

Processing Dependent Influence of the Hole Transport Layer Ionization Energy on Methylammonium Lead Iodide Perovskite Photovoltaics

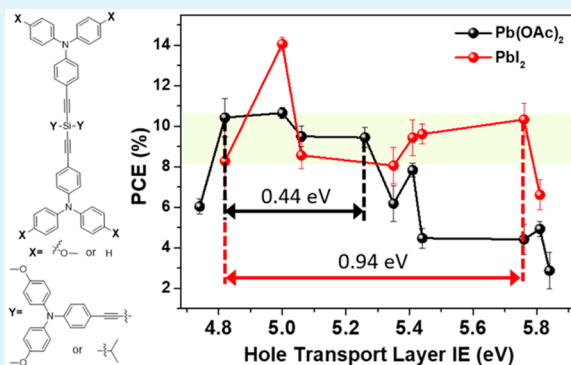
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Supporting Information

ABSTRACT: Organometal halide perovskite photovoltaics typically contain both electron and hole transport layers, both of which influence charge extraction and recombination. The ionization energy (IE) of the hole transport layer (HTL) is one important material property that will influence the open-circuit voltage, fill factor, and short-circuit current. Herein, we introduce a new series of triarylaminioethynylsilanes with adjustable IEs as efficient HTL materials for methylammonium lead iodide (MAPbI₃) perovskite based photovoltaics. The three triarylaminioethynylsilanes investigated can all be used as HTLs to yield PV performance on par with the commonly used HTLs PEDOT:PSS and Spiro-OMeTAD in inverted architectures (i.e., HTL deposited prior to the perovskite layer). We further investigate the influence of the HTL IE on the photovoltaic performance of MAPbI₃ based inverted devices using two different MAPbI₃ processing methods with a series of 11 different HTL materials, with IEs ranging from 4.74 to 5.84 eV. The requirements for the HTL IE change based on whether MAPbI₃ is formed from lead acetate, Pb(OAc)₂, or PbI₂ as the Pb source. The ideal HTL IE range is between 4.8 and 5.3 eV for MAPbI₃ processed from Pb(OAc)₂, while with PbI₂ the PV performance is relatively insensitive to variations in the HTL IE between 4.8 and 5.8 eV. Our results suggest that contradictory findings in the literature on the effect of the HTL IE in perovskite photovoltaics stem partly from the different processing methods employed.

KEYWORDS: organometal halide perovskite, photovoltaic, photoelectron spectroscopy, processing, hole transport layer



INTRODUCTION

Organometal and metal halide perovskites have rapidly emerged as the most competitive third-generation photovoltaic (PV) technology, with record power conversion efficiencies (PCEs) of lead based perovskites increasing from 3.8% in 2009 to 22% in 2017.^{1–3} With these high PCEs, perovskite PVs are of increasing interest for commercialization. This push for commercialization and the development of alternative perovskites, e.g., lead-free perovskites, requires the generation of robust PV cell architectures and materials that can be processed using inexpensive solution based methods with inexpensive and stable materials for every component of the device. One important aspect in meeting the demands for the further development of perovskite PVs is the development of solution-processable, stable, easily prepared charge transport layers that yield high-performing PV devices. Targeted design of these transport layers requires an understanding of the properties necessary to yield such PVs.

The most efficient perovskite PV cells to date, based on either methylammonium lead iodide (MAPbI₃) or similar perovskites (e.g., formamidinium lead iodide), rely on the use

of both hole and electron transport layers.^{2–4} These transport layers typically result in selective extraction of holes or electrons at the appropriate electrodes. Modifications to various properties of these transport layers are predicted to lead to improved PV device performance and are currently a subject of research interest. These transport layer modifications include enhancing the ability of the transport layer to passivate interfacial defect states in the perovskites,^{5,6} optimizing the energy level alignment between transport states in the perovskite and charge transport layer,^{7,8} enhancing the charge-carrier mobility or electrical conductivity of the transport layer,^{9–11} and increasing the stability of the layer under PV cell operating conditions.^{12–14}

The majority of hole transport layers (HTLs) are based on organic materials,^{8,9,13,15,16} with PEDOT:PSS and Spiro-OMeTAD being the most widely used, but inorganic layers such as NiO_x have also demonstrated high performance.^{17,18} All

Received: November 6, 2017

Accepted: April 19, 2018

Published: April 19, 2018

of the commonly used HTLs have their drawbacks. For example, PEDOT:PSS and Spiro-OMeTAD can lead to unstable PV cells, and many of the organic HTLs are expensive due to complicated synthetic routes or intensive purification procedures.^{19–21} Furthermore, optimizing the electronic properties of the HTL is likely to lead to higher PV performance, further motivating the need to develop new HTLs. A wide range of these materials are being investigated, including small molecules such as triarylamine derivatives, carbazole derivatives, and porphyrins^{22–26} and polymers such as polytriarylamines and polyelectrolytes.^{27–31} More extensive reviews of HTLs can be found in the literature.^{16,32}

One parameter of the HTL that is predicted to affect the performance of MAPbI₃ based PV cells is the ionization energy (IE). For example, if the IE of the HTL is significantly higher than the IE of MAPbI₃, then a barrier to hole transfer from the perovskite to HTL may exist. Alternatively, if the IE of the HTL is significantly lower than the IE of the active layer, then the achievable open-circuit voltage (V_{OC}) of the PV cell may be reduced due to a pinning of the quasi-Fermi level of holes to the HTL HOMO energy. A recent literature review, which compiles results from over 50 HTL materials used in MAPbI₃ PV cells, shows that efficient PV devices are generally obtained when the IE or HOMO of the HTL is between 5.0 and 5.35 eV.¹⁶ These results are consistent with work by Belisle et al. and Ishida et al. where HTLs with varying IEs were examined.^{33,34} In these reports high PV performance was observed with HTL IEs between 5.0 and 5.35 eV, and significant performance drops were observed when the IE exceeded 5.4 eV. Other reports suggest a narrower range of IEs is acceptable.^{7,8,35,36} For example, Polander et al. show that perovskite PV performance drops when the HTL IE is lower than 5.1 eV or higher than 5.3 eV,⁷ Cho et al. show a drop in PV performance as the IE changes from 5.19 to 5.32 eV,⁸ and Rakstys et al. show higher PV performance for HTLs with IEs of 5.22 and 5.14 eV than for IEs of 5.09 and 4.96 eV.³⁶ The different reported acceptable HTL IE ranges found in the literature may arise due to variations in MAPbI₃ processing methods, different device architectures, different techniques for measuring IEs or HOMO energies (e.g., photoelectron spectroscopy or electrochemistry), differences in the perovskite layer, or other factors (such as the charge-carrier mobility) of the HTL that may influence PV performance.

