Surface roughness is a key parameter for judging the performance of a given material’s surface quality for its electronic application. A powerful tool to measure surface roughness is 3D laser scanning confocal microscopy (LSM), which will allow you to assess roughness and compare production and finishing methods, and improve these methods based on mathematical models.

Focus on creating high-conductivity electronic devices with minimal power loss using laser scanning microscopy is an effective tool to discern a variety of roughness parameters.
Side-Chain Functionalized Polymer Hole-Transporting Materials with Defect Passivation Effect for Highly Efficient Inverted Quasi-2D Perovskite Solar Cells

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Compared with inverted 3D perovskite solar cell (PSCs), inverted quasi-2D PSCs have advantages in device stability, but the device efficiency is still lagging behind. Constructing polymer hole-transporting materials (HTMs) with passivation functions to improve the buried interface and crystallization properties of perovskite films is one of the effective strategies to improve the performance of inverted quasi-2D PSCs. Herein, two novel side-chain functionalized polymer HTMs containing methylthio-based passivation groups are designed, named PVCz-SMeTPA and PVCz-SMeDAD, for inverted quasi-2D PSCs. Benefited from the non-conjugated flexible backbone bearing functionalized side-chain groups, the polymer HTMs exhibit excellent film-forming properties, well-matched energy levels and improved charge mobility, which facilitates the contact extraction and transport between HTM and quasi-2D perovskite layer. More importantly, by introducing methylthio units, the polymer HTMs can enhance the contact and interactions with quasi-2D perovskite, and further passivating the buried interface defects and assisting the deposition of high-quality perovskite. Due to the suppressed interfacial non-radiative recombination, the inverted quasi-2D PSCs using PVCz-SMeTPA and PVCz-SMeDAD achieve impressive power conversion efficiency (PCE) of 21.41% and 20.63% with open-circuit voltage of 1.23 and 1.22 V, respectively. Furthermore, the PVCz-SMeTPA based inverted quasi-2D PSCs also exhibits negligible hysteresis and considerably improved thermal and long-term stability.

1. Introduction

Organic–inorganic hybrid perovskite solar cells (PSCs) have attracted wide attention in the field of new energy photovoltaic due to their excellent photoelectric performance, low-cost fabrication process and high power conversion efficiency (PCE).[1–6] Among the device architectures, inverted (p–i–n) PSCs have the advantages of long-term stability, small hysteresis effect, low temperature manufacturing, as well as integration with commercial photovoltaic technology (such as crystalline silicon and Copper indium gallium selenide photovoltaic technology).[7–11] which are more suitable for commercial scale-up production in compared with regular (n–i–p) PSCs.[12,13] However, the unfavorable non-radiative recombination energy losses at the interface of perovskite/carrier-transporting layer are serious in the inverted PSCs, which have greatly limited the improvement of device performance for some time.[14–17] Recently, researchers have explored different interface-engineering strategies being focus on passivating the defects at the top surface or buried interface of 3D perovskite films, which leads to the efficiency of inverted PSCs increased significantly to >25%.[18–22]

Despite remarkable progress of efficiency for inverted PSCs, the inherent instability of 3D perovskites under operational environments still limits the commercial development of inverted PSCs.[7] Comparing to the 3D perovskites, quasi-2D perovskites with bulky organic spacer exhibit enhanced thermal and photo stability when they are applied in inverted or regular PSCs.[23,24] However, owing to the efficiency of quasi-2D PSCs still inferior to 3D counterparts, further improvement of PCE is highly required for the inverted quasi-2D PSCs to meet both efficiency and stability requirements. Besides the additive, cation and solvent engineering of quasi-2D perovskite active layers,[25,26] the top surface or buried interface engineering of perovskite to passivate defects and suppress non-radiative recombination are also crucial for optimizing the performance of inverted quasi-2D PSCs.[27]

Hole-transporting materials (HTMs), as the underlying substrate of 3D or quasi-2D perovskite layer in inverted PSCs, not
only affects the interfacial carrier transfer dynamics, but also plays a key role in the crystal growth and defect chemistry of perovskite with different dimensional structures. Compared with small molecules and inorganic HTMs, polymer HTMs have more excellent film-forming properties and solvent resistance, and are more compatible with low-cost printing technology (inkjet and slot-die printing, etc.).

