nature (glass transition temperature (T_g) detected at 147 °C). While Si-OMeTPA shows a melting peak at around 345 °C and crystallization peak at around 323 °C during the heating and cooling process, respectively, which indicates Si-OMeTPA is crystalline after thermal annealing. These results can be further confirmed by the red-shifted maximum absorption peak of the annealed Si-OMeTPA film (at 150 °C for 30 min), while the amorphous SiTP-OMeTPA shows an almost unchanged absorption spectra (see Fig. 2b). The X-ray diffraction (XRD) pattern of the Si-OMeTPA film on silicon wafer (see Fig. 2c) shows (100), (200) and (300) three diffraction peaks, revealing a lamellar molecule packing structure with a long range order in the crystalline state.^{31, 32} Meanwhile, this ordered structure could be well maintained even adding 3 wt% 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) additive. In comparison, the SiTP-OMeTPA films show no diffraction peak even after thermal annealing due to its amorphous nature (Fig. S9 in ESI).

Space-charge-limited current (SCLC) method was then used to investigate the effect of molecular packing structure on hole mobilities (μ_h) of SiTP-OMeTPA and Si-OMeTPA films. As shown in Fig. 2d and Table 1, the μ_h of the thermal annealed Si-OMeTPA film shows more than one order of magnitude higher than that of the as-cast film, due to the formation of long range ordered lamellar structure in the crystalized Si-OMeTPA film after thermal annealing. The μ_h was further enhanced by adding 3 wt% F4-TCNQ additive, resulting in a μ_h

of 2.96×10^{-4} cm²/V·s. The result agrees well with the resistance reduction of PTAA HTL by doping F4-TCNQ.³³ Although the amorphous SiTP-OMeTPA films also showed an increased μ_h after thermal annealing and doping F4-TCNQ, the relatively lower values indicate the molecule arrangement can dramatically influence hole transport ability. Therefore, it can be concluded that the long range ordered lamellar structure of the crystalized Si-OMeTPA film is one of the ideal structures for π -conjugated molecules to facilitate vertical hole transport.



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Fig. 3 (a) Transmission spectra of glass/ITO, glass/ITO/PTAA, glass/ITO/SiTP-OMeTPA and glass/ITO/Si-OMeTPA electrodes. UPS spectra in the cutoff (b) and the onset (c) energy regions of SiTP-OMeTPA and Si-OMeTPA films. (d) The images of the water and DMF droplets contact angles on different surfaces of the HTLs.

Transmittance and matched energy levels of the HTLs are also important factors that significantly affects the current density and charge extraction ability of the pero-SCs. As shown in Fig. 3a, ITO coated with 30-nm-thick Si-OMeTPA film showed almost the same transmittance, while the SiTP-OMeTPA and control PTAA films led to an abviously decreased transmittance in the wavelength range of 340-430 nm. This result reveals that the Si-OMeTPA film is a superior candidate as the HTL of *p-i-n* pero-SC without loss of incident light. Ultraviolet photoelectron spectroscopy (UPS) was then used to accurately evaluate the

highest occupied molecular orbital (HOMO) energy levels³⁴ of the two silicon based HTLs on ITO. The cutoff (E_{cutoff}) and onset (E_i) energy regions in the UPS spectra are shown in Fig. 3b and 3c, respectively. According to the equation ϕ =21.2-($E_{cutoff} - E_i$)³⁵, the HOMO energy levels of SiTP-OMeTPA and Si-OMeTPA were calculated to be -5.34 and -5.39 eV, respectively. The lowest unoccupied molecular orbital (LUMO) levels of -2.30 eV for SiTP-OMeTPA and -1.96 eV for Si-OMeTPA were obtained from their corresponding optical bandgaps (3.04 eV and 3.43 eV) and HOMO energy levels. Compared with the work function or HOMO energy level of conventional HTL, such as -5.12 eV of PEDOT:PSS and -5.13 eV of PTAA,^{36, 37} the deeper HOMO energy level of SiTP-OMeTPA and Si-OMeTPA closing to the valence band (VB) of MAPbI₃ (5.4 eV) could enhance charge transfer from MAPbI₃ to the HTL via an energetically favorable pathway without a significant loss in energy. Meanwhile, the higher LUMO (-2.3 eV and -1.96 eV) of the two silicon based HTLs can also effectively block electrons to prevent recombination at anode.

