Development of Simple Hole-transporting Materials for Perovskite Solar Cells

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Abstract

Three low-cost propeller-shaped small molecules based on a triphenylamine core and the high performance donor molecule $DTS(FBTTh_2)_2$ were investigated as hole-transporting materials in perovskite solar cells. Each hole-transporting material was designed with highly modular side-arms, allowing for different bandgaps and thin-film properties while maintaining a consistent binding energy of the highest occupied molecular orbitals in order to facilitate hole-extraction from the perovskite active layer. Perovskite solar cell devices were fabricated with each of the three triphenylamine-based hole-transporting materials and $DTS(FBTTh_2)_2$ and were compared to devices with spiro-OMeTAD the hole-transporting layers. Each of our triphenylamine hole-transporting materials and $DTS(FBTTh_2)_2$ displayed surface morphologies that were considerably rougher than that of spiro-OMeTAD; a factor that may contribute to lower device

performance. It was found that using inert, insulating polymers as additives with $DTS(FBTTh_2)_2$ reduced the surface roughness, resulting in devices with higher photocurrents.

Introduction

The use of soluble photoactive materials in third-generation photovoltaic (PV) technologies enables low-cost, solution-processed manufacturing. In particular, perovskite solar cells (PSC) combine low-cost materials, solution processing and high efficiencies for a promising PV technology. Since the first report of organometal halide perovskites (e.g., CH₃NH₃PbI₃) as light-harvesters in photovoltaic devices in 2009,¹ vast improvements have been made with power conversion efficiencies now reaching 19%.² It has been shown that hole-extraction from the perovskite active layer is a critical step in charge-separation and current generation.³ Therefore, a key component in the perovskite solar cell is the hole-transporting material (HTM). In fact, the development of an all-solid-state perovskite solar cell (PSC) was a significant advancement toward commercialization of this technology and was made possible by the application of a solid-state hole-transporting material: 2,2',7,7'-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD).⁴

Effective hole-transport from the perovskite to the metal electrode is dependent on a number of factors including electronic compatibility and nanomorphology. More specifically, there must be favourable alignment of the perovskite valence band maximum (VBM) and the highest occupied molecular orbital (HOMO) of the HTM to allow hole-extraction upon carrier generation. Furthermore, the material must form a continuous film over the perovskite tends to be rough with large crystalline domains, especially in a planar device architecture with no mesoporous framework.^{5–8} Spiro-OMeTAD has well-aligned energy levels,⁹ good hole

mobility¹⁰ and the ability to form amorphous and uniform thin films;¹¹ properties that make it a perfect candidate as an HTM in PSCs and the reason for its continued use and high-performance in PSCs.

However, the core starting material (e.g., 2,2',7,7'-Tetrabromo-9,9'-spirobifluorene) is inherently expensive due to its multifaceted synthesis.⁹ Furthermore, spiro-OMeTAD requires the use of p-type dopants (e.g., tert-butylpyridine (tBP) and lithium trifluoromethanesulfonate (Li-TFSI)) to increase conductivity and hole-mobility to yield high-performance devices.^{12–14} However, such dopants are hygroscopic and detrimental to the long-term stability of the cell and thus not practical as agents in commercial solar cells.¹⁵ It is therefore important to develop efficient, yet dopant-free,¹⁶ economical HTMs.

Development of alternative HTMs from low-cost starting materials is an active area of research and a strategy for reducing the overall cost of perovskite solar cells. Simple, easy-to-synthesize HTMs have emerged with efficiencies rivalling spiro-OMeTAD in PSCs.^{17–19} For example, a simple HTM known as "H101" was synthesized with a 3,4-ethylenedioxythiophene (EDOT) core and shown to achieve give respectable *PCE* of 10.6 % without the use of dopants.¹⁷ In a subsequent paper, the same group reported a derivative of H101 with a tetra-substituted thiophene core (aka "H111") that achieved a *PCE* of 14.9 %.¹⁹

Other materials that show promise as cheap building blocks for HTMs are based upon triphenylamine (TPA). A polytriarylamine HTM has already demonstrated potential in PSCs, out-performing other polymeric HTMs based on thiophene and carbazole units.²⁰ On the other hand, small molecules with a single TPA unit have been used as hole conductors in a variety of the organic electronic applications.^{20–24} In these compounds, the central TPA "core" adopts a pseudotetrahedral geometry.²⁵ Each of the three phenyl groups can be functionalized at *para*

positions forming the three "side-arm" units. The result is a three-dimensional (3D) propellershaped molecule. This design motif has already been applied for HTMs in PSCs. ^{26,27} For example, Choi *et al.* synthesized a TPA-based HTM that achieved a 7.45% without the use of dopants. Sung *et al.* achieved an impressive *PCE* of 13.86% with a TPA-based HTM employing carbazole branching units in PSCs.²⁷ However, these cells were fabricated with the use of p-type HTL dopants and the stand-alone performance of the HTMs is not revealed.