In this work we introduce a novel family of triarylamino-ethynylsilyl (TAAES) derivatives as HTL materials for perovskite PVs and investigate the influence of the HTL IE, as measured with ultraviolet photoelectron spectroscopy (UPS), on the performance of MAPbI₃ based PV cells. We expand our investigation of HTL materials from the TAAES derivatives to a variety of HTL materials with IEs spanning a 1.1 eV range. We find that the V_{OC} is surprisingly high for HTL IEs down to 4.74 eV, and with Pb(OAc)₂ as the source of lead the PCE values are maximized for HTL IEs of 4.8–5.3 eV due primarily to changes in the fill factor (FF) and short-circuit current density (J_{SC}). With a different processing procedure using PbI₂ as the source of lead the PCE is less sensitive to HTL IE, with champion PCEs over 10% for a nearly 1 eV range in the HTL IE.

EXPERIMENTAL SECTION

Materials. Lead acetate trihydrate (Pb(OAc)₂·3H₂O, 99.0–103.0%) and lead iodide (PbI₂, 99.9985%) were purchased from Alfa Aesar. Methylammonium bromide (MABr) was purchased from

Lumtec. Methylammonium iodide (MAI) was bought from Dyesol and used after recrystallizing twice in ethanol and drying in a vacuum oven overnight at 60 °C. *N,N*-Dimethylformamide (anhydrous, 99.8%), dimethyl sulfoxide (anhydrous, 99.8%), and ethyl ether (anhydrous, 99.0%) were purchased from EMD Millipore Corp. Chlorobenzene (anhydrous, 99.8%) was bought from Sigma-Aldrich. Hole transport materials include Spiro-OMeTAD (Jilin OLED), rubrene (TCI, >99.9%), α -sexithiophene (6T, TCI), *N,N'*-di(1-naphthyl)-*N,N'*-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPD, Sigma-Aldrich, 99%), and tris(8-hydroxyquinoline)aluminum (Alq₃, TCI, 98%). The electron transporting layers and electrodes include [6,6]-phenyl C₆₁-butyric acid methyl ester (PC₆₁BM, Nano-C), C60 (Nano-C, 99.5%), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, TCI, >99.0%), Al (99.99%, Angstrom Engineering), Ag (99.99%, Angstrom Engineering), and MoO₃ (Alfa Aesar, 99.998%).

Synthesis of TAAES-2. Ethynyltriphenylamine³⁷ (2 g, 6.75 mmol) was dissolved in dry THF and cooled to 0 °C. Lithium hexamethyldisilazane (LiHMDS, 7 mL, 7.00 mmol, 1 M in THF) was added, and the mixture was stirred for 3 min at 0 °C. Next, diisopropyl-dichlorosilane (0.555 g, 3.00 mmol) was diluted in 5 mL of hexane, and the solution was added slowly over 10 min to the reaction mixture at 0 °C. The mixture was allowed to warm to rt with stirring for 2 h, after which it was quenched with solid ammonium chloride and the solvent was removed by rotary evaporation. The recovered material was then partitioned between ethyl acetate and water, and the organic phase was washed with 3 × 150 mL of water and once with brine. The organic phase was concentrated, and the crude product was purified by column chromatography (silica gel, 6:1 hexanes/DCM) and recrystallized from 1,2-dichloroethane/hexane to give a slightly yellow crystalline solid. Single crystals suitable for X-ray analysis were grown by slow evaporation in 1,2-dichloroethane. Yield: 48%. ¹H NMR (400 MHz, CDCl₃) δ_H : 7.34 (m, 4H); 7.25 (m, 8H); 7.05 (m, 12H); 6.94 (m, 4H); 3.78 (s, 12H); 1.16 (m, 14H). ¹³C NMR (100 MHz, CDCl₃) δ_C : 156.3; 149.0; 140.1; 133.1; 127.0; 119.0; 114.8; 113.7; 107.7; 86.1; 55.5, 17.8, 12.7.

Synthesis of TAAES-2OMe. Ethynyltrimethoxytriphenylamine³⁸ (0.500 g, 1.52 mmol) was dissolved in dry THF (25 mL) and cooled to 0 °C. LiHMDS (1.60 mL, 1.60 mmol, 1 M in THF) was added, and the mixture was stirred for 30 min at 0 °C. Next, diisopropyl-dichlorosilane (0.130 g, 0.760 mmol) was diluted in 5 mL of hexane, and the solution was added over 10 min to the reaction mixture at 0 °C. The mixture was allowed to warm to rt with stirring for 2 h, after which it was quenched with solid ammonium chloride, and the solvent was removed by rotary evaporation. The recovered material was partitioned between ethyl acetate and water, and the organic phase was washed with 3 × 150 mL of water and once with brine. The organic phase was concentrated, and the crude product was purified by column chromatography (silica gel, 6:1 hexanes/ethyl acetate) to give a colorless solid. Single crystals suitable for X-ray analysis were grown by slow diffusion of methanol vapor into a saturated solution of TAAES-2OMe in THF. Yield: 37%. ¹H NMR (400 MHz, CDCl₃) δ_H : 7.27 (d, *J* = 5.4 Hz, 4H); 7.03 (d, *J* = 5.4 Hz, 8H); 6.82 (d, *J* = 5.6 Hz, 8H); 6.78 (d, *J* = 5.4 Hz, 4H); 3.78 (s, 12H); 1.04 (m, 14H). ¹³C NMR (100 MHz, CDCl₃) δ_C : 156.3; 149.0; 140.1; 133.1; 127.0; 119.0; 114.8; 113.7; 107.7; 86.1; 55.4, 17.8, 12.7.