In addition, surface wettability of HTLs has a significant impact on the quality of the subsequent growth of perovskite film on it in the fabrication of the *p-i-n* pero-SCs. Generally, polar solvents have good wettability on the surface of conventional HTLs like PEDOT:PSS, as confirmed by the small contact angles of water droplet (19.7°, Fig. 3d). Recent reports reveal that the non-wetting HTL (such as PTAA) surface can facilitate the growth of high-aspect-ratio crystalline grain perovskite films and thus lead to higher photovoltaic performance of the pero-SCs.³⁸ Fortunately, as shown in Fig. 3d, the two silane-containing HTLs exhibit a comparable surface wettability with that of PTAA (contact angle of water droplet (θ)=87.2°), particularly Si-OMeTPA shows a same contact angle (θ =87.2°) with that of PTAA. We then further used DMF droplet instead of water to measure contact angles for accurately evaluating wettability of PbI₂ precursor. It can be seen that the contact angles of DMF droplet on different HTL surfaces are obviously smaller than those of water droplet due to the lower polarity of DMF, but exhibit a similar trend except that the contact angles on the

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surfaces of Si-OMeTPA and SiTP-OMeTPA are slightly lower than that on PTAA surface.⁵ Therefore, it can be expected that the improved hydrophily of two silane-containing HTL materials will facilitate the PbI₂ deposition from DMF solution leading to a full coverage of perovskite materials.³⁹ Such HTLs with balanced wettability should be beneficial for achieving high-quality perovskite films.

2.2 Photovoltaic Properties

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Based on the above results, we then fabricated planar *p-i-n* pero-SCs with a structure of glass/ITO/HTL/MAPbI₃/PCBM/Al. As shown in Fig. 4a, the MAPbI₃ film can well grow on the hydrophobic surfaces of SiTP-OMeTPA and Si-OMeTPA films showing compact and homogeneous perovskite morphologies, in particular for the MAPbI₃ film grown on Si-OMeTPA showing a larger average grain size over ~600 nm. Accordingly, in the crosssection SEM image of Si-OMeTPA based device, a thick perovskite layer (~420 nm) with grain boundaries perpendicular to the substrate is obtained, which can effectively minimize the grain boundary energy.⁵ It can be seen from Fig. 4a that all functional layers can be clearly distinguished, confirming that the planar heterojunction configuration was well formed in the pero-SCs. XRD patterns are commonly used to evaluate the quality of perovskite film in the pero-SCs. Fig. S10 in ESI shows the XRD patterns of MAPbI₃ grown on the Si-OMeTPA and SiTP-OMeTPA HTLs. It can be seen that diffraction peak at 12.4° (assigned to the (001) plane of PbI₂) is weaker for the MAPbI₃ film grown on Si-OMeTPA than that on SiTP-OMeTPA, indicating a lower PbI_2 content and more complete perovskite phase of the photoactive layer prepared on the Si-OMeTPA HTL. Low PbI_2 content has been found to be beneficial for perovskite photovoltaics due to its passivation effect at grain boundaries that reduces charge recombination.⁴⁰ Fig. 4b provides the energy-level diagram of the related materials in the pero-SCs. As the CB of perovskite is -5.40 eV,⁷ both SiTP-OMeTPA and Si-OMeTPA HTLs show a perfect energy band alignment with the perovskite photoactive layer

with small HOMO energy level offset, for efficient hole transfer and collection from the photoactive layer to the HTL.

HTL ETL/Cathode FF PCE Treatment $V_{\rm oc}$ $J_{\rm sc}$ μ_h (mA/cm^2) (%) $(cm^2/V \cdot s)$ (V) (%) SiTP-OMeTPA^a 1.39×10^{-6} PCBM/Al 0.81 58.42 14.54 6.85 as-cast 1.27×10-5 SiTP-OMeTPA^a PCBM/Al 0.98 63.31 18.10 11.28 annealed SiTP-OMeTPA^a doped/annealed PCBM/Al 0.99 71.69 19.85 14.15 6.3×10⁻⁵ 4.24×10-6 Si-OMeTPA^a as-cast PCBM/Al 0.98 57.48 15.29 8.58 8.8×10⁻⁵ Si-OMeTPA^a PCBM/Al 1.01 12.89 annealed 64.86 19.77 2.96×10⁻⁴ Si-OMeTPA^a doped/annealed PCBM/Al 1.07 74.23 22.96 18.23 Si-OMeTPA^a doped/annealed PCBM/C₆₀/BCP/Ag 1.07 77.17 23.08 19.06 Si-OMeTPA^b doped/annealed PCBM/C₆₀/BCP/Ag 1.07 75.97 22.98 18.68

