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TOC graph

Two different triphenylamine-substitutions on 9,9-bis(4-diphenylaminophenyl)fluorene (FLTPA) core has been synthesized successfully from cost-efficient commercially available starting materials. Afterwards, they are employed in the inverted perovskite solar cells. The 2,7-linear substituted compound (4,4'-(2,7-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-9*H*-fluorene-9,9-diyl)bis(*N*,*N*-diphenylaniline, namely TPA-2,7-FLTPA-TPA)-based devices have achieved the highest power conversion efficiency of 17.1%. Meanwhile, those of the 3,6-twisted ones are 13.9%.



Boosting Inverted Perovskite Solar Cells Performance by Using Functionalized 9,9-bis(4-diphenylaminophenyl)fluorenes with Triphenylamine as Dopant-free Hole Transporting Materials

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18 Abstract

19 In this study, two newly developed small molecules based on functionalized 9,9-bis(4-20 diphenylaminophenyl)fluorenes and triphenylamine moieties, namely TPA-2,7-FLTPA-TPA 21 and **TPA-3,6-FLTPA-TPA** are designed, synthesized and fully characterized successfully. 22 The electrochemical, optical and thermal properties of both materials are investigated using 23 various techniques. Afterwards, these materials are employed as dopant-free hole transporting 24 materials (HTMs) in planar inverted perovskite solar cell devices with the aim of determining 25 the device performance and studying their stability in comparison with the standard $N^4, N^4, N^{4''}, N^{4''}$ -tetra([1,10-biphenyl]-4-yl)-[1,1':4',1''-terphenyl]-4,4''-diamine (TaTm) based 26 27 devices. Under 1 sun condition, the TPA-3,6-FLTPA-TPA based devices achieve a power conversion efficiency (PCE) of 13.9% whereas TPA-2,7-FLTPA-TPA exhibits the highest 28 29 PCE of 17.1% mainly due to an improvement in the fill factor (FF). Meanwhile, the devices 30 prepared using TaTm as reference HTM exhibit an overall efficiency of 15.9%. In addition to 31 the higher efficiency, our newly developed HTM TPA-2,7-FLTPA-TPA-based devices 32 demonstrate better stability which is comparable to that with TaTm using similar aging test 33 conditions.

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Keywords: 9,9-bis(4-diphenylaminophenyl)fluorenes, triphenylamine, molybdenum trioxide,
 hole transporting materials, perovskite solar cells

37

38 INTRODUCTION

39 Compared to inorganic semiconductors, organic counterparts have been developed and 40 employed intensively either as active layer or charge transporting layer for various 41 optoelectronic devices including organic light emitting diodes (OLEDs), organic solar cells 42 (OSCs), organic thin-film transistors (OTFTs), perovskite solar cells (PSCs) and other types of 43 devices. Organic semiconducting materials offer several benefits such as versatility of 44 synthesis, which allows great scope for tuning optoelectronic properties, lowering the 45 production cost, compatibility with several substrates (transparent glass, flexible plastic, paper 46 and clothes), light weight and low-temperature fabrication and large scale processing.¹⁻⁴On this line, Li's research group has provided a great overview of OSC materials for commercialization 47 48 based on high performance, simple device fabrication process, stability, cost and green 49 processing.⁵ In addition to OSC, recently, PSC have attracted much attention due to their 50 promising power conversion efficiency (PCE) which has recently reached 23.7%. This device 51 efficiency is now close to that of commercially used silicon solar cells.⁶ This high efficiency 52 can only be achieved with the use of solid-state organic hole transporting layers (HTLs) in such 53 PSC devices where the organic semiconducting material plays an extremely critical role. The 54 efficiency and stability of PSC devices are major device parameters and they are being 55 continuously improved. This would have not been possible without the exploration of new high 56 hole mobility charge transporting layers incorporated in the PSC devices. The performance can 57 be enhanced with the use of an HTL because this layer assists in the collection of holes upon 58 dissociation of excitons created after light absorption. In addition to their role of extraction and 59 transport of holes, which is necessary to boost the open circuit voltages (V_{oc}) and achieve highperformance devices,⁷⁻¹⁰ these HTL also protects the perovskite layer from the penetration of 60 61 harmful elements such as moisture and ion ingress from the contact electrodes. In addition to 62 this HTL's dual role, it also plays a key role in achieving fabrication of perovskite solar cell devices on large scale, first in the form of prototypes, and ultimately to push this technology to 63 64 the next level - commercial use.

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65 Basically, perovskite devices can be categorized into the conventional/regular (n-i-p) structure and the planar inverted (p-i-n), based on their configuration.¹¹ In the first layout, a compact or 66 67 mesoporous metal oxide electron transporting layer (ETL, n-type) is deposited first followed 68 by the active perovskite layer (i) and then the p-type HTL layer (p). Meanwhile, the inverted 69 (p-i-n) structure consists of a hole transporting layer (HTL, p-type) followed by the perovskite 70 active layer (i) and then the electron transporting layer (ETL, n-type). For the n-i-p devices, 71 usually high performing n-type mesoporous TiO₂ needs to be deposited at a high temperature 72 (around 400 °C) which restricts the use of flexible plastics as substrate. But there are some 73 exceptional oxides such as SnO2 which does not require high temperature annealing and it 74 exhibits higher solar cell performance.¹² For the p-i-n architecture, on the other hand, all layers 75 can be simply fabricated via low-temperature solution-processing techniques, which is 76 beneficial to fabricate large-scale devices using various substrates.¹³⁻¹⁵ Moreover, this kind of 77 devices can cope with some limitations of the regular ones, including (a) the increase in the 78 production cost due to the requirement of high temperature processing and (b) high instability 79 and large hysteresis.¹⁶