In this contribution we have developed a series of three propeller-shaped smallmolecules, each with a TPA core and different side-arm compositions, for use as HTMs in PSCs and have studied the utility of the known high performance donor DTS(FBTTh₂)₂ as a HTM. All three new compounds were synthesized in-house and built with side-arms consisting of different donor (i.e., electron-donating) and acceptor (i.e., electron-withdrawing) functionalities (see **Figure 1** for molecular structures). By applying this design strategy, it was possible to keep the HOMO at an energy level consistent with that of spiro-OMeTAD to allow for efficient holeextraction from the perovskite active layer while modifying the molecular structures. In this way, the effect of both molecular composition and film-forming properties on the performance TPA-based HTMs in perovskite solar cells can be investigated.

The molecular structures of all organic materials used in this study are given in **Figure 1**. The first hole-transporting material is tris(4-(5-hexylthiophen-2-yl)phenyl)amine, designated as "HTM01". HTM01 is the simplest of the three materials with a TPA core flanked by a thiophene unit for the purpose of extending π -conjugation. Although it has been previously synthesized via lithiation and transmetallation,²⁸ we report an alternative and facile synthetic approach yielding HTM01 via direct arylation (synthetic details are provided in the **ESI**). The second compound in this study is 5,5',5"-(5,5',5"-(nitrilotris(benzene-4,1diyl))tris(furan-5,2-diyl))tris(2-octylisoindoline-1,3-dione), or "HTM02". HTM02 has two structural differences compared to HTM01: i) a furyl unit replaces the thienyl unit, and ii) phthalimide groups are added to the ends of the side-arms as additional acceptor units. The furyl units were selected for two reasons. First, it is considered to be a sustainable and "green" alternative to thiophene as a building block in functional materials since it is derived from biological feedstocks.^{29–31} Second, substitution of furan for thiophene as electron-rich donor units in organic semiconductors can result in an increase in hole mobility, as demonstrated by our recent work³² and others.^{33,34} The phthalimide groups are electron-withdrawing and result in a stabilization of the frontier energy levels of HTM02 relative to HTM01, and corresponding decrease in the bandgap energy. Conveniently, solubility can be tuned using the phthalimide unit via simple modification of the alkyl chain attached to the nitrogen atom.

The third compound, HTM03, has a diketopyrrollopyrrole (DPP) unit in the center of the side-arm units. DPP-based polymers have proven effective as HTMs in PSCs, ³⁵ making DPP a good choice for a donor building block. The insertion of DPP into the side-arm further stabilizes the frontier molecular orbitals and reduces the bandgap energy (E_g) of HTM03 relative to both HTM01 and HTM02. Large branched alkyl chains (i.e., 2-ethylhexyl) help to disrupt strong π - π intermolecular interactions between DPP units,³⁶ which improves solubility. 1-ethylpropyl or "swallowtail" end caps were used in place of the hexyl chains present in HTM01 and HTM02 and HTM03 are provided in the **ESI**.

The fourth HTM utilized is 7,7'-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[*c*]-

[1,2,5]thiadiazole), which is also known as p-DTS(FBTTh₂)₂, but is labelled as "HTM04" herein. HTM04 is well-known as a high-performance donor material in bulk-heterojunction smallmolecule organic solar cells.³⁷ HTM04 was selected as an HTM in this study since has similar HOMO energy levels to HTM01, HTM02 and HTM03 and displays high hole-mobility, but has a very different molecular geometry.³⁸

Herein, we investigate the four HTMs in terms of optical and electronic properties and film-formation using a combination of UV-Visible absorption spectroscopy (UV-Vis), cyclic voltammetry (CV), and atomic force microscopy (AFM). The performance of the PSCs fabricated with the new HTMs is subsequently tested.