 Table 1. Summary of Photovoltaic Parameters of the Pero-SCs.

^a Reverse scan: 1.2 V \rightarrow 0 V, scan-rate 200 mV/s, delay time 100 ms. ^bForward scan: 0 \rightarrow 1.2 V, scan-rate 200 mV/s, delay time 100 ms. ^c $\mu_{\rm h}$ calculated from *J-V* curves of hole-only devices.



Fig. 4 (a) Cross-section SEM images of the planar p-*i*-n pero-SCs based on Si-OMeTPA HTL (left). Top-view SEM images of the perovskite films grown on Si-OMeTPA HTL (right top) and SiTP-OMeTPA HTL (right bottom). (b) The corresponding energy-level diagram of pero-SCs. (c) *J*-*V* curves of the planar p-*i*-n pero-SCs based on different HTLs. (d) The steady-state PL spectra and (e) TRPL decay transient spectra of the perovskite films prepared on ITO or

different HTLs coated substrate. ^aThermal annealed HTL at 150 °C for 30 min. ^bHTL doped with 3 wt% F4-TCNQ then thermal annealed at 150 °C for 30 min.

Fig. 4c shows the current density-voltage (J-V) characteristics of the pero-SCs with SiTP-OMeTPA and Si-OMeTPA HTLs treated by different conditions, under the illumination of AM1.5G 100 mW/cm², and Table 1 listed the photovoltaic parameters data of the corresponding pero-SCs. The pero-SCs with the as-cast HTL exhibited quite poor PCE of 6.85% for the device with SiTP-OMeTPA HTL and 8.58% for Si-OMeTPA HTL with the low V_{oc} , short circuit current density (J_{sc}), and fill factor (FF), which could be attributed to the low hole mobilities of the as-cast HTLs (1.39×10⁻⁶ for SiTP-OMeTPA HTL and 4.24×10⁻⁶ cm²/V•s for Si-OMeTPA HTL).⁴¹ After thermal annealing of the HTLs at 150 °C for 30 min before depositing perovskite films, the PCEs of the SiTP-OMeTPA and Si-OMeTPA based devices were dramatically increased to 11.2% and 12.89%, respectively, which could be ascribed to the significantly enhanced hole mobilities of the HTLs that improves Ohmic contact and charge extraction ability of the device. For the devices based on the HTLs with 3 wt% F4-TCNQ and thermal annealing (doped/annealed), the PCEs of the pero-SCs with SiTP-OMeTPA and Si-OMeTPA HTLs were further improved to 14.15% and 18.23%, respectively. Notably, the Si-OMeTPA HTL based pero-SCs exhibits ~30% higher PCEs than that of the SiTP-OMeTPA based devices. The superior photovoltaic performance of the Si-OMeTPA HTL could be attributed to its higher μ_h and higher transparency originating from long range ordered lamellar phase structure and more fully delocalized electron in Si-OMeTPA.

The charge transfer properties of the pero-SCs were further investigated by steady-state PL spectra and time-resolved PL (TRPL) measurements, as showed in Fig. 4d and 4e, and Table S1 in SI. The perovskite film shows the strongest PL quenching and reduced life time (22.35 ns) when depositing it on the doped/annealed Si-OMeTPA HTL in comparison to

those on the as-cast Si-OMeTPA, annealed Si-OMeTPA, and even the doped/annealed SiTP-OMeTPA HTLs. This means that the excitons produced in the perovskite film can be easily dissociated and the holes can be more efficiently extracted by the doped/annealed Si-OMeTPA HTL. The results agree with the improved photovoltaic performance of the pero-SCs with the doped/annealed Si-OMeTPA HTL. In addition, from the obviously improved J_{sc} and FF for the doped/annealed Si-OMeTPA based device, we can also conclude that the crystalized Si-OMeTPA with dopant has less traps in it or at the surface of Si-OMeTPA/perovskite, which facilitates charge transportation and suppresses charge recombination.