These strategies may increase the instability and cost of PTAA based inverted PSCs. Thus, it is necessary to develop high-performance polymer HTMs that can simultaneously modulate the crystallinity and improve the buried interface of perovskite to replace PTAA in inverted 3D or quasi-2D PSCs.

To date, several main-chain conjugated, π-conjugation interrupted and cross-conjugated polymer HTMs with efficient defect passivation effects have been developed for commonly 3D perovskite based inverted PSCs, which could optimize the interfacial energy levels and efficient defect passivation effects are highly necessary for inverted quasi-2D PSCs, in order to minimize the problems of interfacial energy level mismatch and high non-radiative charge recombination in the devices.

Side-chain polymer HTMs with excellent film-forming ability, suitable energy level and high hole mobility demonstrate great application potential for inverted quasi-2D PSCs, although the ability of them to passivate perovskite defects still needs to be enhanced. In this work, based on the non-conjugated flexible backbone, we successfully synthesized two side-chain functionalized polymer HTMs (PVClz-SMeTPA and PVClz-SMeDAD) containing methylthio-based passivation groups. The methylthio groups in the side-chain of PVClz-SMeTPA and PVClz-SMeDAD can passivate defects, improve the crystallinity and buried interface properties of quasi-2D perovskite via dipole intermolecular interaction between a lone pair electron and Pb2+. The PVClz-SMeTPA and PVClz-SMeDAD were synthesized via radical polymerization, and methylthioarylamine-functionalized vinylcarbazole monomers were obtained from Suzuki coupling or Buchwald–Hartwig reactions. The synthetic routes of two polymers are shown in Scheme S1 (Supporting Information). The structure of the intermediate monomers was characterized by 1HNMR and 13CNMR (Figures S10–S16, Supporting Information). The synthetic cost of PVClz-SMeTPA and PVClz-SMeDAD is estimated to be low at $24.94 and $11.34 g⁻¹, providing substantial cost advantages compared to PTAA ($423.3 g⁻¹) (detailed cost analysis, Tables S1 and S2, Supporting Information). PVClz-SMeTPA and PVClz-SMeDAD were obtained with a number-average molecular weight (Mₙ) of 20477 and 18650, as well as polydispersity index (PDI) of 1.81 and 1.24 for them, respectively. Both polymers exhibit good solubility in common organic solvents, such as dichloromethane, ethyl acetate, tetrahydrofuran, toluene, and chlorobenzene, which would be beneficial for device fabrication. Both PVClz-SMeTPA and PVClz-SMeDAD have excellent thermodynamic stability (Figure S1, Supporting Information). The thermal decomposition temperatures (T_d) of the two polymers are 415 and 411 °C, respectively, which reflects good thermal stability of the polymers.

The optical properties of PVClz-SMeTPA and PVClz-SMeDAD films are studied by ultraviolet–visible (UV–vis) and photoluminescence (PL) spectroscopy (Figure 2a). According to the spectra, the two polymer HTMs show absorption peaks at 339 and 328 nm. The maximum emission peaks of PVClz-SMeTPA and PVClz-SMeDAD in PL spectrum are 395 and 425 nm, respectively. PVClz-SMeTPA shows a blue-shift of 30 nm compared with PVClz-SMeDAD, which may be due to the weaker electron-donating ability of methylthio-based triphenylamine units than diphenylamine moieties substituted in the 3,6 position of carbazoles. Compared to the solution state (Figure S2, Supporting Information), the UV–vis and PL spectra of PVClz-SMeTPA and PVClz-SMeDAD films shifted significantly, indicating that there have obvious π-π stacking phenomenon in the film state of PVClz-SMeTPA and PVClz-SMeDAD molecules. The optical bandgaps (E_g) of PVClz-SMeTPA and PVClz-SMeDAD evaluated from the onset of absorption were 3.12 and 3.34 eV, respectively.