Synthesis of TAAES-4OMe. Ethynyltrimethoxytriphenylamine (0.500 g, 1.42 mmol) was dissolved in dry THF and cooled to 0 °C in an ice bath. LiHMDS (1.6 mL, 1.6 mmol, 1 M in THF) was added, and the mixture was stirred for 3 min at 0 °C. Next, tetrachlorosilane (0.0510 g, 0.300 mmol) was diluted in 5 mL of hexane, and the solution was added slowly over 10 min to the reaction mixture at 0 °C. The reaction was allowed to warm to rt with stirring for 2 h. The reaction mixture was then quenched with solid ammonium chloride, and the solvent was removed by rotary evaporation using minimal heating. The recovered material was partitioned between ethyl acetate and DI water, and the organic phase was washed with 3 × 150 mL of DI water and once with brine. The organic phase was concentrated, and the crude product was purified by column chromatography (silica gel, 3:1 hexanes/ethyl acetate) to give a slightly yellow solid. Single crystals suitable for X-ray analysis were grown by slow evaporation of

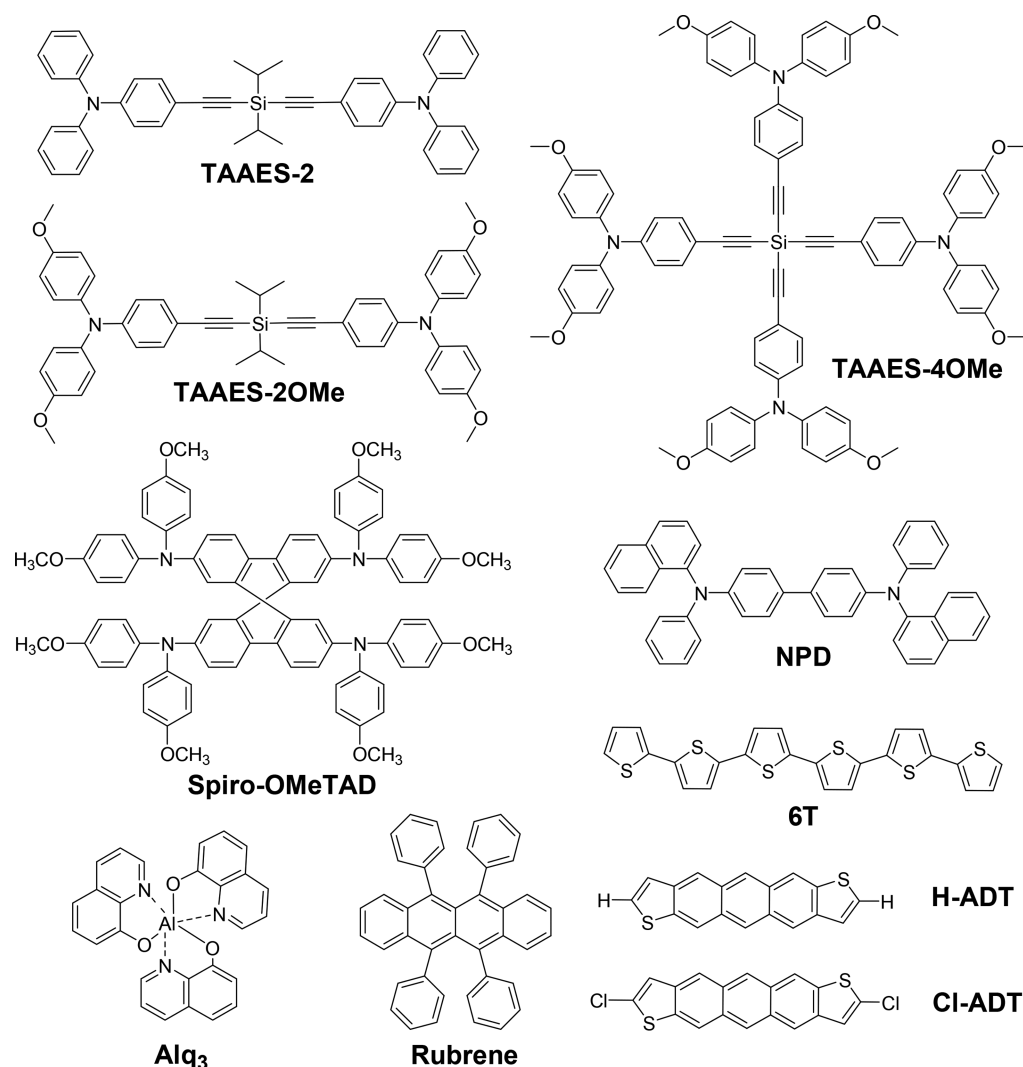


Figure 1. Chemical structures of the molecules utilized as HTLs in this work.

1,2-dichloroethane. Yield: 23%. ^1H NMR (500 MHz, CDCl_3) δ_{H} : 7.33 (m, 10H); 7.03 (m, 14H); 6.81 (m, 24H); 3.77 (m, 24H); 3.77 (m, 24H). ^{13}C NMR (100 MHz, CDCl_3) δ_{C} : 156.4; 149.5; 139.9; 133.4; 127.2; 118.4; 114.8; 112.6; 107.0; 85.3; 55.5.

Synthesis and Purification of Methylammonium Iodide. Methylamine (27.8 mL, 40 wt %, Alfa Aesar) and hydriodic acid (30 mL, 57 wt %, Alfa Aesar) were combined and allowed to react in an ice bath for 2 h with stirring. The solution was then evaporated at 60 °C with a rotary evaporator, leaving only methylammonium iodide (MAI). The precipitate was washed with diethyl ether several times until the color of precipitate was white. The obtained precipitate was dried under vacuum for 24 h and stored in a nitrogen-filled glovebox (<0.3 ppm of H_2O and O_2) until use. Both house synthesized MAI and recrystallized MAI from Dyesol showed similar performance in photovoltaic devices.