Fig. 5 (a) Charge collection probability as a function of internal voltage; (b) light intensitydependence of V_{oc} for the pero-SCs with the doped/annealed SiTP-OMeTPA or Si-OMeTPA HTLs.

In order to understand the device operation mechanism of the *p-i-n* pero-SCs. The plots of photocurrent (J_{ph}) versus the effective applied voltage (V_{eff}) for the devices were measured to investigate the influence of different HTLs (doped/annealed SiTP-OMeTPA and Si-OMeTPA) on the exciton dissociation and charge collection. As can be seen from Fig. 5a, when V_{eff} arrives at ~2 V, J_{ph} values for two devices reach saturation (J_{sat}) , suggesting that charge recombination is minimized at higher voltage due to the high internal electric field in the devices. The charge extraction probability (CEP) can be calculated from the ratio of J_{ph}/J_{sat} .⁴² We can find that the CEP increases from 0.923 to 0.944 by changing doped/annealed SiTP-OMeTPA to doped/annealed Si-OMeTPA HTL. This result indicates better charge extraction ability of pero-SC can be achieved by using the crystalized Si-OMeTPA HTL with long range ordered lamellar structure.

Fig. 5b shows the charge recombination kinetics of devices by measuring V_{oc} at varied logarithmically (ln(I)) with light intensity. The slopes for the devices with the doped/annealed SiTP-OMeTPA and doped/annealed Si-OMeTPA HTL are 1.43 kT/e and 1.19 kT/e, respectively. The significant decreased slope of the device with the doped/annealed Si-OMeTPA HTL, that are closed to the trap-free device with a slope of 1.0 kT/e^{43, 44}, indicates the reduced trap state in the perovskite film. This result could be ascribed to that the doped/annealed Si-OMeTPA HTL is more beneficial for the growth of MAPbI₃ with less traps, which can effectively depress the charge carriers recombination thus achieve higher device performance.

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Fig. 6 (a) *J-V* curves of the pero-SCs with Si-OMeTPA as HTL and C₆₀/BCP as double cathode buffer layers in reverse and forward scan measured under the illumination of AM1.5G, 100 mW/cm². Forward scan: -0.2 V \rightarrow 1.2 V, scan rate 200 mV/s, delay time 100

ms; Reverse scan: 1.2 V \rightarrow -0.2 V, scan rate 200 mV/s, delay time 100 ms. (b) EQE spectra of the corresponding pero-SCs. (c) Histograms of device PCE measured for 50 corresponding pero-SCs. (d) The plot of PCE values versus synthetic steps of organic HTLs used for the MAPbI₃ based *p-i-n* pero-SCs reported in literatures and this work.

In order to further improve photovoltaic performance of the *p-i-n* pero-SCs with the doped/annealed Si-OMeTPA as HTL, we used the thermally evaporated C_{60} /bathocuproine (BCP) double layers as cathode buffer layer in the device, in considering that the BCP film as an exciton-transporting and hole-blocking layer could realize ehancement of device performance.⁴⁵ The device structure is glass/ITO/Si-OMeTPA/MAPbI₃/PCBM/C₆₀ (20 nm)/BCP (5 nm)/Ag. As shown in Fig. 6a and Table 1, the devices showed a further improved PCE of 19.06 % measured in the reverse scan direction, with a J_{sc} of 23.08 mA/cm², a V_{oc} of 1.07 V, a FF of 77.17%. which is quite consistent with the PCE measured in the forward scan direction (18.68%), with a J_{sc} of 22.98 mA/cm², a V_{oc} of 1.07 V, a FF of 75.97%, indicating negligible *J-V* hysteresis. The performance enhancement and negligible hysteresis behavior could be attributed to the well-grown perovskite film on the Si-OMeTPA HTL and the improved electron-collection and hole-blocking property of the C₆₀/BCP double cathode buffer layers.