In order to determine the HOMO energy levels of PVClz-SMeTPA and PVClz-SMeDAD, we used the IPS-4 ionization energy measurement system to conduct photoelectron yield spectroscopy (PYS) analysis of PVClz-SMeTPA and PVClz-SMeDAD in N₂ atmosphere (Figure 2b). The HOMO levels of two polymers were measured to be −5.61 and −5.51 eV, respectively. As shown in Figure S3 (Supporting Information), cyclic voltammetry (CV) was also used to measure PVClz-SMeTPA and PVClz-SMeDAD films, obtaining HOMO levels of −5.58 and −5.47 eV for them, which are in accordance with PYS results.

2. Results and Discussion

Figure 1 shows the chemical structures of PVClz-SMeTPA and PVClz-SMeDAD containing methylthio-based passivation groups, which could improve the crystallinity and buried interface properties of perovskite through the dipole intermolecular interaction between methylthio groups and Pb₂⁺. The PVClz-SMeTPA and PVClz-SMeDAD were synthesized via radical polymerization, and methylthioarylamine-functionalized vinylcarbazole monomers were obtained from Suzuki coupling or Buchwald–Hartwig reactions. The synthetic routes of two polymers are shown in Scheme S1 (Supporting Information). The structure of the intermediate monomers was characterized by 1HNMR and 13CNMR (Figures S10–S16, Supporting Information). The synthetic cost of PVClz-SMeTPA and PVClz-SMeDAD is estimated to be low at $24.94 and $11.34 g⁻¹, providing substantial cost advantages compared to PTAA ($423.3 g⁻¹) (detailed cost analysis, Tables S1 and S2, Supporting Information). PVClz-SMeTPA and PVClz-SMeDAD were obtained with a number-average molecular weight (Mₙ) of 20477 and 18650, as well as polydispersity index (PDI) of 1.81 and 1.24 for them, respectively. Both polymers exhibit good solubility in common organic solvents, such as dichloromethane, ethyl acetate, tetrahydrofuran, toluene, and chlorobenzene, which would be beneficial for device fabrication. Both PVClz-SMeTPA and PVClz-SMeDAD have excellent thermodynamic stability (Figure S1, Supporting Information). The thermal decomposition temperatures (T_d) of the two polymers are 415 and 411 °C, respectively, which reflects good thermal stability of the polymers.

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Compared with our previous synthesized methoxylamine-functionalized polymers, PVCz-SMeTPA and PVCz-SMeDAD show downshifted HOMO levels due to the π-acceptor capability of the sulfur atom. Figure 2c shows the energy levels distribution of PVCz-SMeTPA, PVCz-SMeDAD, and PTAA in the inverted Quasi-2D PSCs. By introducing methylthioarylamine groups, the HOMO energy levels of two polymer HTMs can be optimized to match well with the VB of quasi-2D perovskite (Figure S4, Supporting Information), and the energy level barrier between different functional layers in the inverted quasi-2D PSCs can be reduced, which is good for hole extraction, as well as reducing charge accumulation and recombination at buried interface.[50,51] According to the $E_h$ and corresponding HOMO levels, the lowest unoccupied molecular orbital (LUMO) energy levels of PVCz-SMeTPA and PVCz-SMeDAD are calculated to be $-2.49$ and $-2.17$ eV, respectively. Their LUMO levels are high

![Figure 1](image1.png)

**Figure 1.** Chemical structures of PVCz-SMeTPA and PVCz-SMeDAD, and schematic illustration of buried interface passivation of quasi-2D perovskite by the PVCz-SMeTPA.

