Highly Stable, Solution-Processable Phenothiazine Derivative as Hole Collection Material for Organic Solar Cells
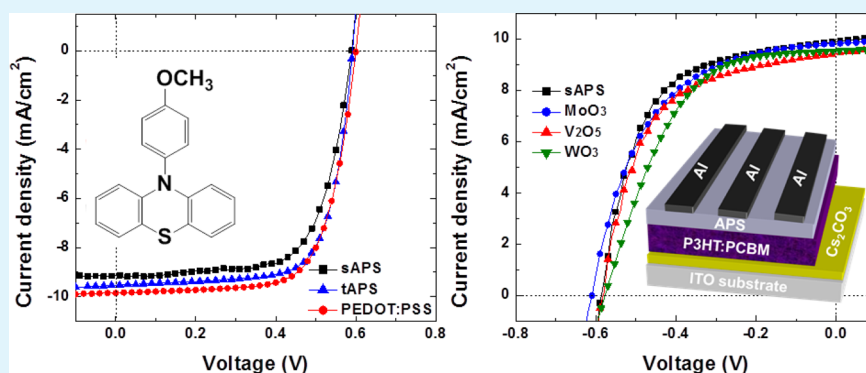
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S *Supporting Information*

ABSTRACT: In this study, we have synthesized a solution-processable phenothiazine, 4-phenothiazin-10-yl-anisole (APS), as hole collection material in organic solar cells (OSCs). The APS reveals unique optical and electronic properties which can efficiently modify the work function (Φ_W) of indium tin oxide (ITO) electrode to enhance the electron blocking capability. Moreover, the results indicate that the APS is highly air-stable which can significantly enhance the long-term stability of OCSs. The inverted device based on APS reached a power conversion efficiency (PCE) of 3.56% and exhibited much better stability under ambient conditions relative to that of the corresponding PEDOT:PSS based device.

KEYWORDS: *solar cells, solution process, buffer layer, interface, mobility, electron blocking*

INTRODUCTION

Over the past decade, the technological developments for renewable energies have become increasingly important to meet the word's rising demand for energy and environmental issues. Among all the different kinds of technologies, application of conjugated polymer as solar cells has attracted great attention because of the ease of fabrication, promising flexibility, large scale, and low cost.[1,2] Many works have been proposed to enhance the performance of OSCs, such as the use of thermal or solvent annealing or additive to improve the crystallization of polymer,[3-5] synthesis of conjugated materials with low band gap,[6-10] adjusting the work function of electrode through interfacial engineering. Recently, the efficiencies of bulk heterojunction (BHJ) polymer solar cell over 10% have been demonstrated using conjugated polymer and fullerene derivatives as donor and acceptor materials,[11,12] respectively, showing its potential as next generation of solar cells.

For the typical BHJ solar cells, an active layer composed of polymer donor and acceptor material is sandwiched between transparent (indium tin oxide, ITO) and metal electrodes. To match the band structure between the active layer and electrodes, the ITO and metal electrodes are modified with suitable buffer layer. For a convectional device, the ITO and

metal electrodes are modified with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and metal with low work function (like Ca and Ba), respectively. However, both PEDOT:PSS and low-work-function metals are air-sensitive leading to oxidation which cause degradation of OSCs. Moreover, PEDOT:PSS is highly acidic which corrodes the ITO layer chemically. Although much metal oxides (WO_3, VO_X, MoO_3, and NiO) have been demonstrated to be efficient candidates as the replacement for PEDOT:PSS,[13-17] their deposition process require vacuum condition which are incompatible with solution process. Therefore, it is desirable to develop a suitable alternative that is compatible with air-stability, solution-processable fabrication and also has good hole collection property.