METHODS

Materials Characterization. X-ray diffraction data were collected for the TAAES crystals using either a NoniusKappa CCD ($\text{Mo K}\alpha$) or a Bruker X8 Proteum ($\text{Cu K}\alpha$) diffractometer. UV–vis absorbance measurements were recorded on thin films in a nitrogen-filled glovebox using an Ocean Optics fiber-optic spectrometer with a thermoelectric cooled CCD detector coupled with an integrating sphere. Films for UV–vis measurements were prepared on clean glass slides. Thin films for ultraviolet photoelectron spectroscopy (UPS) were prepared with thicknesses of 15–25 nm for the HTLs and ca. 200

nm for the perovskite by thermal evaporation or spin-coating on nonpatterned ITO-coated glass substrates (Tinwell Tech., $15 \Omega/\square$), using similar procedures as those reported for the PV device fabrication. Devices for SCLC measurements were fabricated with the structure ITO/PEDOT:PSS/HTL/ MoO_3 /Ag. Prior to spin-casting the HTL, ITO-coated glass substrates were cleaned and coated with PEDOT:PSS as detailed in the [PV Device Fabrication](#) section. Films of the TAAES derivatives (30 mg/mL in chlorobenzene) were prepared by spin-casting at 4000 rpm for 30 s in the nitrogen-filled glovebox without further annealing. MoO_3 (7 nm) and Ag (100 nm) were thermally evaporated through shadow masks to define 8 independently addressable pixels per substrate. Differential scanning calorimetry (DSC) measurements were measured with a TA Instruments Q20, with a heating ramp of 20 °C/min rate under a nitrogen atmosphere. UPS measurements were taken with an Excitech H Lyman- α photon source (10.2 eV) coupled with a PHI 5600 ultrahigh vacuum system with a hemispherical electron energy analyzer, as detailed in our previous publication.³⁹ A sample bias of −5 V and a pass energy of 5.85 eV were used for the UPS measurements. Uncertainties in IEs are typically ± 0.05 eV based on sample-to-sample and spot-to-spot variation. X-ray photoelectron spectroscopy (XPS) measurements were performed with the same PHI 5600 system and analyzer using a Mg $\text{K}\alpha$ source (1253.6 eV, PHI 04-548 dual anode X-ray source) for excitation and a pass energy of 23.5 eV. The samples for HTL and ITO reactivity studies using XPS were prepared by depositing the HTL on ITO, as detailed in the [PV Device Fabrication](#) section, probing the HTL with XPS, depositing the

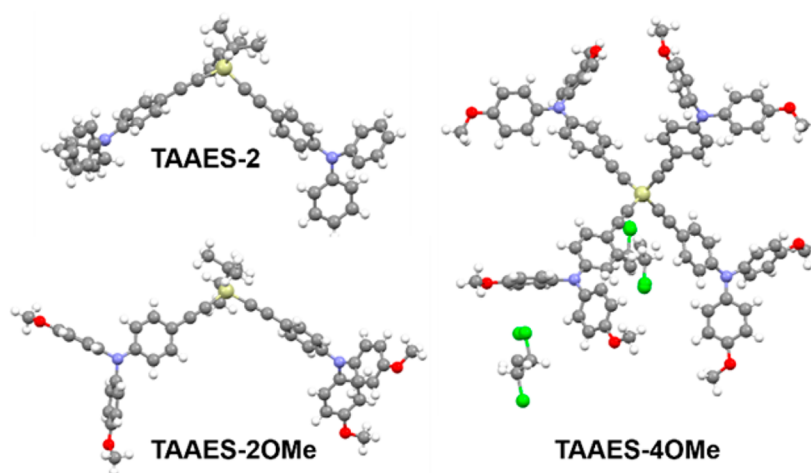


Figure 2. Molecular geometries of the TAAES derivatives based on the crystal structures. In TAAES-4OMe solvent molecules (1,2-dichloroethane) are present.

perovskite (as detailed in the PV device fabrication section) onto the HTL or ITO, and rinsing the perovskite off with dimethylformamide. Following perovskite removal, the HTL or ITO was again probed with XPS. Samples for scanning electron microscopy (SEM) were prepared on ITO-coated glass and probed with a Hitachi S-4300 SEM with an accelerating voltage of 2 or 10 kV.

PV Device Fabrication and Characterization. Patterned ITO-coated glass substrates (Tinwell Tech., $15 \Omega/\square$) were sequentially sonicated in aqueous detergent (sodium dodecyl sulfate, Sigma-Aldrich), deionized water, acetone, and 2-propanol each for 10 min. After drying with nitrogen the substrates were exposed to UV-ozone treatment for 10 min to remove organic contaminants. PEDOT:PSS (Clevios P VP AI 4083) was spun-cast at 5000 rpm for 30 s and then annealed on a hot plate at 130°C for 15 min in air. Rubrene, NPD, 6T, H-ADT, Cl-ADT, and Alq₃ (25 nm) were deposited by thermal evaporation to a thickness of 25 nm with rates of 0.5 or $1 \text{ \AA/s}$ at a typical pressure of 1×10^{-7} mbar. Spiro-OMeTAD and the TAAES derivatives (30 mg/mL chlorobenzene) were spun-cast at 4000 rpm for 30 s and annealed at 70°C for 5 min. With the exception of PEDOT:PSS, all HTLs were prepared inside a N_2 -purged glovebox (<0.1 ppm of O_2 and H_2O). All further processing was also done in this glovebox for the $\text{Pb}(\text{OAc})_2$ procedure, whereas in the PbI_2 procedure the perovskite films were cast in air.

$\text{Pb}(\text{OAc})_2$ Based MAPbI_3 Preparation. MAI and $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ were dissolved in anhydrous DMF at 3:1 molar ratio. The final concentration of solution was 46 wt % before adding 1 mol % MABr to $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ in DMF. This solution was spun-cast at 4000 rpm for 30 s on top of the different HTLs and then allowed to dry for 15 s. During this 15 s delay the perovskite film started to change from transparent to light brown. Then, the substrates were put on a hot plate at 70°C for 10 min. Substrate appearance changed rapidly to a mirror-like dark brown upon putting on the hot plate. The MAPbI_3 film on Cl-ADT was inhomogeneous, resulting in few working cells. To improve MAPbI_3 film formation, 80 μL of 1-butanol was dripped on the Cl-ADT-coated substrate and spun cast at 4000 rpm for 30 s immediately before coating the perovskite layer. The yield of working devices improved significantly with 1-butanol, but the PV performance with and without 1-butanol was similar.