External quantum efficiency (EQE) spectra of the corresponding pero-SCs are shown in Fig. 6b. The J_{sc} value calculated from the integration of the EQE spectrum was 21.9 mA/cm², which agrees well with the J_{sc} value obtained from the J-V curve within 5% deviation. Fig. 6c shows a histogram of the PCE values of 50 devices. Half of the devices based on the doped/annealed Si-OMeTPA as HTL and with the C_{60} /BCP double cathode buffer layers demonstrated PCEs over 18.0%. Fig. 6d plots PCE values *versus* synthetic steps of the HTLs used for the *p*-*i*-*n* pero-SCs reported in literatures and this work. It can be seen that 19.06% is the highest PCE in the planar *p*-*i*-*n* pero-SCs with the HTL synthesized by only two steps, indicating that Si-OMeTPA is a promising cheap HTL material for future application of the *p*-

i-n pero-SCs. It is worth noting that this PCE is only lower than the highest reported value of the device with PTAA HTL for the MAPbI₃ system, where additive and antisolvent dripping treatments were simultaneously employed to further improve the quality of MAPbI₃ film.¹² However, these treatments need stringent processing and toxic solvent, in particular for the antisolvent technology, which are unfavorable for large-area solar cell fabrication and device reproducibility. Encouragingly, when fabricating devices under the same condition (without additional treatments to MAPbI₃), the Si-OMeTPA HTL based device showed an approximately 10% enhanced PCE and slightly higher V_{oc} compared to that of the device using PTAA as HTL (PCE of 17.47% consistent with previous reports.^{10, 33}, see in Fig. S11, ESI), which probably attributes to the well grown perovskite film on Si-OMeTPA as well as better matched device energy levels.



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Fig. 7 (a) Stability of the *p-i-n* pero-SCs in (a) nitrogen atmosphere and (b) ambient atmosphere with 70-80% RH.

Stability of the pero-SCs is an another critical issue for their application. First of all, we investigated the the effect of intrinsic thermal annealing stability of the Si-OMeTPA HTL on the performance of the *p-i-n* pero-SCs. Considering the decomposition of perovskite film and F4-TCNQ at high thermal annealing temperature, Si-OMeTPA without dopant was thermal annealed at different temperatures (100-200 $^{\circ}$ C) with different time (5-30 min), then used as HTL to fabricate the device directly. As shown in Fig. S12 in ESI, the PCEs of the devices

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with the Si-OMeTPA HTL exhibit only slight variation with increasing the thermal annealed temperature and with extending the annealing time on the HTL, indicating a promising thermal stability of the Si-OMeTPA HTL without influencing its long range ordered lamellar structure as well as electronic coupling between Si-OMeTPA and MAPbI₃. For the planar *p-in* pero-SCs, the chemical stability of HTL is also particularly important due to its influence on the interfaces between the HTL and perovskite film and between the HTL and ITO or FTO bottom transparent electrode. The storage stability of the *p-i-n* pero-SCs based on Si-OMeTPA HTL and control PEDOT:PSS HTL without encapsulation were studied in the nitrogen and ambient atmosphere, respectively, as shown in Fig. 7. In the nitrogen atmosphere, the PCE of the control pero-SC based on PEDOT:PSS HTL degraded to 74% of its initial value when keeping in the dark condition for 500 h (see Fig. 7a), while the Si-OMeTPA HTLbased device retained over 92% of its initial PCE. One possible reason responsible for the improved device stability could be ascribed to the neutral characteristic of the Si-OMeTPA HTL, which can effectively prevent the corrosion agaist ITO and perovskite film. For investigation of the stability of the devices in ambient atmosphere, we fabricated the pero-SCs using a structure of ITO/PEDOT:PSS or Si-OMeTPA/perovskite/PCBM/C₆₀/BCP/Ag, and the unencapsulated devices were stored under ambient atmosphere with a ~60-80% relative humidity (RH). As shown in Fig. 7b, after 130 h exposure, the Si-OMeTPA based device retained almost 90% of its initial PCE, while the PCE of the PEDOT:PSS based devices dramatically degraded to 49%. We could attribute the obviously enhanced stability of the Si-OMeTPA based devices to the hydrophobicity of the Si-OMeTPA HTL, which will protect the MAPbI₃ layer from water ingress.