A desired interfacial layer used for OSCs should have a number of properties, that is, (1) high transparency, (2) suitable energy levels to enhance the collection of the photogenerated charge, (3) solution processability, (4) excellent air stability and nonreactivity, and (5) solvent

resistance. To meet the demands mentioned above, in this study, we have synthesized a small molecule, 4-phenothiazin-10-yl-anisole (APS). The APS can be applied as an efficient hole collection layer in OSCs. We used APS as buffer layer to fabricate poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) based OSCs with convectional and inverted structures. The PCE of the devices based on APS can rival that of the corresponding conventional device (PEDOT:PSS). Moreover, the APS based devices also exhibited much better stability under ambient conditions relative to that of the corresponding conventional device. Our work indicates that the APS is a promising candidate for cathode interlayer for OSCs.

■ EXPERIMENTAL SECTION

Synthesis of 4-Phenothiazin-10-yl-anisole (APS). A mixture of phenothiazine (9.96 g, 50 mmol), 4-iodoanisole (14.04 g, 60 mmol), copper powder (2.68 g, 50 mmol), potassium carbonate (13.82 g, 100 mmol), and triethylene glycol dimethyl ether (TEGDME) (60 mL) was stirred under the protection of dry nitrogen at 180 °C for 24 h outlined in Scheme 1. The reaction mixture was cooled, filtered, and

Scheme 1. Synthesis Routes of 4-Phenothiazin-10-yl-anisole (APS) Molecule
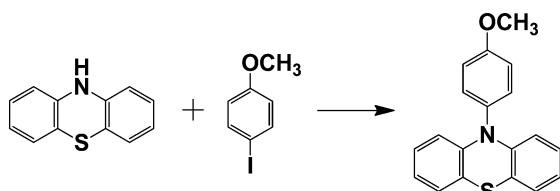
poured into ice water. The brown precipitate was collected by filtration. Recrystallization from Ethyl Acetate (EA) and then dried at 80 °C to give yellowish crystalline (11.52 g, 75%): (mp = 176−177 °C; lit. 172−173 °C) by DSC at 10 °C/min.

FTIR (KBr pellet, cm^{-1}): 1242, 1034 (aromatic −C−O−C−stretch). 1H NMR (300 MHz, CDCl$_3$, δ, ppm): 3.86 (s, −OCHH$_3$), 6.14 (d, 2H), 6.84 (t, 2H), 6.90 (t, 2H), 7.04 (d, 2H), 7.21 (d, 2H), 7.34 (d, 2H). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 55.6, 115.7, 116.3, 118.9, 122.6, 126.7, 127.4, 132.1, 132.6, 144.2, 159.1. MS (FAB) m/z found: M$^+$, 305.2.

Solar Cell Devices. Before device fabrication, the ITO glasses (1.5 × 1.5 cm^2) were ultrasonically cleaned in detergent, deionized water, acetone and isopropyl alcohol before the deposition. After routine solvent cleaning, the substrates were treated with UVO (ultraviolet ozone cleaner, Jelight Company, USA) for 15 min. Then a modified ITO surface was obtained by spin-coating a layer of PEDOT:PSS (~30 nm) or APS (~10 nm). After baking at 130 °C for 1h, the substrates were then transferred into a nitrogen-filled glovebox. The solar cell devices were fabricated by spin-coating blend of P3HT:PCBM on the PEDOT:PSS or APS modified ITO surface. Prior to the deposition, the blend of P3HT:PCBM was prepared by dissolving it in 1,2-dichlorobenzene, followed by stirring the solution for 12 h at 50 °C. The active layer was obtained by spin-coating the blend at 600 rpm for 60 s. The active layer was then dried in covered glass Petri dishes to control the film growth rate. Subsequently, the films were annealed on the top of hot plate at 130 °C for 30 min. A 30 and 100 nm thick of calcium and aluminum were thermally evaporated under vacuum at a pressure below 6 × 10^{-6} Torr thorough a shadow mask. The active area of the device was 0.12 cm^2.