![Figure 2](image2.png)

**Figure 2.** a) Normalized UV–vis absorption and PL emission spectra of PVCz-SMeTPA and PVCz-SMeDAD films. b) PYSoft of two polymers. c) Structure and energy level diagram of functional layers in inverted PSCs. d) Hole-injection characteristics measured by the SCLC method based on the device structure of ITO/PEDOT:PSS/HTMs/MoO$_3$/Au.
enough for electron blocking. As shown in Figure 2d, space charge-limited current (SCLC) method was used to evaluate the hole-mobilities of new polymer HTMs. The hole-mobility values of PVCz-SMeTTPA was calculated to be $6.59 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ higher than that of PVCz-SMeDAD ($4.37 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and PTAA ($3.69 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Table 1 summarizes detailed data on the optical, thermodynamic, electrochemical, and photoelectric properties of PVCz-SMeTTPA and PVCz-SMeDAD.

Moreover, polymer HTMs with uniform morphology and wettability are of great significance for the buried interface contact and crystal growth of perovskites. According to the atomic force microscopy (AFM) images of ITO substrate coated with PVCz-SMeTTPA, PVCz-SMeDAD, and PTAA films (Figure S5), all of them exhibit uniform surface morphologies with low root-mean-square (RMS) roughness of 1.3–1.4 nm. Figure S6 (Supporting Information) shows the dimethylformamide (DMF) contact angle test of PVCz-SMeTTPA, PVCz-SMeDAD, and PTAA to study the wettability of the perovskite precursor solution on the polymers, which is crucial to the crystal growth of perovskites. The DMF contact angle values of PVCz-SMeTTPA, PVCz-SMeDAD, and PTAA films are only 9.3°, 11.7°, and 20.4°, respectively, implying better spreading of the perovskite precursor solution on our two polymers than PTAA. Owing to enhanced wettability of our side-chain functionalized polymers, we are able to deposit perovskite directly on the polymer HTMs without additional surface treatment, and the buried interfacial contact between PVCz-SMeTTPA/PVCz-SMeDAD and perovskite will also be enhanced. We also investigated the morphology, back contact and crystallinity of quasi-2D perovskites growing on different HTMs. AFM was used to investigate the influence of different HTMs substrates on the crystallization growth of perovskite, as shown in Figure 3a–c. The root mean square (RMS) roughness of perovskite films based on PVCz-SMeTTPA and PVCz-SMeDAD substrates are 12.5 and 14.3 nm, respectively, compared to the perovskite film on the control PTAA (17.1 nm).

The smoothness of the quasi-2D perovskite films based on our polymer HTMs will benefit the charge extraction and transport in the inverted PSCs. Figure 3d–f exhibits the top-view SEM images of the perovskite films on different polymer HTMs, and the corresponding grain size distributions are illustrated in the Figure 3g–i. All SEM images show dense film morphologies and smooth flatness of the perovskite films. The average grain sizes of PVCz-SMeTTPA/Perovskite and PVCz-SMeDAD/Perovskite films are $\approx 2.38$ and $\approx 2.10 \text{ nm}$, respectively, while the average grain size grown on the control PTAA/Perovskite film is $\approx 1.78 \text{ nm}$. The relative larger grain size of perovskite based on PVCz-SMeTTPA and PVCz-SMeDAD as compared to PTAA may attribute to the excellent passivation effects, as well as wettability of polymer HTMs, which could promote the uniform film formation and growth of quasi-2D perovskites. Figure 3j is used to further explain the proposed crystal growth processes and passivation mechanisms of perovskites based on different polymers.