PbI_2 Based MAPbI_3 Preparation. For the perovskites processed using a PbI_2 precursor solution, 461 mg of PbI_2 , 159 mg of MAI, and 78 mg of DMSO (1:1:1 molar ratio) were added to 600 mg of DMF solution and stirred at room temperature for 1 h before use in the glovebox. This solution and the HTL-coated substrates were transferred from the glovebox to a fume hood in ambient atmosphere (humidity $47 \pm 3\%$) immediately prior to spin-coating. The perovskite precursor solution was spun-cast at 4000 rpm for 25 s with a 2 s ramp, and 0.5 mL of diethyl ether was rapidly injected onto the substrate 5 s into the spin-coating process. Immediately following spin-coating the

substrates were heated at 65°C for 1 min and 100°C for 5 min. After annealing, the films were brought back into the nitrogen-filled glovebox for further processing.

PC_{61}BM (20 mg/mL chlorobenzene) was spun-cast on top of the perovskite thin films at 4000 rpm for 30 s. The films were transferred to the thermal evaporator without air exposure, and C_{60} (20 nm) and BCP (10 nm) were deposited sequentially with a rate of $1 \text{ \AA/s}$ at a pressure of ca. 1×10^{-7} mbar. Finally, aluminum (100 nm) electrodes were evaporated through a shadow mask that defined 4 cells of 0.1 cm^2 area and 4 cells of 0.2 cm^2 area per substrate. Solar cell performance was measured using a solar simulator (ABET Technologies, 11002) at 100 mW/cm^2 illumination (AM 1.5G). The intensity was adjusted to (100 mW/cm^2) using a photodiode calibrated with a KG5 filter (ABET Technologies). The PV cell data reported are typically an average of 16 or more cells, with error bars representing ± 1 standard deviation.

RESULTS AND DISCUSSION

Materials. The molecular structures of the HTLs utilized in this work are depicted in Figure 1. These molecules include the solution-processed TAAES derivatives, the commonly used PEDOT:PSS (not shown) and Spiro-OMeTAD materials, and a series of thermally evaporated small organic molecules that were selected to span a wide range of IEs. Within these materials, there are multiple sets that show similar structural characteristics and thus are more directly comparable. These include the TAAES family, where the IE is varied by introducing methoxy groups on the phenyl rings and increasing the number of triarylamine groups bound to the central silicon atom. In part, this TAAES family was inspired by dimeric versions of ethynyltriarylamines, which show reasonable efficiencies when used as hole transport layers in dye-sensitized PVs.³⁸ By building off of a tetrahedral silane based scaffolding, we are able to vary both the solubility and geometry of the HTL material by simple chemistry. The ADT derivatives are also structurally similar molecules with widely differing IEs. Here, substitution of the reactive thiophene ends with chlorines is used to alter the IE.

The TAAES derivatives were synthesized according to the procedures described in the Experimental Section, H-ADT was synthesized following literature procedures,⁴⁰ and Cl-ADT was synthesized based on the procedure reported in the Supporting Information. Single-crystal X-ray diffraction data were recorded

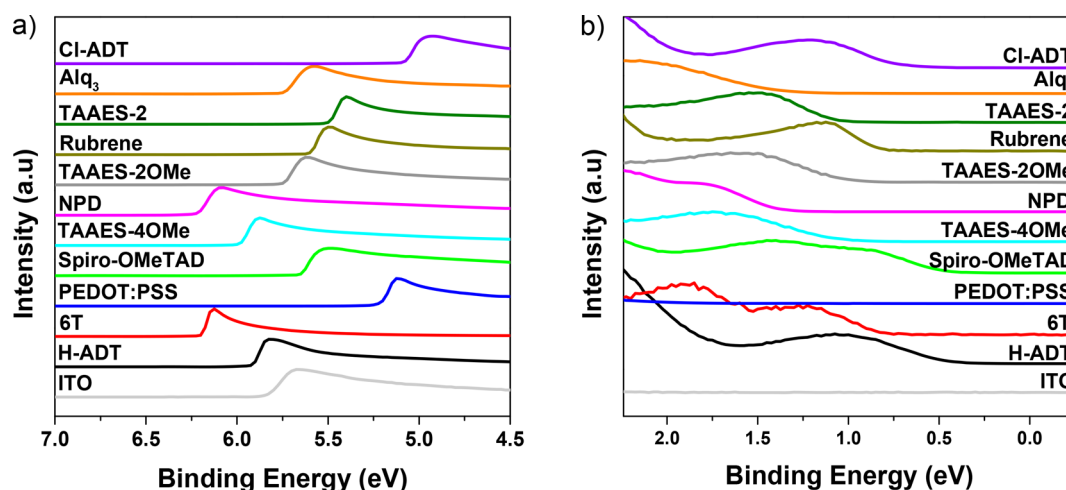


Figure 3. UPS spectra showing the secondary electron cutoff (a) and HOMO onset (b) regions for the HTLs applied in this work.

for the TAAES derivatives, confirming the expected structures (Figure 2).

The UV–vis absorbance measurements for thin films of these TAAES derivatives, as shown in Supporting Information Figure S1, show that these derivatives absorb at wavelengths shorter than ca. 400 nm, thus allowing most visible light to be absorbed by MAPbI₃ in the PV cells.

Ultraviolet Photoelectron Spectroscopy. Films of the MAPbI₃ perovskite and varying HTLs were prepared on ITO-coated glass substrates using two different processing methods and examined with UPS to determine the work functions (WFs) and IEs. Reported IEs (or valence band maxima energies) for MAPbI₃ measured with UPS range from 5.2 to 6.6 eV.^{41–48} This massive variation in reported values may stem from the sample preparation method, an excess of Pb or MAI, underlying substrate work function, sample damage during measurement, and the method used to define the IE. Endres et al. combined DFT calculations with UPS data and suggested that the most appropriate way to define the IE (or valence band position) of MAPbI₃ is based on the valence band onset as determined from a semilog plot.⁴⁴ Using a linear fit to the VB edge on a semilog plot, we measure an IE of 5.80 ± 0.07 eV for MAPbI₃ processed using Pb(OAc)₂ and 5.56 ± 0.06 eV for MAPbI₃ processed using PbI₂, as shown in Figure S2. These IE values are averages (±standard deviations) from three or four separately prepared films for each processing method, with all measured IE values and work functions listed beneath Figure S2.