Figure 1 depicts the molecular structures of the HTMs while **Figure 2** depicts the relevant energy levels of all components in our PSCs. HOMO energy levels of the HTMs were estimated using the oxidation potentials determined by CV (see **Figures S6-S10** in the **ESI** for CV plots of the HTMs) The valence-band maximum (VBM) energy of the perovskite (MAPbI₃) was previously determined by others using ultraviolet photoelectron spectroscopy (UPS) and is shown for comparison.⁴ The conduction band minimum of -5.5 eV (versus the energy of an electron in vacuum) for an air-exposed film of MoO₃ is representative of n-type MoO₃ charge-transport layers used in organic electronic devices.³⁹ In perovskite solar cells, MoO₃ is used as an n-type material to assist charge transport/hole-blocking layer with a work function of 4.0 eV.⁴⁰ The work function of fluorine-doped tin-oxide (FTO), the electron-collecting electrode, is 4.5 eV based on measurements conducted using ultraviolet photoelectron spectroscopy (UPS).⁴¹



Figure 1. Molecular structures of the five HTMs investigated in this study. TPA and thiophene units are highlighted in blue and red, respectively.



Figure 2. Energy level diagram for all components in the PSCs. The HOMO and LUMO levels for HTM01-04 were determined by CV, with coloured bars representing the bandgap. Only the HOMO level was measured for spiro-OMeTAD. The CBM and VBM for CH₃NH₃PbI₃ were determined by others.⁷

Results and Discussion

Optical Characterization. UV-Vis spectra for thin films of the five hole-transporting materials are shown in **Figure 3**, with a summary of electronic parameters given in **Table 1**. The optical bandgap energy (E_g) is defined by the onset wavelength of light absorption (λ_{onset}). Spiro-OMeTAD and HTM01 have similar absorption profiles with maximum absorption in the near-UV region (373 and 377 nm, respectively). HTM02 has an intermediate optical bandgap, with maximum absorption at 445 nm for the thin film. HTM03 and HTM04 have the smallest E_g with onset of absorption at 715 and 759 nm, respectively.

CV was used to determine the oxidation potential of each of the HTMs. Individual CV traces for each HTM are included in the **ESI** and show that all of the HTMs undergo multiple

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reversible oxidations. These values (E_{ox}) are reported in **Table 1** with respect to the oxidation potential of ferrocene (Fc), which has been measured previously to be 4.80 eV.⁴² It was confirmed that the HOMO levels of all five HTMs were similar (~5 eV below the vacuum) and at an appropriate level for hole-extraction at the perovskite interface.



Figure 3. UV-Vis absorption spectra acquired for thin-film samples of each HTM.

НТМ	E _{ox} vs. Fc (V)	E _{HOMO} (eV) (relative to E _{vac})	$E_{ m g, film} \left(m eV ight)$	$\lambda_{onset, film} (nm)$
Spiro-OMeTAD	0.20	-5.00	2.96	419
HTM01	0.14	-4.94	2.95	420
HTM02	0.26	-5.08	2.38	520
HTM03	0.24	-5.04	1.73	715
HTM04	0.23	-5.03	1.63	759

Table 1. Summary of optical and electrochemical properties of the HTMs used in this study.

PSC Device Fabrication and Characterization.

The photovoltaic properties of the HTMs were investigated by fabricating planar heterojunction PSC devices (see **ESI** for a description of the fabrication procedure). Control devices were fabricated with both doped (tBP and Li-TFSI) and undoped spiro-OMeTAD as the HTMs. Our best-performing devices made with doped spiro-OMeTAD delivered a power conversion efficiency (*PCE*) of 13.4%, which is comparable to PSC devices made by others using a similar method of perovskite deposition.⁴³ It was confirmed that the use of dopants with spiro-OMeTAD afforded devices with lower series resistance (by a factor of two) and higher *PCE* and fill-factor (*FF*) (**Figure 4a**)). However, no p-type dopants were used with the four new HTMs in this study, and therefore the PV performance is compared only to undoped spiro-OMeTAD.