3. Conclusion

In conclusion, we synthesized two low-cost X-shaped organic molecules Si-OMeTPA and SiTP-OMeTPA with silicon core and TPA branches, and used them as HTL in the planar *p-i-n* pero-SCs. Among the two HTLs, Si-OMeTPA can be simply synthesized by two steps from commercial raw materials with a total yield of over 60%, and possesses excellent thermal stability, high crystallinity with a long range ordered lamellar structure and higher μ_h . Therefore, the Si-OMeTPA HTL allows us simultaneously address several major challenges of the *p-i-n* pero-SCs, including facilitating the growth of high-quality and less trap states polycrystalline perovskite films as well as improving hole extracting ability and band alignment at interface. As a result, the *p-i-n* pero-SCs with the doped/annealed Si-OMeTPA as HTL and C₆₀/BCP as double cathode buffer layers showed significantly enhanced PCE of 19.06% with negligible hysteresis behavior and high stability. The results indicate that Si-OMeTPA is a promising low-cost HTL materials for future application of the *p-i-n* pero-SCs.

4. Experimental Section

4.1 Materials synthesis

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4.1.1 Synthesis of SiTP-OMeTPA

4-bromo-N,N-bis(4-methoxyphenyl)aniline (OMeTPA-Br) 4-bromoaniline (5.00 g, 29.2 mmol), 4-iodoanisole (14.4 g, 61.3 mmol), CuI (0.28 g, 1.46 mmol), KOH (12.8 g, 228 mmol), and 1,10-phenanthroline (0.26 g, 1.46 mmol) were added in degassed anhydrous toluene (50 mL) and the reaction mixture was heated to 110 °C. Reaction was continued for 36 h and then the reaction mixture was cooled to room temperature, diluted with CH₂Cl₂ (100 mL), and washed three times with 150 mL water. The combined organic phases were dried over anhydrous MgSO₄, and the solvent was evaporated subsequently. The crude product was purified by silica gel chromatography using petroleum ether/dichloromethane (3/1, v/v) as eluent to afford the final product as yellow solid (6.02 g, 53.8%). ¹H NMR (300 MHz, *d*₆-DMSO) δ 7.31 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.9 Hz, 4H), 6.92 (d, J = 8.9 Hz, 4H), 6.67 (d, J = 8.9 Hz, 2H), 3.74 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 156.06, 147.93, 140.56, 131.77, 127.74, 126.58, 114.79, 55.50.

4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

yl)phenyl)aniline (OMeTPA-BPIN) OMeTPA-Br (2.0g, 5.2 mmol) was added into a dry 250 ml Schlenk flask, and 50 mL anhydrous THF was transferred into the flask, immediately. 2.72 mL (6.53 mmol) 2.4 M *n*-BuLi solution was then injected dropwise by syringe into the THF solution, and kept stirring at -78 °C for 2 hours. After that, isopropoxyboronic acid pinacol ester (1.21 g, 6.53 mmol) was added dropwise into the above solution by syringe. The reaction mixture was firstly kept stirring at -78 °C for 1 hour and then warmed up to room temperature for overnight. Deionized water (20 mL) is added to quench the reaction. The phases are separated and the aqueous layer is extracted with dichloromethane (3×100 mL). The combined organic phases are dried over anhydrous MgSO₄, the solvent was removed by rotor-vapor. The crude product was purified by silica gel chromatography using petroleum ether/dichloromethane (3/1-1/1, v/v) as eluent to afford the final product as white solid (1.63 g, 72.6%). ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, J = 8.6 Hz, 2H), 7.10 - 7.02 (m, 4H), 6.89 - 6.78 (m, 6H), 3.79 (s, 6H), 1.32 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 156.20, 151.39, 140.42, 135.77, 127.14, 118.64, 114.73, 83.40, 55.47, 24.86.