Ultraviolet photoelectron spectra measured for the various HTLs are shown in Figure 3. The photon source for the UPS measurements emits from the H Lyman- α transition at 10.2 eV, and we previously demonstrated that this lower energy source reduces sample damage.³⁹ Here, the intersection of a tangent to either the final 50% of the secondary electron cutoff edge or HOMO edge and the background is used to extract the work function (WF) and HOMO onset, respectively. The IEs are calculated by adding the difference between the HOMO onset and Fermi energy (E_{Fermi} is at 0 eV) to the WF. Since PEDOT:PSS is a highly doped material, the WF is used in place of the IE. These measured IEs are depicted schematically in Figure 4 along with a simplified device energy diagram.

The UPS measurements of the TAAES derivatives show IEs ranging from 5.26 to 5.76 eV. For these TAAES derivatives, the addition of methoxy groups to TAAES-2 results in a 0.34 eV

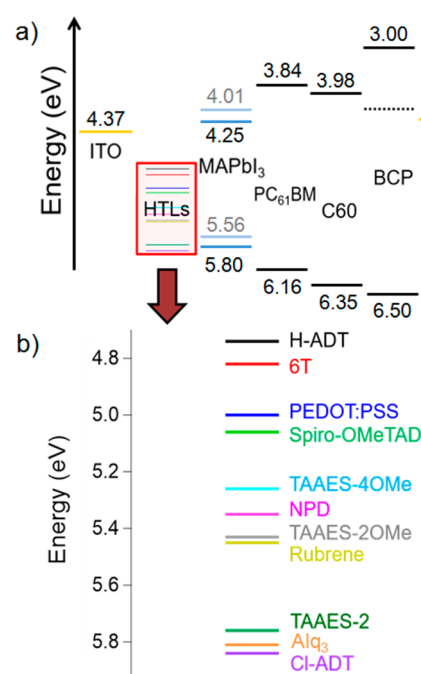


Figure 4. Simplified device energy level schematic showing the electrodes, HTLs, MAPbI₃, and ETLs (a) and the measured IEs of the various HTLs used in this work (b). The IEs, electron affinities, and/or work functions for PC₆₁BM,⁵² C₆₀,⁵² BCP,⁵³ and Al⁵⁴ are taken from the literature.

decrease in the IE. This trend is explained by the π -electron-donating nature of the methoxy groups and is consistent with the 0.31 eV decrease in IE observed by Planells et al.³⁸ upon adding methoxy groups to similar triarylaminoethynes. Adding two more triarylamino groups to the central silicon atom further lowers the IE by 0.16–5.26 eV, which is in the range of other HTL materials that show high performance in MAPbI₃ PV cells.¹⁶ For the ADT derivatives, substitution of the two terminal hydrogens with chlorines results in a massive increase in the IE of 1.1 eV, from 4.74 eV for H-ADT to 5.84 eV for CI-ADT. The IEs of the other materials are in agreement with previously reported values.^{33,41,49–51}

TAAES Derivatives as HTLs in PV Devices. Photovoltaic devices were initially fabricated based on previously reported methods that use lead acetate and methylammonium iodide as

precursors in a one-step perovskite film formation process,⁵⁵ as detailed in the [Experimental Section](#). The TAAES derivatives and Spiro-OMeTAD layers were solution processed in a nitrogen-filled glovebox, while PEDOT:PSS was processed in air. Spiro-OMeTAD was not doped, thus permitting a more direct comparison to the other undoped HTLs investigated in this paper. Illuminated and dark current–voltage characteristics are displayed for the solution-processed HTL layers in [Figure 5](#).

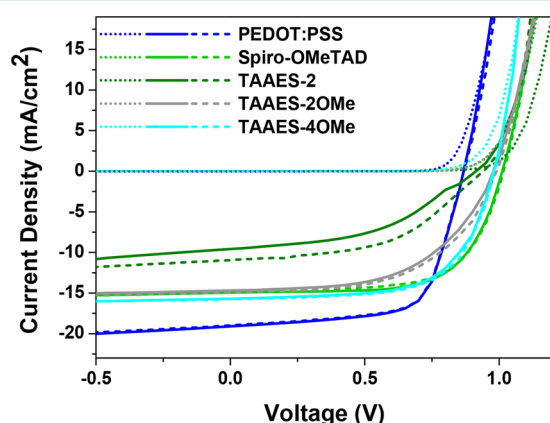


Figure 5. Illuminated and dark current–voltage characteristics for the solution-processed HTLs with $\text{Pb}(\text{OAc})_2$ as the Pb source precursor. Dotted lines are in the dark, solid lines are forward scans, and dashed lines are reverse scans.

The highest performing TAAES derivative is TAAES-4OMe, which shows slightly lower PV performance than PEDOT:PSS

and on par performance with Spiro-OMeTAD. Here, the V_{OC} of TAAES-4OMe (0.98 ± 0.01 V) is similar to Spiro-OMeTAD (1.00 ± 0.01 V) and greater than PEDOT:PSS (0.90 ± 0.02 V). The HTLs all show similar fill factors of 0.62 – 0.66 and short circuit current densities (J_{SC}) of 15 – 18 mA/cm^2 . As a result, the average PCEs for these three devices are 9.45 ± 0.48 , 9.50 ± 0.51 , and $10.66 \pm 0.28\%$ for TAAES-4OMe, Spiro-OMeTAD, and PEDOT:PSS, respectively. Additionally, there is minimal hysteresis in the J – V curves, with TAAES-4OMe and Spiro-OMeTAD showing almost none. This data indicates that TAAES-4OMe is a suitable alternative to the more commonly used Spiro-OMeTAD and PEDOT:PSS transport layers. The simple and scalable route to these TAAES derivatives, although not optimized for this report, make them attractive as lower-cost replacements for Spiro-OMeTAD. Further, the ease of synthetic tunability of both the core and periphery of these systems makes them a versatile platform for determining structure–function relationships that govern the performance of HTL materials used in perovskite photovoltaics.