Characterization. The cell performance was tested under simulated AM 1.5 G irradiation at 100 mW cm^{-2} using a Xe lamp-based solar simulator (Thermal Oriel 1000 W). The light intensity was calibrated using a monosilicon photodiode equipped with a Hamamatsu KG-5 color filter. The whole measurement process was performed at room temperature in a glovebox filled with N$_2$. The

absorption spectra were obtained from Jasco-V-670 UV−visible spectrophotometer. The surface morphologies of the polymer films were investigated using an atomic force microscope (Digital Instrument NS 3a controller equipped with a D3100 stage). XPS/UPS spectra were recorded using a PHI 5000 VersaProbe (ULVAC-PHI, Chigasaki, Japan) system with the He(I) ($h\nu$ = 21.2 eV) as energy source.

■ RESULTS AND DISCUSSION

UV−vis spectroscopy was used to evaluate the absorption of the APS solution and transmittance of APS film coated on ITO substrate as shown in Figure 1. The absorption peak of APS
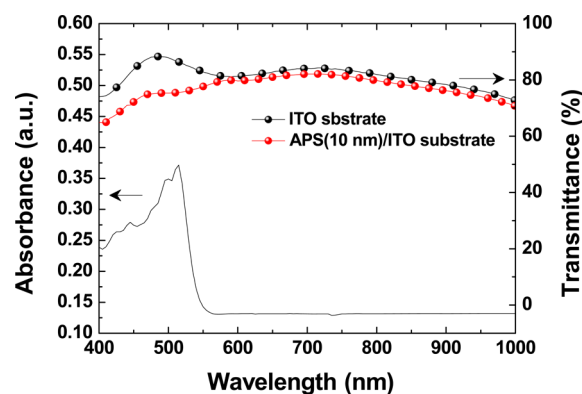

Figure 1. Absorbance and transmittance spectrum of APS film.

solution was located at 520 nm, suggesting APS is highly transparent in the visible region. The optical transmittance of the APS thin film (10 nm) and bare ITO are also shown in Figure 1. Compared to the bare ITO substrate, the APS film reveals a slight decrease in transmittance when the wavelength is shorter than 550 nm which is contributed from the absorbance of APS film. For the wavelength between 550 and 800 nm, the transmittance of APS film is above 80%. The highly transparent property indicates that the APS is a very good candidate for the buffer layer of polymeric solar cells. The thermal properties of APS molecule are also shown in the Supporting Information.

Figure 2a presents UPS (He I) spectra, collected using He I radiation ($h\nu$ = 21.2 eV), of the APS modified ITO electrodes prepared from spin coating (sAPS) and thermal evaporation (tAPS). The absolute value of Φ_W was determined by measuring the shift in the secondary electron cutoff of APS thin films. The results indicate that the Φ_W of sAPS and tAPS are almost the same, which is around 5.1 eV. This value is very close to that of PEDOT:PSS (5.2 eV).[18] The schematic energy levels of APS together with others materials used in our study are also shown in Figure 2c. According to the energy level alignment in the inset, not much of an energetic barrier is expected for hole transfer between active layer and the APS modified electrode. In order to investigate the durability of the APS, the UPS spectra analysis was also performed with various standing times as shown in Figure 2b. The cast APS films were kept in a chamber controlled at 85 °C/85% relative humidity condition. Surprisingly, the values of Φ_W for the samples with various standing times are almost unchanged. These results indicate that the new hole-transporting material is highly stable and suitable to be integrated into OSCs.