4',4''',4''''',4''''''-silanetetrayltetrakis(N,N-bis(4-methoxyphenyl)-[1,1'-biphenyl]-4-amine)

(SiTP-OMeTPA) Tetra(4-bromophenyl)silane (0.5 g, 0.77 mmol), OMeTPA-BPIN (1.6 g, 3.70 mmol), Pd(PPh₃)₄ (0.027 g, 0.023 mmol) were dissolved in a mixture of Toluene (30 mL) and 2M K₂CO₃ aqueous solution (10 mL). This solution was proted by N_2 and then stirred at 100 °C for 48 hours. After cooling to room temperature, the reaction solution was diluted with 20 mL CH₂Cl₂, and washed three times with 50 mL water. The combined organic phases were dried over anhydrous MgSO₄, and the solvent was evaporated subsequently. The purified by silica gel chromatography crude product was using petroleum ether/dichloromethane (4/1-1/1, v/v) as eluent to afford the final product as light green solid (0.837 g, 70.2%). ¹H NMR (300 MHz, CDCl₃) δ 7.67 (d, J = 8.1 Hz, 8H), 7.58 (d, J = 8.1 Hz, 7.58 (d, J 8H), 7.44 (d, J = 8.6 Hz, 8H), 7.07 (t, J = 8.6 Hz, 16H), 6.98 (d, J = 8.4 Hz, 8H), 6.89-6.78 (m, 16H), 3.80 (s, 24H). MS (MALDI-TOF): calcd for $C_{104}H_{88}N_4O_8Si [M]^+$, 1548.64; found, 1548.73.

4.1.2 Synthesis of Si-OMeTPA

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Tetrakis(4-bromophenyl)silane (Si-TBP) 1,4-dibromobenzene (4.00 g, 16.95 mmol) and 50 mL anhydrous THF were added into a dry 250 ml Schlenk flask. Then 7.41 mL (17.8 mmol) 2.4 M *n*-BuLi solution was injected dropwise by syringe at -78 °C, and the mixture was stirring at -78 °C for 2 hours. After that, a 5 mL THF solution of SiCl₄ (0.65 g, 3.85 mmol) was added into the mixture and kept stirring at -78 °C for 1 hour, then warmed up to room temperature for overnight. The reaction solution was quenched by 50 mL deionized water, and obtained aqueous solution was extracted by dichloromethane (100 mL) for three times. The combined organic phase were dried over anhydrous MgSO₄, the solvent was removed by rotor-vapor. The crude product (2.06 g, 82.3%). ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 7.9 Hz, 8H), 7.34 (d, J = 7.9 Hz, 8H). ¹³C NMR (150 MHz, CDCl₃) δ 137.58, 131.43 (d, J = 7.0 Hz), 125.42.

4,4',4",4"'-silanetetrayltetrakis(N,N-bis(4-methoxyphenyl)aniline) (Si-OMeTPA) Si-TBP (0.5 g, 0.77 mmol), bis(4-methoxyphenyl)amine (bis-OMeAm) (1.26 g, 3.85 mmol), Pd₂(dba)₃ (0.022 g, 0.023 mmol) and sodium tert-butoxide (0.44 g, 4.62 mmol) were dissolved in 10 ml of refined-anhydrous toluene in a 50 mL two-necked flask, and then the solution was protected with N₂. Then a solution of tri-tert-butylphosphine in toluene (1 M, 46 μ l, 0.046 mol) was injected. The mixture was heated to 110 °C and stirred for 48 h. After cooling to room temperature, the mixture was diluted with dichloromethane and washed by brine for three times. The organic phase was combined and dried over MgSO₄. After the solvent was removed, the crude product was purified by silica gel chromatography using petroleum ether/dichloromethane (4/1-1/1, v/v) as eluent to afford the final product as white power

(0.696 g, 72.6%). ¹H NMR (300 MHz, CDCl₃) δ 7.33 (d, J = 8.5 Hz, 8H), 7.09 - 7.02 (m, 16H), 6.88 - 6.78 (m, 24H), 3.78 (s, 24H). ¹³C NMR (75 MHz, CDCl₃) δ 155.99, 149.47, 140.65, 137.04, 127.02, 125.58, 118.83, 114.65, 55.48. MS (MALDI-TOF): calcd for C₈₀H₇₂N₄O₈Si [M]⁺, 1244.51; found, 1244.39.