Furthermore, the X-ray diffraction (XRD) spectra measurements were carried out to reveal the structure and crystallinity of perovskite films deposited on PVCz-SMeTTPA, PVCz-SMeDAD, and PTAA films. As presented in Figure 4a, the XRD patterns of all polymer/perovskite films display the same diffraction peaks at 14.14° and 28.50°. The perovskite grown on the PVCz-SMeTTPA substrate has higher crystal diffraction peaks compared to PVCz-SMeDAD and PTAA based ones, indicating that PVCz-SMeTTPA/perovskite film has better crystal orientation. We also study the impact of three polymers on the absorbance of quasi-2D perovskites, as shown in Figure 4b. Compared with perovskite films with PTAA, the light absorption of perovskite films with PVCz-SMeTTPA and PVCz-SMeDAD are enhanced, which may attribute to the increase in the grain size of perovskite. To explore the defect passivation effect of PVCz-SMeTTPA, PVCz-SMeDAD, and X-ray photoelectron spectroscopy (XPS) was used to further analyze the chemical-bonding states between the two polymer HTMs and the perovskite interface. Figure 4c shows the XPS spectra of pristine perovskite film and the perovskite films covered by different polymer HTMs. The signals of the Pb 4f orbitals exhibit two main peaks at 138.51 eV $(4f_{7/2})$ and 143.41 eV $(4f_{5/2})$ for the pristine perovskite film. As compared, the Pb 4f peaks of the perovskites with PVCz-SMeTTPA and PVCz-SMeDAD all show a 0.9 eV shift to the lower binding energy. For the pristine polymer films in Figure 4d, two main single peaks assigned to the S 2p$_{3/2}$ and S 2p$_{1/2}$ orbitals are observed for PVCz-SMeTTPA (162.78 and 163.98 eV) and PVCz-SMeDAD (162.85 and 163.96 eV), while bilayered perovskite/polymer HTM films show the peaks of S 2p shift to higher binding energy. The above Pb 4f and S 2p peak shift in the XPS spectra indicate the coordination and interaction between the polymer and Pb$^{2+}$ in the perovskite, demonstrating that PVCz-SMeTTPA and PVCz-SMeDAD can passivate the buried interface defects and improve the crystallinity of perovskite films.

In order to further evaluate the photoelectric properties of PVCz-SMeTTPA and PVCz-SMeDAD, these two polymers were used as HTMs for inverted PSCs. As shown in Figure 5a, we used an inverted quasi-2D PSCs structure of ITO/polymer HTM/ quasi-2D perovskite/PC$_{71}$BM/Cr/Au, $(3FBMA)_{m}MA_{n}Pd_{1/2}$ (3FBMA = 3-fluorobenzylammonium, MA = methylammonium) based quasi-2D perovskite was adopted as the absorber material, PC$_{71}$BM is used as electron-transporting material (ETM), and Cr acts as a charge barrier layer. Figure 5b shows the cross-sectional
Figure 3. AFM images of perovskite films on a) PTAA, b) PVCz-SMeTPA, and c) PVCz-SMeDAD. d–f) SEM images of the perovskite films on different polymers. g–i) The corresponding grain size distributions of perovskites on the different polymers. j) The proposed crystal growth process and passivation mechanism of perovskites influenced by different polymers.
Figure 4. a) XRD patterns and b) UV-vis absorption spectra of perovskite films deposited on PVCz-SMeTPA, PVCz-SMeDAD, and PTAA. XPS spectra of c) Pb 4f and d) S 2p levels in the perovskite film, pristine polymer HTMs, and the bilayered perovskite/polymer HTMs films.

Figure 5. a) The device architecture of inverted quasi-2D PSC. b) SEM of the cross-sectional structure of PSC with PVCz-SMeTPA. c) J–V curve of champion cells based on three polymers recorded under AM1.5G (100 mW cm$^{-2}$). d) IPCE spectra and integrated $j_{oc}$ of three polymer HTMs based PSCs. e) Histogram of efficiency distribution of three polymer HTMs based PSCs. f) The stable output at the maximum power points for devices based on three polymer HTMs.
SEM image of inverted PSCs based on PVCz-SMeTPA. The thickness of the perovskite film is ~500 nm, and its excellent crystallinity promotes the formation of larger sized regular grains. Compared with the perovskite thin films on the PTAA (Figure S7, Supporting Information), the perovskite thin films on the surfaces of PVCz-SMeTPA and PVCz-SMeDAD are more dense and uniform, with fewer defects.