We measured the surface morphology of the APS layer by AFM to investigate the effect of process method (solution-process or thermal evaporation). Figure 3 shows the AFM
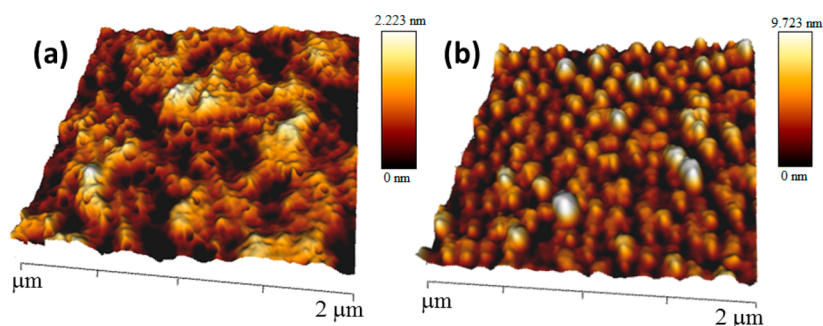
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Figure 2. (a) Measurment of the values of Φ_w of the APS films for different deposition methods. (b) comparison of the Φ_w of the APS films stored in 85 °C/85% relative humidity condition with various times and (c) energy levels of the materials involved in the OSCs.
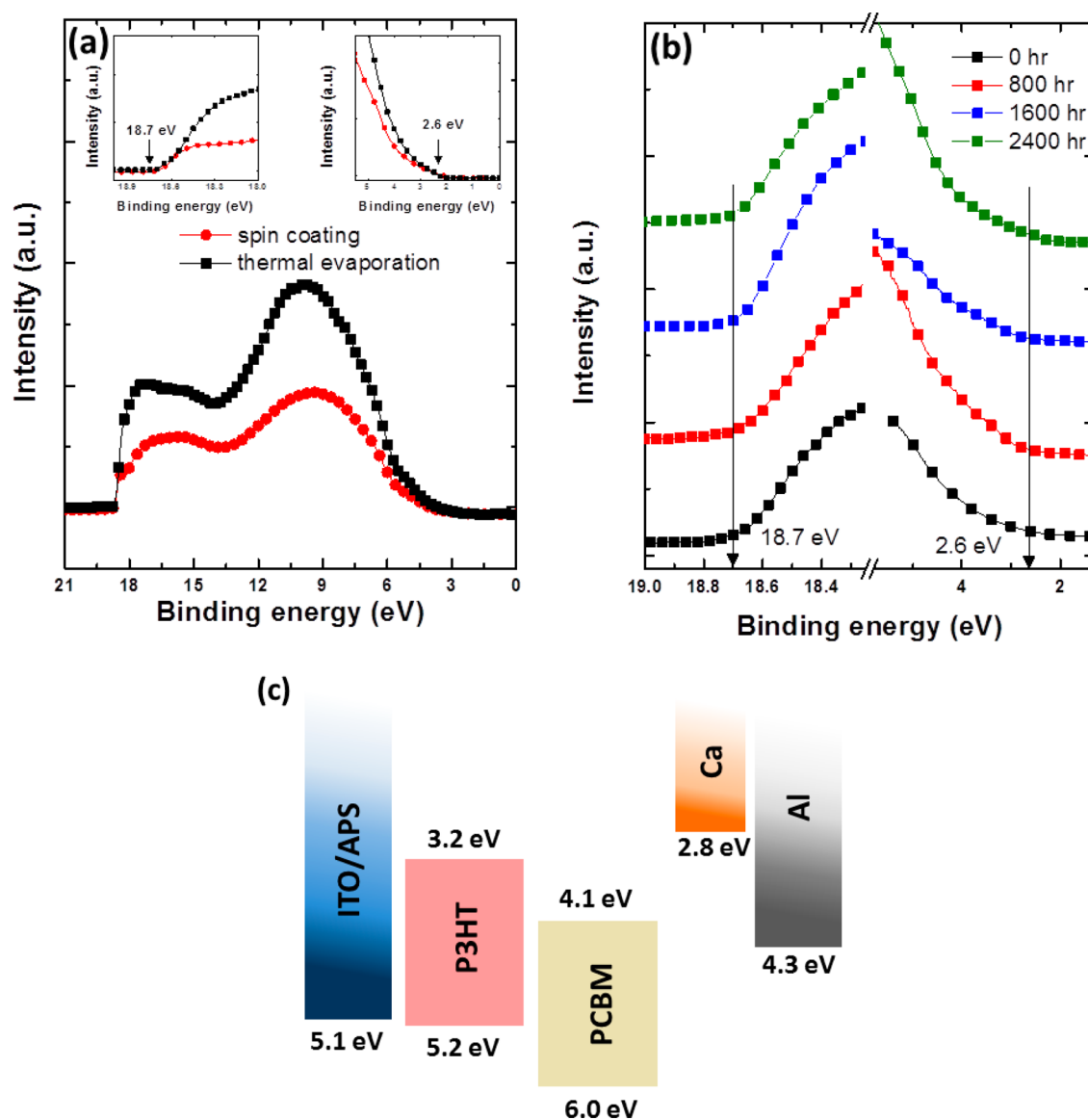