The *J*-*V* curves of the best-performing devices with each of the undoped HTMs are shown in **Figure 4b**) with corresponding performance metrics listed in **Table 2**. The best device with spiro-OMeTAD reached a *PCE* of 6.6%, an open-circuit voltage (V_{oc}) of 0.88 V, a shortcircuit photocurrent density (J_{sc}) of 17.2 mA cm⁻² and a *FF* of 0.43. HTM01 performed the best among the TPA-based HTMs with a *PCE* of 3.5 % and J_{sc} of 8.8 mA cm⁻². Devices made with HTM02 and HTM03 display lower J_{sc} and correspondingly lower *PCE*. HTM04 devices offered the highest J_{sc} among HTMs at 10.0 mA cm⁻². However, the high series resistance and low *FF* ultimately resulted in low PCEs (2.8%) for even the best-performing HTM04 devices. Comparing the PV data between all of the HTLs, it is evident that all of the devices display a similar V_{oc} as a result of the similar HOMO levels of the HTMs. Others have shown that the V_{oc} of PSC devices is strongly dependent on the HOMO level of the HTM.⁴⁴ Although it is possible to enhance the V_{oc} of devices by utilizing HTMs with low-lying HOMOs, such materials offer poor electron-blocking capabilities leading to recombination and low current densities poor device efficiencies.⁴⁵

In the present study, the J_{sc} is the parameter that shows the most variability among devices utilizing different HTMs. One can reason that factors influencing photocurrent,

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including HTL morphology, hole-transport properties, and HTL-perovskite interfacing are critical for realizing high-performance devices. It was also observed that all devices displayed some degree of hysteresis with scan direction (see **Figure S2** in the **ESI**), a phenomenon that is described by others throughout the literature.^{46–48}



Figure 4. a) *J-V* curves of the best-performing PSCs fabricated with doped and undoped spiro-OMeTAD. b) *J-V* curves of the best-performing PSCs fabricated with four new HTMs and undoped spiro-OMeTAD.

Table 2. Summary of performance metrics for champion cells with different HTLs. The plots were obtained by scanning from +2.0 V to 0.0 V at a rate of 1 V per second under 100 mW/cm² AM1.5 G illumination. The average metrics for five sample devices (each with a different HTL) are also provided with standard deviations in the brackets. The shunt and series resistances listed are for the best-performing devices only.

HTL		$V_{ m oc}\left({ m V} ight)$	J _{sc} (mA cm ⁻²)	PCE (%)	FF	Shunt Resistance (Ω/cm ²)	Series Resistance (Ω/cm ²)
Doped spiro- OMeTAD	Best	1.06	17.8	13.4	0.71	1.0×10 ⁶	1.9×10 ⁻²
	Average	1.04(0.02)	17.3(0.4)	12.2(0.7)	0.68(0.03)	-	-
Undoped spiro- OMeTAD	Best	0.88	17.2	6.6	0.43	1.6×10 ⁶	3.7×10 ⁻²
	Average	0.85(0.04)	16.4(1.3)	5.6(0.7)	0.40(0.03)	-	-
HTM01	Best	0.97	8.8	3.5	0.41	2.5×10^{5}	3.6×10^{-2}
	Average	0.94(0.03)	8.0(0.6)	2.8(0.4)	0.38(0.02)	-	-
HTM02	Best	0.92	4.2	2.0	0.52	5.7×10^2	2.0×10^{1}
	Average	0.88(0.08)	3.9(1.0)	1.6(0.4)	0.48(0.13)	-	-
HTM03	Best	0.85	3.4	0.9	0.31	3.4×10^{5}	8.5
	Average	0.87(0.04)	3.3(0.4)	0.9(0.1)	0.30(0.01)	=	-

HTM04	Best	0.89	10.0	2.8	0.31	1.7×10^{5}	2.3×10 ⁻²
	Average	0.80(0.08)	7.5(3.0)	1.8(0.9)	0.28(0.03)	-	-

Hole-transporting layer (HTL) Surface Morphology.

The surface morphologies of the HTLs were probed to further investigate the source of the differences in PV performance. **Figure 5** shows atomic force microscope (AFM) images of the HTL surfaces acquired after device fabrication and testing. An image of the bare perovskite layer is shown for comparison. The bare perovskite film consists of micron-sized crystalline grains with large height deviations that resemble "mountains" and "valleys."