By optimizing the fabrication conditions of perovskite and HTM layers (Figure S9, Supporting Information), efficient and stable quasi-2D inverted PSCs based on PVCz-SMeTPA, PVCz-SMeDAD, and PTAA were prepared and investigated. The corresponding forward and reverse current voltage (J–V) characteristic of champion devices with different polymer HTMs presents in Figure 5c, with corresponding parameters summarized in Table 2. PVCz-SMeDAD based quasi-2D PSCs exhibit a slightly higher PCE of 20.63% due to the improved $V_{oc}$ of 1.23 V and fill factor (FF) of 0.82, while PTAA based devices show efficiency of 19.38% with $V_{oc}$ of 1.19 V and FF of 0.80. PVCz-SMeTPA based devices show an excellent PCE of 21.41% with $V_{oc}$ of 1.23 V, a short-circuit current density ($J_{sc}$) of 20.88 mA cm$^{-2}$ and FF of 0.83, which not only outperforms the PVCz-SMeDAD and PTAA based devices, but also is among the highest values for inverted quasi-2D PSCs. The enhanced performance of PVCz-SMeTPA based devices could be explained by its better energy level alignment and hole mobility. Specifically, the methylthio-based groups in our polymer are favorable for the interfacial defect passivation and crystal growth control of perovskite films, which can effectively reduce charge accumulation and suppress non-radiative recombination at the buried interface, and thereby achieving excellent device performance with higher $V_{oc}$, FF, and PCE. And smaller hysteresis between forward and reverse scans was also observed for the PVCz-SMeTPA and PVCz-SMeDAD based quasi-2D inverted PSCs. According to the incident photon-to-electron conversion efficiency (IPCE) spectra in Figure 5d, PVCz-SMeTPA and PVCz-SMeDAD based device all show higher photo-response in a broad spectral range between 300–800 nm. The integrated $J_{sc}$ values for devices with PVCz-SMeTPA, PVCz-SMeDAD, and PTAA are 21.11, 20.65, and 20.00 mA cm$^{-2}$, respectively, which are consistent with the $J_{sc}$ data obtained from the $J$–V curve test. The difference in $J_{sc}$ obtained from the $J$–V curve and IPCE spectrum is only within 5%. In addition, we also investigated the reproducibility of photovoltaic performances based on two polymer HTMs. Under the same testing conditions, we selected 50 devices from each polymer for analysis. As demonstrated in the histogram of PCEs in Figure 5e, PVCz-SMeTPA based PSCs present higher average PCE of 20.37% with narrower efficiency distribution as compared to PVCz-SMeDAD and PTAA based devices, suggesting the excellent reproducibility of high-performance devices. Besides, we found that the $V_{oc}$, FF, and PCE of PVCz-SMeTPA and PVCz-SMeDAD devices are higher than those of PTAA based devices (Figure S8, Supporting Information). Figure 5f exhibits that devices with PVCz-SMeTPA, PVCz-SMeDAD, and PTAA can continuously and stably output photocurrent for >120 min at maximum power points of 20.75, 19.70, and 19.61 mA cm$^{-2}$, confirming the reliability of the device performance.

The influence of different HTMs on charge recombination and transfer properties in perovskite films was evaluated by photoluminescence (PL) and time-resolved PL (TRPL) measurements, as shown in Figure 6a, the PL of the perovskite film with PVCz-SMeTPA and PVCz-SMeDAD exhibits a significantly quenching effect compared to the perovskite film coated on ITO glass, indicating an effective charge transfer between the perovskite and the HTM layer. By using TRPL to characterize the carrier lifetime in perovskite thin films, further exploring charge extraction and transfer in perovskite thin films. In Figure 6b, the attenuation process is defined by a double exponential attenuation fitting with Equation (1):

$$Y = A_1 \exp \left( -\frac{t}{\tau_1} \right) + A_2 \exp \left( -\frac{t}{\tau_2} \right) + y_0$$

The fast decay lifetime $\tau_1$ is related to the charge extraction speed between HTM and perovskite interface, and the slow decay lifetime $\tau_2$ is caused by the non-radiative recombination in perovskite. Compared to pristine perovskite thin films on ITO substrates ($\tau_1 = 23.07$ and $\tau_2 = 108.52$ ns), the carrier lifetime of perovskite films deposited on polymer HTMs is significantly shortened. The $\tau_1$ and $\tau_2$ of perovskite deposited on PTAA are 17.92 and 86.75 ns, respectively. In addition, the perovskite on PVCz-SMeDAD displays a shorter $\tau_1$ of 9.82 and $\tau_2$ of 54.67 ns. Among them, PVCz-SMeTPA/perovskite film shows the best decay with $\tau_1$ of 7.99 and $\tau_2$ of 43.97 ns. The results indicate that PVCz-SMeTPA can well promote the charge extraction and passivate defects at the buried of perovskite films, thereby suppressing non-radiative recombination.