Figure 3. Representative images of the surface morphologies of the APS films prepared from solution process and thermal evaporation.

images for the APS films on top of ITO substrate prepared from spin-coating and thermal deposition. It was found that both methods could form continuous films with a root-mean-square (rms) roughness of ~0.9 nm for sAPS and ~2.1 nm for tAPS. The rougher surface of tAPS film is believed to offer a larger interfacial area for charge transfer between the active and

buffer layer. Moreover, the tAPS film showed more crystalline features than that of sAPS which is likely due to the self-organization of APS molecule during evaporation process, resulting in stronger intermolecular $\pi-\pi$ interactions. The X-ray diffraction patterns of sAPS and tAPS were also shown in the Supporting Information. To further study the electronic
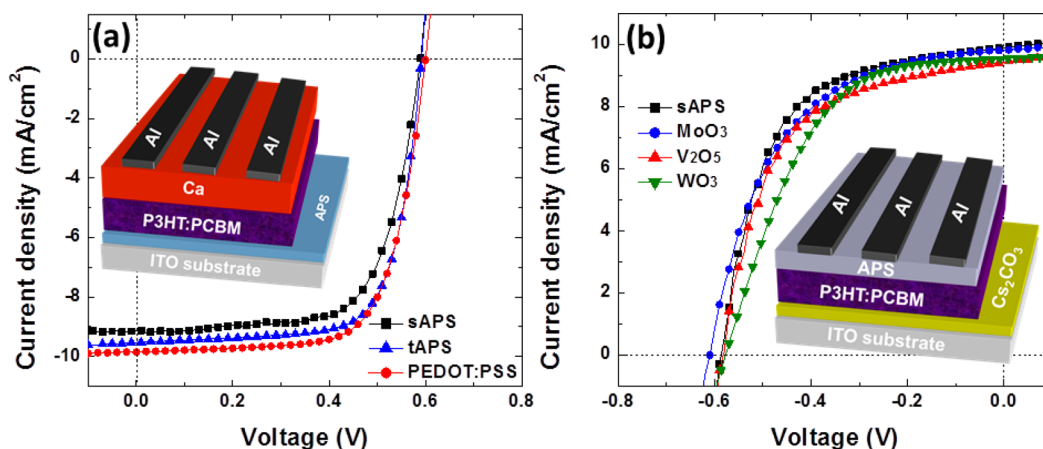
Figure 4. Cell performance tested under AM 1.5G (100 mW cm^{-2}) for (a) conventional structure with APS and PEDOT:PSS as hole collection layers. (b) inverted structure with APS and TMOs as hole collection layers.

characteristic of APS films, we also measured the hole mobility. The mobility of sAPS and tAPS films was evaluated by space charge limited current (SCLC) measurements (see as Supporting Information). The hole only devices were fabricated with the structure of ITO/PEDOT:PSS/APS/MoO$_3$/Al. The SCLC hole mobilities for sAPS and tAPS were calculated to be 7.6 × 10^{-5} and 3.1 × 10^{-4} cm^2 V^{-1} s^{-1}, respectively.