4.2 Measurements and Instruments

¹H NMR and ¹³C NMR spectra were measured using a Varian Mercury-400 NMR. Time-of-flight mass spectra were recorded with a Broker MALDI-TOF mass system. Thermal gravimetric analysis (TGA) was carried out on Discovery-TG, with a heating rate of 10 °C/min under nitrogen flow. Differential scanning calorimetry (DSC) was performed under nitrogen flushing at a heating rate of 10 °C/min with Discovery-DSC Q20. Electrochemical measurements of the two HTL materials were performed with a Bioanalytical Systems BAS100 B/W electrochemical workstation. The cyclic voltammetry (CV) diagrams of the HTMs were obtained by using *n*-Bu₄NPF₆ as supporting electrolyte in acetonitrile solution with a glass carbon working electrode, a platinum wire counter electrode and a Saturated calomel electrode (SCE) reference electrode under N_2 atmosphere. UPS was tested by Kratos Axis Ultra DLD. PL was tested by FLS980 (Edinburgh Instrument, UK), and the transient photoluminescence also used FLS980 (Edinburgh Instrument, UK) at the wavelength of 768 nm. XRD patterns were collected using X'Pert Pro MPD (PANalytical B.V.). The SEM images were collected on SU8010 produced by Hitachi, where the electron beam accelerated at 5kV. The J-V characteristics of the devices was measured with a computer-controlled Keithley 2400 Source Measure Unit under the illumination of AM1.5G white light source, the optical power at the sample was 100 mW/cm². And the light intensity was corrected by a standard silicon solar cell. The EQE was obtain using a solar cell spectral response measurement system (Enli Technology Co., Ltd., QE-R3011). The light intensity at each wavelength was also calibrated with a standard Si solar cell. The transmittance and reflection

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spectra were measure with Ultraviolet Spectrometer (Agilent Technologies Cary 5000 UV-Vis-NIR).

4.3 Device Fabrication

ITO glass substrates were sequentially washed with isopropanol, acetone, distilled water, and ethanol for 20 min, then dried with N_2 . The sythesized HTL materials (Si-OMeTPA and SiTP-OMeTPA) and control PTAA were dissolved in CB with a concentration of 5 mg/mL and 10 mg/mL, respectively. Then, they were spin-coated on the ITO/glass substrates at the speed of 6000 rpm for 30 s. For the doped HTLs, the 3 wt% and 1 wt% F4-TCNO were added into sythesized HTL materials and PTAA solution, respectively, before depositing. The resulting HTLs were thermally annealed at 150 °C for 30 min (Si-OMeTPA and SiTP-OMeTPA) and 100 °C for 10 min (PTAA). The perovskite layer was fabricated by two-step method. PbI₂:MAI precursor solution (35 μ L, molar ratio = 1.3:0.3, dissolved in DMF/DMSO, volume ratio = 9:1) was stirred at 70 $^{\circ}$ C overnight on the hot plate. On the top of HTL, the PbI₂:MAI precursor solution was firstly spin-coated at 6000 rpm for 15s. Then MAI solution (40 µL, 35 mg/mL, dissolved in 2-propanol) was spin-coated at 3700 rpm for 45 s on PbI₂:MAI film. After that, the deposited films were thermal annealed at 100 °C for 30 min in a nitrogen-filled glove-box. The resulting perovskite films were coated with PCBM film by spin-coating 20 mg/mL PCBM solution (in CB) at 2000 rpm for 30s. Finally, Al (100 nm) electrode or C_{60} (20 nm)/BCP (5 nm)/Ag (100 nm) were deposited on PCBM by vacuum evaporation under 1*10⁻⁶ mbar.

Electronic supplementary information Materials synthesis and device fabrication. Characterization figures showing ¹H NMR, ¹³C NMR, TGA, DSC, XRD of SiTP-OMeTPA and Si-OMeTPA. Characterization of perovskite film including XRD and TRPL data. PCE evolution of pero-SCs with thickness and annealing time, cost analysis of HTL materials.

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Acknowledgment

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51673138 and 91633301), the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), the Jiangsu Provincial Natural Science Foundation (Grant No. BK20160059), and Natural Science Foundation of the Jiangsu Higher Education Institutions of China (16KJB430027). Project Funded by China Postdoctoral Science Foundation (Grant No. 2017M610347).

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Table of Contents

We synthesized a low-cost silicon containing HTL materials, achieving an excellent PCE of 19.06% for planar p-i-n perovskite solar cells.