Due to the large height deviations in the thin-film samples, acquisition of AFM tapping-mode images proved challenging and tip convolution artifacts are apparent in the roughest images. Nevertheless, information about the morphology of the HTL surfaces and quantification of the roughness parameters was possible. It is observed that spiro-OMeTAD forms the smoothest, most planar film over the underlying perovskite layer with the lowest value of root-mean square roughness (R_{RMS}) (see Table 3). Among the three propeller HTMs, the roughness of the films increases from HTM03 to HTM02 to HTM01. Considering the trend in PV performance of the devices shown in Figure 4, J_{sc} also increases from HTM03 to HTM02 to HTM01. This result is counterintuitive as one would expect that the smoothest film (i.e., one that is similar to the spiro-OMeTAD HTL) would lead to higher J_{sc} values and overall better PCE. This suggests that many other factors are at play. Indeed, the layers formed by HTM03 and HTM04 have surfaces of comparable roughness ($R_{RMS} = 17$ and 20, respectively), however, PSC devices with HTM04 can generate threefold higher photocurrent than those with HTM03, indicating that surface roughness cannot be the only factor contributing to photovoltaic performance. Other important structural details, including the film morphology at the HTL-perovskite interface and the HTL thickness, cannot be determined by AFM, yet are likely critical factors. Interestingly, both HTM01 and HTM04 bear similar alkyl-thiophene endcapping units as opposed to phthalimide-based endcapping units, suggesting a possible material composition effect. Further experiments are needed.



Figure 5. 2D AFM images of HTL surfaces of the five materials under study. An image of a neat perovskite film (i.e., no HTL) is shown for comparison.

Table 3. Roughness parameters of HTL films on perovskite obtained from 2D AFM images. . The parameters were calculated over an area of $25 \,\mu m^2$.

	No HTL (Neat perovskite)	Spiro- OMeTAD	HTM01	HTM02	HTM03	HTM04
Surface Area (µm ²)	26	24	28	24	25	24
$R_{\rm RMS}^{a}$ (nm)	35	12	58	28	17	20
R_{a}^{b} (nm)	28	10	40	21	13	14
$R_{\rm max}^{\ \ c} ({\rm nm})$	246	86	445	228	132	170

^{*a*} R_{RMS} , the root mean square (RMS) average of height deviations relative to the mean image data plane. ^{*b*} R_{a} , the average of the absolute values of the surface height deviations relative to the mean plane. ^{*c*} R_{max} , the vertical distance between the highest and lowest data points in the image.

As shown in **Figure 4b**), HTM04 displays the highest J_{sc} among the new HTMs and is known to have excellent hole mobility.³⁸ HTM04 is also unique among the HTMs in this study; it is the only HTM that displays crystallinity (see thin-film XRD patterns in **Figure S3** in the **ESI**). AFM images in **Figure 5** reveal that HTM04 has a rougher, textured surface morphology over the perovskite layer when compared to the Spiro-OMeTAD HTL. Therefore, it is of interest to investigate methods for improving the planarity of the HTL. Since HTM04 is spincasted from a hot solution at its solubility limit, it is not possible to increase the concentration in an attempt to generate a thicker, more-planar film. Alternatively, high-molecular weight nonconjugated polymers can be used as inert solvent additives to increase the viscosity of the spincoating solution in an attempt to increase the thickness and coverage of the HTL.

Following this approach, two non-conjugated insulating polymers were selected as additives: polystyrene (PS) and trimethyl-terminated polydimethylsiloxane (PDMS). The concentration of HTM04 was kept at 25 mg/mL and the amount of polymer additive was equivalent to 2% of the HTM by weight (i.e., 0.5 mg/mL). PS was selected because it has been shown to improve the performance of small-molecule bulk-heterojunction organic solar cells with HTM04 by inducing phase separation.⁴⁹ PDMS is also known to improve the morphology and PV performance of small-molecule bulk-heterojunction active layers in organic solar cells⁵⁰ and has also been demonstrated as an inert additive in HTLs of PSCs for the purpose of surface planarization.¹⁵

PSC devices were fabricated with HTM04 as the hole-transporting material combined with either PS or PDMS as inert additives. The *J-V* curves for the best-performing devices containing HTM04 with and without polymer additives are shown in **Figure 6**, with corresponding performance metrics listed in **Table 4**. Addition of PS to the HTL film results in

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a slight decrease in J_{sc} and V_{oc} compared to the devices with a neat HTM04 layer. On the other hand, devices with PDMS as an HTM-additive display both higher photocurrent ($J_{sc} = 11.9$ mA/cm²) and a higher *FF* than those without the additive, resulting in an increase in *PCE* (3.3 % versus 2.8 % for the HTM04 neat film).