To examine the feasibility of applying the APS as buffer layer in OSCs, the P3HT:PCBM based solar cells were fabricated. Figure 4a presents the current–voltage (J–V) curves of solar cells incorporating APS and PEDOT:PSS as hole collection layer. For comparison purpose, the devices based on sAPS and tAPS were both fabricated. Table 1 lists the average device

Table 1. Photovoltaic Characteristics of Convenctional and Inverted P3HT:PCBM Solar Cells Incorporating APS, PEDOT:PSS, and TMOs as Hole Collection Layer

conventional device				
sample	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
sAPS	9.15	0.59	67.8	3.66
tAPS	9.52	0.60	70.7	4.04
PEDOT:PSS	9.85	0.60	72.1	4.11
inverted device				
sample	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
sAPS	9.89	0.59	58.8	3.43
MoO$_3$	9.81	0.60	54.7	3.22
V$_2$O$_5$	9.43	0.59	56.2	3.13
WO$_3$	9.54	0.58	53.3	2.95

parameters (from a minimum of three devices). The tAPS based device delivered a short-circuit current (J_{SC}) of 9.52 mA cm^{-2}; with an open-circuit voltage (V_{OC}) of 0.60 V and a fill factor (FF) of 70.7%, the power conversion efficiency (PCE) was 4.04%. These values can rival that of PEDOT:PSS based device (4.11%). Furthermore, the PCE of tAPS based device is slightly larger than that of sAPS based device (3.66%). The higher PCE for the tAPS based device is attributed to the higher mobility and larger interfacial area relative to that of sAPS.[19−21] These data suggest that both the thermally evaporated and solution processed APS films could be used as substitutes for PEDOT:PSS buffer layers between the ITO and the polymer layer, with comparable device performance. (The effect of the APS thickness on cell performance is also

shown in the Supporting Information.) We have also investigated the application of APS as an interfacial layer in inverted solar cells. The good solubility of APS in methanol and acetonitrile allowed us to fabricate the inverted cells with APS via solution-process. (The solubility of APS in other organic solvents was also tested and the results are shown in Supporting Information) Figure 4b reveals the cell performance of P3HT:PCBM inverted devices with sAPS and other transition metal oxides (TMOs) as hole collection layer. The TMO layers were prepared through thermal evaporation. Among these buffer layers, the sAPS deliver the highest J_{SC} of 9.89 mA/cm^2 and FF of 58.7% leading to the PCE of 3.43%. All the cell parameters are displayed in Table 1. The results show that the APS is a promising hole collection material which can be integrated into conventional and inverted cells by solution-process.

To further test the compatibility of APS with other conjugated polymers, the OSCs based on polyfluorene copolymer (F8T2)[22,23] and cyclopentadithiophene polymer (Si-PCPDTTBT)[24,25] with sAPS as buffer layer were also fabricated. The cell performance and the chemical structure of F8T2 and Si-PCPDTTBT are shown in Figure 5. The J_{SC} values are 3.59, 8.71 mA/cm^2 for F8T2:PCBM and Si-PCPDTTBT:PCBM based OSCs, and 3.78, 8.64 mA/cm^2 for sAPS and PEDOT:PSS based devices, respectively. The PCEs of F8T2:PCBM and Si-PCPDTTBT:PCBM based OSCs are 1.81%, 3.30%, and 1.92%, 3.12% for sAPS and PEDOT:PSS based devices. The results indicate that the APS based OSCs can deliver rival cell performances compared with the PEDOT:PSS based devices. This suggests that the APS buffer layer is suitable not only for P3HT based OSCs but also for other conjugated polymers.