In order to further understand the charge transfer and recombination process of polymers based PSCs and thus reveal the charge carrier dynamics in the devices, the relationship of $V_{oc}$ versus light intensity was further studied. The $V_{oc}$ could be fitted by the following Equation (2):

$$V_{oc} = \frac{nK_B T \ln(I)}{q} + \text{constant}$$

where $n$ is the diode ideality factor, $T$ is the absolute temperature, $K_B$ is the Boltzmann constant, $q$ is the elementary charge, and $I$ is the light intensity. $n$ values can be calculated from the slope. As displayed in Figure 6c, the devices based on PVCz-SMeTPA, PVCz-SMeDAD, and PTAA show the slope of 1.62, 1.90, and 2.01 $K_B T q^{-1}$, respectively. Compared to PTAA based PSCs, devices with PVCz-SMeTPA and PVCz-SMeDAD have lower ideality factors, suggesting that the Shockley–Read–Hall (SRH) non-radiative recombination is mitigated at the buried interface of perovskite layer in the devices.

<table>
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Table 2. Photovoltaic metrics of the champion devices based on PVCz-SMeTPA, PVCz-SMeDAD, and PTAA.
Figure 6. a) Steady-state PL spectra and b) Time-resolved PL of PVCz-SMeTPA/perovskite, PVCz-SMeDAD/perovskite, PTAA/perovskite, and original perovskite films. c) Light dependence of V_{oc} in PSCs with three polymer HTMs. d) Dark current of PSCs with three polymer HTMs. e) Trap density characterization based on the SCLC analysis of hole-only devices for PVCz-SMeTPA, PVCz-SMeDAD, and PTAA. f) Stability tests of three polymer HTMs based inverted quasi-2D PSCs kept in inert atmosphere for heat stability at 60 °C continuous annealing and long-term stability.

We adopted dark current analysis to further explore the non-radiative recombination in the PVCz-SMeTPA, PVCz-SMeDAD, and PTAA based devices. The asymmetric J–V curves of devices in the Figure 6d are divided into three regions. Region I (from negative voltage to low positive voltage) represents the leakage (shunt) current, where the J–V curve is straight and the slope is controlled by 1/R_{sh} (R_{sh} is the shunt resistance). Region II represents diffusion current and recombination current of the diode space-charge region, and region III represents the high-voltage region in the devices. The R_{sh} of PVCz-SMeTPA and PVCz-SMeDAD based PSCs is larger than that of PTAA in the region I, indicating that the first two have smaller leakage current. It can be attributed to the larger grain size of the perovskite layer, as well as the better passivation of interface defects in perovskite by PVCz-SMeTPA and PVCz-SMeDAD. According to Shockley equation, we can use Equation (3) to evaluate V_{oc}:

\[ V_{oc} = \frac{n K_B T}{q} \ln \left( \frac{J_{sc}}{J_0} \right) \]  

where \( n \) is the ideality factor, \( K_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( q \) is the elementary charge, \( J_{sc} \) is the photogenerated short-circuit current density, and \( J_0 \) is the reverse saturation current density. The lower reverse saturation current density corresponds to the higher \( V_{oc} \). The \( J_0 \) value of devices containing PVCz-SMeTPA and PVCz-SMeDAD ranges from 10^{-10} to 10^{-11} mA cm^{-2}, while the \( J_0 \) value of devices containing PTAA is \( \approx 10^{-10} \) mA cm^{-2}. This indicates that devices with PVCz-SMeTPA and PVCz-SMeDAD have higher \( V_{oc} \) compared to PTAA based device, and the results are consistent with the photovoltaic performance of the devices (Table 2).