Figure 6. A comparison *J*-*V* curves of best-performing perovskite solar cell devices with HTM04 as the HTM, with and without non-conjugated polymer additives. The plots were obtained by scanning from +2.0 V to 0.0 V at a rate of 1 V per second under 100 mW/cm² (1.0 sun) AM1.5 G illumination.

Table 4. A summary of *J*-*V* characteristics of perovskite solar cell devices with HTM04 as the HTM, with and without non-conjugated polymer additives. The average metrics for five sample devices (each with a different HTL) are also provided with standard deviations in the brackets. The shunt and series resistances listed are for the best-performing devices only.

HTL		$V_{ m oc}({ m V})$	J _{sc} (mAcm ⁻²)	PCE (%)	FF	Shunt Resistance (Ω/cm^2)	Series Resistance (Ω/cm ²)
HTM04 neat	Best	0.89	10.0	2.8	0.31	1.7×10^{5}	7.5×10 ⁻²
	Average	0.80(0.08)	7.5(3.0)	1.8(0.9)	0.28(0.03)	-	-
HTM04 + 2% PS	Best	0.87	9.4	2.7	0.33	2.1×10^5	7.3×10 ⁻²
	Average	0.77(0.06)	9.2(1.4)	2.0(0.5)	0.29(0.03)	-	-
HTM04 + 2% PDMS	Best	0.85	11.9	3.3	0.33	2.2×10^{5}	7.6×10 ⁻²

	Average	0.89(0.03)	10.1(1.6)	3.1(0.5)	0.34(0.01)	-	-
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AFM was used to further probe the effect of non-conjugated polymers of the morphology of the HTLs (see **Figure 7**). AFM images of the HTL surfaces reveal that films with HTM04 and PDMS on a perovskite active layer are 25% less rough than HTM04 neat films on perovskite (see **Table 5** for R_{RMS} values). The images suggest that the addition of PDMS reduces the roughness of the HTL by filling in the deep "valleys" in the perovskite film. Further evidence for changes in self-assembly and crystallinity within the HTL are provided in the **ESI**; **Figure S4** shows that the XRD peak intensity for HTM04 decreases upon addition of either polymer. Interestingly, addition of either polymer improved the shunt resistance of the devices, which provides further evidence that the blends provide better coverage of the perovskite layer, thus passivating shunt pathways.

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Figure 7. 2D AFM images of HTL surfaces of HTM04 with and without polymer additives on a perovskite film. An image of a neat perovskite film is shown for comparison.

Table 5. Roughness parameters for HTL films on perovskite obtained from 2D AFM images. The parameters were calculated over an area of $25 \,\mu m^2$.

	No HTL	HTM04 Neat	HTM04 + 2% PS	HTM04 + 2% PDMS
Surface Area (µm ²)	26	23	24	25
$R_{\rm RMS}$ (nm)	35	20	17	14
$R_{\rm a}({\rm nm})$	28	14	12	11
R_{\max} (nm)	246	170	139	139

Conclusions and Future Work

We have investigated three new triphenylamine-based materials and the popular donor $DTS(FBTTh)_2$ as hole transport materials for perovskite solar cells. The highly modular molecular framework of the triphenylamine-based materials allows for facile synthesis and

straight forward structural modifications. All of the HTMs investigated had a HOMO level on par with spiro-OMeTAD, but with different optical and electrochemical properties. Unfortunately devices utilising HTM 01-03 demonstrated inferior performance compared to the control device using spiro-OMeAD as the HTM.J-V measurements of perovskite solar cell devices fabricated with each HTM shows that low photocurrent is the primary reason for the poor performance relative to spiro-OMeTAD. The low photocurrents are attributed to the rough HTL surfaces (as revealed by AFM), potentially incomplete coverage, and resulting shunt pathways. Further optimization of the triphenylamine-based HTMs, HTM01, HTM02 and HTM03, will include adjustments in molecular design to enhance solubility, thus allowing for spin-casting at greater solution concentrations, generating thicker and more planar HTLs with more complete coverage. The fourth HTM investigated, HTM04 (DTS(FBTTh)₂), showed slightly better performance than HTM 01-03, but still worse than spiro-OMeTAD. Through the addition of non-conjugated polymer additives to the HTM04 casting solution, we have demonstrated that the roughness of the HTL layer can be decreased resulting in an improvement in photocurrent generation. . This is a simple yet effective strategy for increasing solution viscosity for HTMs with low-solubility, resulting in smoother HTL films and better device performance.

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