To investigate the stability of APS, we performed durability tests under ambient conditions for the devices without encapsulation. Figure 6 compares the PCEs with respect to exposure time in the ambient atmosphere for the convencional solar cells based on sAPS (ITO/sAPS/P3HT:PCBM/Cs$_2$CO$_3$/Al) and PEDOT:PSS (ITO/PEDOT:PSS/P3HT:PCBM/Cs$_2$CO$_3$/Al). After 2400 h, obvious decay of PEDOT:PSS based device was observed, the efficiency decreased 93% (PCE from 3.78% to 0.27%). The decay is mainly resulted from the decrease in J_{SC} and FF. The erosion of ITO by PEDOT:PSS could be one of the main reasons. The erosion of ITO would cause the poorer interface which impedes the charge carrier
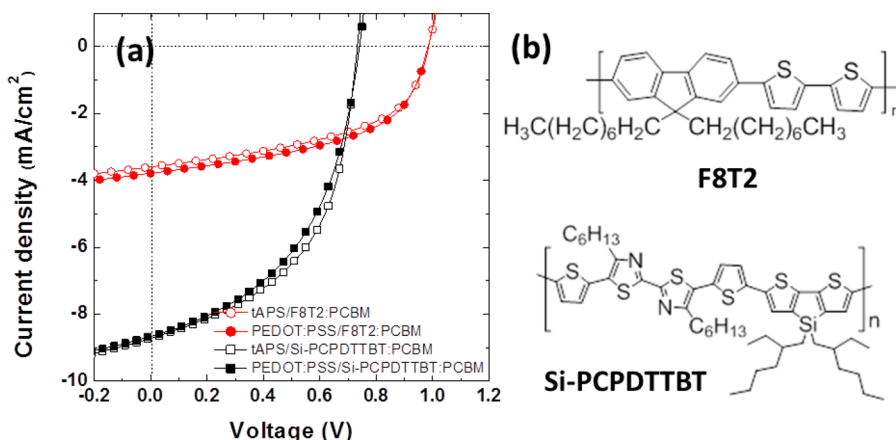
Figure 5. (a) Cell performance tested under AM 1.5G (100 mW cm^{-2}) for tAPS and PEDOT:PSS based-devices with F8T2:PCBM and Si-PCPDTTBT:PCBM as active layers. (b) the chemical structure of F8T2 and Si-PCPDTTBT copolymers.
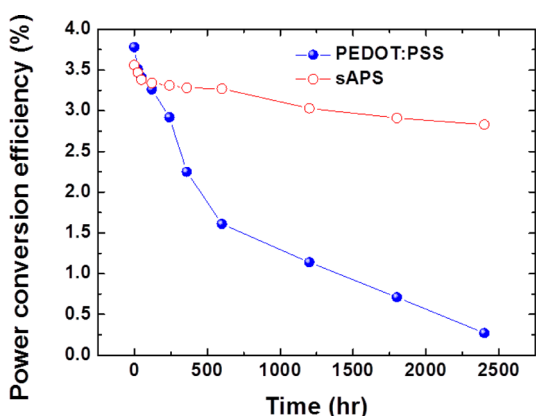

Figure 6. Durability tests under ambient conditions for the APS and PEDOT:PSS-based devices without encapsulation.

collection leading to larger series resistance. In contrast, the device incorporated with sAPS as hole collection layer exhibits highly stable property. The air stable sAPS acts not only as hole collection layers but also as protection layers for the active materials; therefore, the PCE for the inverted cell remained at 79.5% of its original value (2.83%) after 2400 h of air storage.

CONCLUSIONS

In summary, we have synthesized, characterized, and evaluated a solution processable, transparent, organic hole collection material, APS. The APS can efficiently modify the Φ_W of ITO electrode to enhance the electron and exciton blocking properties. Its excellent hole extracting capability was clearly demonstrated in polymeric solar cells with high PCEs (4.04%). Moreover, the APS is highly air-stable compared with PEDOT:PSS which can significantly enhance the long-term stability of OSCs. The inverted cells fabricated with APS were air-stable, maintaining a PCE of ~2.83% after 2400 h of durability testing in air without encapsulation; in contrast, the corresponding device based on PEDOT:PSS almost lost its efficiency after 2400 h of ambient exposure. These results suggest that the APS can be an alternative material as replacement for PEDOT:PSS in OSCs.

ASSOCIATED CONTENT

Ⓢ Supporting Information

DSC, TGA, XRD, solubility, mole mobility, and effect of APS thickness on cell performance. This material is available free of charge via Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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