[Figure 5](#) shows that TAAES-2OMe and TAAES-2 exhibit lower performance than TAAES-4OMe, with PCE values of 7.83 ± 0.34 and $4.42 \pm 0.74\%$, respectively. Multiple properties of the HTL may influence the PV performance, including the IE, charge-carrier mobility,^{56,57} and its influence on the morphology of the perovskite film.²⁸ The hole mobilities of the TAAES derivatives were extracted from space-charge limited current measurements fit with the Mott–Gurney equation,⁵⁸ as shown in [Figure S3](#). These hole mobilities are all similar to average values of 4×10^{-6} , 5×10^{-6} , and 2×10^{-6} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for TAAES-2, TAAES-2OMe, and TAAES-4OMe,

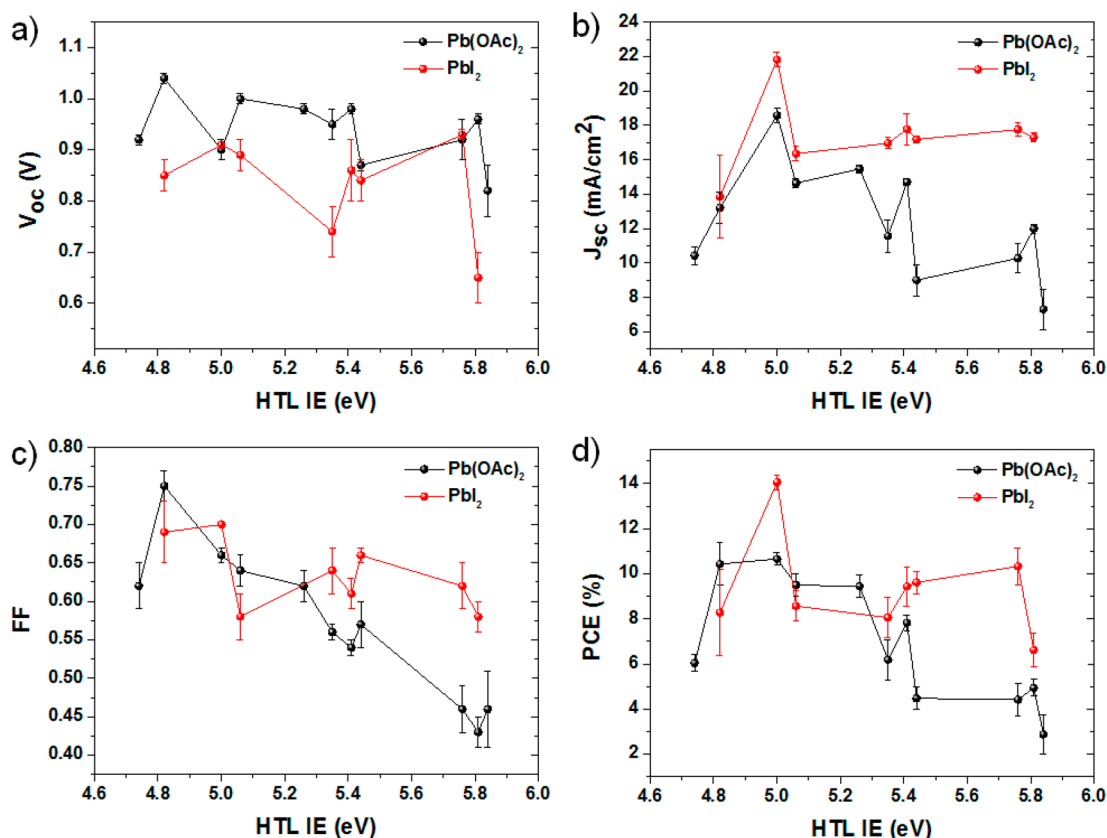


Figure 6. Average V_{OC} (a), J_{SC} (b), FF (c), and PCE (d) for MAPbI_3 PV cells as a function of HTL IE. The error bars correspond to $\pm$ the standard deviations from typically 16 or more individual PV cells for each HTL.

respectively. These similar hole mobilities suggest that the mobility of the HTL materials are not responsible for the observed performance differences. Scanning electron microscopy images show that the MAPbI₃ morphologies are similar on all the TAAES derivatives, with average grain sizes falling between 108 and 119 nm, as shown in Figures S4 and S5 and Table S1. Furthermore, the TAAES derivatives all have glass transition temperatures (T_g s) of 80 ± 2 °C, as shown by the DSC data presented in Figure S6. These T_g s are below the annealing temperature of the MAPbI₃ film, and thus we do not expect significant differences in the degree of perovskite precursor diffusion within the HTLs during thermal annealing. With similar hole mobility and perovskite morphology, the most apparent difference in the measured and expected physical properties of the three TAAES derivatives is the IE, which varies from 5.26 to 5.76 eV. Neglecting changes in material energetics at the interface, TAAES-2 has an IE that is nearly identical to that of the perovskite, whereas TAAES-2OMe and TAAES-4OMe have IEs that are 0.34 and 0.50 eV lower than that of the perovskite. However, TAAES-2 shows the lowest performance. To determine whether these differences in IEs are a major reason for the variation in PV performance, we extended our HTL study to include six more materials spanning a larger range of IEs.

HTL IE Influence on PV Performance. The additional HTL materials selected to further probe how the IE effects the PV performance of MAPbI₃ devices include H-ADT (IE = 4.74 eV), 6T (IE = 4.82 eV), NPD (IE = 5.35 eV), rubrene (IE = 5.44 eV), Alq₃ (IE = 5.81 eV), and Cl-ADT (IE = 5.84 eV). One of the goals is to determine if HTLs with low IEs (i.e., 6T and H-ADT) result in V_{OC} losses, as has been previously observed and suggested to account for lower V_{OC} values in perovskite PVs.^{7,36,59} Another goal is to determine if HTLs with higher IEs result in V_{OC} , FF, or J_{SC} losses due to a barrier to hole extraction.

Figure 6 shows the average PV performance parameters for the MAPbI₃ PV cells as a function of HTL IE. First, we analyze the trends with Pb(OAc)₂ as the Pb source. Surprisingly, the V_{OC} remains high (>0.92 V) even when the HTL IE drops to 4.74 eV. The J_{SC} plateaus at ca. 15 mA/cm² when the IE is between 5.06 and 5.41 eV but drops off as the IE ventures outside of this range. The FF stays above 0.62 with HTL IEs of 4.74–5.26 eV and decreases steadily as the IE climbs above 5.26 eV. As a result, the PCE is greatest for HTL materials with IEs between 4.82 and 5.26 eV with Pb(OAc)₂.