Meanwhile, we used SCLC measurement to characterize the trap density of perovskite films on different polymer HTMs. Figure 6e shows the J–V curves of hole-only devices with structure of ITO/PEDOT:PSS/polymer HTM/perovskite/PTAA/Ag. The J–V curves can be divided into three regions: the Ohmic region (\( n = 1 \)), the trap-filling limit (TFL) region (\( n > 3 \)), and the Child region (\( n = 2 \)). In the TFL stage, the defect trap state can be filled by the injected charge, and the defect density \( N_{defects} \) can be calculated by Equation (4):

\[ N_{defects} = \frac{2 \varepsilon \varepsilon_0 V_{TFL}}{e L^2} \]  

where \( \varepsilon \) and \( \varepsilon_0 \) are the relative dielectric constant and vacuum dielectric constant, respectively, \( L \) is the thickness of the perovskite film, \( V_{TFL} \) is the trap filled limit voltage. The \( V_{TFL} \) values of PVCz-SMeTPA, PVCz-SMeDAD, and PTAA devices are 0.31, 0.48, and 0.5 V, respectively. Therefore, the \( N_{defects} \) for devices with PVCz-SMeTPA, PVCz-SMeDAD, and PTAA are calculated to be 2.83 \times 10^{12}, 4.38 \times 10^{13}, and 4.57 \times 10^{13} cm^{-3}, respectively, indicating that PVCz-SMeTPA can efficiently passivate defects on buried interfaces and in the bulk of perovskite films, which is beneficial to suppressing non-radiative recombination, thus achieving the best device performance.

The long-term device stability of PVCz-SMeTPA, PVCz-SMeDAD, and PTAA based inverted quasi-2D PSCs were further investigated. Figure 6f describes the stability of three
polymers based unpackaged devices under continuous annealing at 60 °C nitrogen atmosphere. Unencapsulated devices with PVCz-SMeTPA, PVCz-SMeDAD, and PTAA maintained 87%, 84%, and 78% of the initial efficiencies after continuous annealing at 60 °C for >1000 h, respectively. When stored in inert environment, the unencapsulated devices based on both PVCz-SMeTPA shows better stability with >90% of the initial PCE than PVCz-SMeDAD and PTAA based devices, after maintained for >1000 h. The results show that the perovskite devices of PVCz-SMeTPA and PVCz-SMeDAD have higher efficiency and better stability compared to devices with PTAA.

3. Conclusion

In summary, based on the non-conjugated flexible backbones, we have designed and synthesized two novel side-chain functionalized polymer HTMs containing methylthio-based passivation groups for inverted quasi-2D PSCs. The methylthio-based groups in PVCz-SMeTPA and PVCz-SMeDAD can act as a Lewis base to passivate the buried interface defects of quasi-2D perovskite, which is beneficial for the formation of high-quality perovskite films and suppression of non-radiative recombination. Meanwhile, PVCz-SMeTPA and PVCz-SMeDAD exhibit excellent film-forming ability and hole mobility, as well as deeper HOMO levels that matching with VB of quasi-2D perovskite, which facilitate the charge extraction and transport. As results, PVCz-SMeTPA based inverted quasi-2D PSCs could achieve a champion PCE of 21.41% with high Voc of 1.23 V, which is one of the highest values for inverted quasi-2D PSCs. This work provides an effective strategy for the buried interface engineering of quasi-2D perovskites and optimizing the performance of inverted quasi-2D PSCs.

Supporting Information

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

Acknowledgements

Z.P. and D.P. contributed equally to this work. This work was financially supported by the National Natural Science Foundation of China (grant no. 62288103 and 61974066), the Joint Funds of the National Natural Science Foundation of China (U21A2078), and the Synergetic Innovation Center for Organic Electronics and Information Displays.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

hole-transporting materials, interface defects passivation, inverted quasi-2D perovskite solar cells, side-chain functionalized polymers

References