To determine if these trends were generally applicable, we tested many of the HTLs using a different method to process the MAPbI₃ films. When the processing method is altered to include PbI₂ as the Pb source, as shown in Figure 6, the J_{SC} , FF, and PCE become less sensitive to the HTL IE, as indicated by champion PCEs of above 10% for HTL IEs at 4.82 and 5.76 eV. The reduced sensitivity of the HTL IE using this PbI₂ processing method may potentially arise due to the dependence of the interfacial chemistry and associated energetics on the lead precursor and processing environment. Additionally, the significantly lower concentrations of MAI needed with the PbI₂ source (a 1:1 MAI:PbI₂ molar ratio, as opposed to a 3:1 MAI:Pb(OAc)₂ ratio) may influence material and interface energetics. These hypotheses are in part supported by the processing method dependent IE and work function for MAPbI₃, as well as the IE dependence on the MAI:Pb ratio used in the precursor solution, as reported in the literature and evidenced by our UPS data in Figure S2.^{48,60,61}

Both MAPbI₃ processing methods show that the V_{OC} does not correlate with the HTL IE for materials with IEs below 5.8 eV. This trend indicates that the quasi-Fermi level of holes is not primarily limited by the HTL IE, as some previous observations suggested.^{7,36,59} Our observation is consistent with previous reports that show a nearly constant V_{OC} over the 5.0–5.35 eV IE range,^{33,34} but to the best of our knowledge this is the first report of high V_{OC} values extending to HTLs with IEs significantly outside of this range. Notably, the V_{OC} does fluctuate within a 0.15 V window for HTLs with IEs less than 5.8 eV for devices processed with either Pb precursor. However, these fluctuations in V_{OC} do not correspond with the HTL IE.

Other properties of the HTL, such as the charge-carrier mobility, are also likely to influence the PV performance. However, it does not appear that there is a large correlation with the HTL mobility over this series. For example, the charge-carrier mobilities in these HTLs span over 2 orders of magnitude,^{38,40,59,62,63} with no correlation with the IE. Furthermore, the low-mobility material Spiro-OMeTAD is one of the best performing HTLs.^{38,59,63} Differences in MAPbI₃ film morphology brought about by processing on the different HTLs may also contribute to the observed PV performance differences. For the Pb(OAc)₂ procedure, scanning electron microscopy (SEM) images indicate that the morphologies of MAPbI₃ are similar on all the HTLs with the exception of 6T, as shown in Figures S4 and S5. For most HTLs the average grain size ranges from 100 to 160 nm, and these differences in grain size do not correlate with device performance as evident in Figure S11. 6T shows an average grain size of 300 nm, which likely explains the larger fill factor. For the PbI₂ procedure, the grain sizes are slightly larger with averages between 130 and 230 nm, as shown in Figures S9 and S10. Again, over this range of grain sizes there does not appear to be a strong correlation with PCE, as shown in Figure S11. Overall, the minimal correlation between grain size and PCE for the observed grain sizes, combined with a lack of correlation between PCE and mobility, leads us to conclude that much of the observed performance differences are due to the IE and the range of acceptable HTL IEs is strongly dependent on the MAPbI₃ processing method.

Recently it was observed that diffusion of perovskite precursors into or through organic transport layers can lead to degradation of the HTL or to chemical reactions with metal electrodes.^{64–66} It is also possible that diffusion of the perovskite precursors through these HTLs may lead to reactions with the indium tin oxide bottom electrode or the HTLs themselves, which may alter the energetics, introduce trap states, and influence recombination dynamics. To probe whether reactions with ITO or the HTL are influencing the PV performance, we recorded XPS spectra of the ITO, 6T, and Cl-ADT films prior to perovskite deposition and after perovskite deposition and removal (i.e., after the perovskite film was rinsed off of the HTL). XPS analysis of the sulfur 2p and chlorine 2p regions of the HTLs shows no evidence of reactions between either HTL and the perovskite for perovskites processed with Pb(OAc)₂ or PbI₂ as the Pb source, as shown in Figure S12. Furthermore, the S 2p peaks from 6T do not change after perovskite deposition and removal for either Pb source. Both the Cl 2p and S 2p peaks for Cl-ADT shift by ca. 0.25 eV after perovskite deposition and removal from Pb(OAc)₂ and PbI₂, but the similarity for both precursors indicates that the energetic shifts are equivalent for the perovskites processed

from both precursors. Additionally, to probe if the different perovskite precursor solutions lead to reactions with ITO, we recorded XPS measurements of ITO before perovskite coating and after perovskite coating and removal, as shown in Figure S13. All XPS peaks from ITO fall at nearly identical positions before and after perovskite exposure and removal. Thus, our data suggest that the observed differences in device performance for the different HTLs are not due to various extents of HTL degradation or reactions between the perovskite precursors and ITO.

CONCLUSIONS

With appropriate IEs, the TAAES derivatives investigated as HTLs show comparable PV performance to the state-of-the-art HTLs PEDOT:PSS and Spiro-OMeTAD. Further investigations into the stability of these derivatives will determine if they may provide suitable replacements for PEDOT:PSS or Spiro-OMeTAD. It is well-known that the performance of MAPbI₃ perovskite photovoltaics are highly sensitive to MAPbI₃ processing conditions, and our work demonstrates that these processing conditions even influence the optimum IE range of the HTL materials. Moving forward, it will be important to identify why this range depends on MAPbI₃ processing conditions and why the IE of MAPbI₃ varies with processing conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b16894.

Synthetic details, absorbance spectra, ultraviolet photoelectron spectroscopy data, current–voltage characteristics, scanning electron microscope images, grain size histograms, and a plot of power conversion efficiency vs grain size (PDF)

Crystal structure file for TAAES-2 (CIF)

Crystal structure file for TAAES-2OMe (CIF)

Crystal structure file for TAAES-4OMe (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

K.R.G. acknowledges the University of Kentucky for providing start-up funds. This material is based upon work partially supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, and the EPSCoR program, under Award DE-SC0018208. J.E.A. thanks the National Science Foundation (CHE 1609974) for supporting chemical synthesis. The X8 Proteum diffractometer was obtained with funds from the NSF MRI program (CHE-0319176).

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