Generally, organic hole transporting materials (HTMs) for PSCs can be divided in two main
groups: polydispersed polymers and monodispersed small molecules. The latter ones offer
various advantages, including defined molecular structure, tunable energetics and good batch-

to-batch reproducibility in comparison with polymeric ones.^{16,17} Among reported various small 83 84 molecular based HTMs, molecularly engineered fluorene-dithiophene (FDT) core substituted 85 by N,N-di-p-methoxyphenylamine donor groups based HTM with a simple dissymmetric structure has been successfully used with state-of-the-art devices and achieve power conversion 86 87 efficiencies of 20.2% and this one is one of the higher performance devices reported in the literature.¹⁸ Though the higher efficiency is achieved using this dopant but it requires dopant. 88 89 Though commercial polymeric HTM based p-i-n perovskite devices, such as poly(3,4-90 ethylenedioxythiophene : polystyrene sulfonate) (PEDOT : PSS) and poly[bis(4-phenyl)(2,4,6trimethylphenyl)amine] (PTAA), displayed high performance,^{19, 20} but they suffer from 91 92 limitations which impact the practical production of PSCs. While the hydrophilic and strong 93 acidic nature of PEDOT: PSS cause the negative impact on the device long-term stability, the 94 use of PTAA is limited due to its extremely expensive price which costs about 50 times the 95 price of gold.¹⁶ Thus the exploration of novel small molecular HTMs for inverted p-i-n PSCs 96 has been emerged.

97 Up to date, even though small molecular HTMs based planar inverted devices have achieved some promising PCEs [such as Trux-OMeTAD (18.05%),²¹ TPA-TVT-TPA (16.32%),¹⁶ 98 99 TPASB (16.2%)²² TPAC3M (16.58%)²³, the stability of the devices is still low or not clear. 100 Recent studies showed that the combination between molybdenum trioxide (MoO_3) and the suitable organic semiconductors may enhance the stability and efficiency of PSCs.²⁴ Indeed, 101 102 Bolink's research group reported that the combination between MoO₃ and a derivative of an arylamine (N^4, N^4, N^4) tetra([1,10-biphenyl]-4-yl)-[1,1':4',1''-terphenyl]-4,4''-diamine or 103 104 TaTm) results in great performance and good stabilities, avoiding the use of doped HTMs in 105 the inverted PSCs.²⁵ MoO₃ which has a deep work-function was showed to induce a free hole 106 density at the interface of organic semiconductors and was found to improve the current density 107 and fill factor (FF) in perovskite cells, by minimizing the sheet resistance.^{26, 27} The use of TaTm 108 in a doped charge transport layer has just been found to be beneficial for the performance of 109 vacuum deposited perovskite solar cells.²⁸ In that case, in order to avoid recombination at the 110 interface between the perovskite and the doped layers, a thin layer of the pure organic charge 111 transport molecules was inserted between the perovskite and the doped layer. However, the 112 stability of solar cells using doped transport layers has been shown to be below that of those 113 employing non-doped layers.²⁹

Fluorene is one of the most promising building blocks for synthesizing light emitting conjugated materials due to its high photoluminescence quantum yield, good thermal and 116 chemical stability, high solubility in common organic solvents, and good film-forming 117 properties.³⁰⁻³² It has been shown that upon substitution of bulky aromatic group such as 118 triphenylamine at the central position of fluorine inhibits keto defect formation, which further 119 gives stable blue emission in OLED devices. Additionally, such molecular design also 120 enhances the thermal stability of both the material and the device.³³ Apart from OLED 121 applications, various fluorene derivatives based HTMs for perovskite solar cells have been developed.³⁴⁻⁴⁶ However, they rely on additives which damage the long-term stability of the 122 123 devices and are mainly employed in conventional/regular (n-i-p) structures. There are hardly 124 any studies regarding fluorene-based HTMs fabricated for inverted devices.

125 Herein, we are reporting two new fluorene-based small molecules, 4,4'-(2,7-bis(4-(bis(4-126 methoxyphenyl)amino)phenyl)-9*H*-fluorene-9,9-diyl)bis(*N*,*N*-diphenylaniline) (coded as 127 **TPA-2,7-FLTPA-TPA**) 4,4'-(3,6-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-9Hand 128 fluorene-9,9-diyl)bis(N,N-diphenylaniline) (coded as **TPA-3,6-FLTPA-TPA**). These 129 molecules were designed and synthesized successfully by varying the substitution position of 130 triphenylamine (TPA) groups via the bromine atoms at the 2 and 7 positions or at the 3 and 6 131 positions on the 9,9-bis(4-diphenylaminophenyl)fluorenes core (FLTPA). After characterizing 132 the materials properties, they were implemented as dopant-free hole transporting materials in 133 inverted CH₃NH₃PbI₃ devices. A thin layer of MoO₃ was deposited in order to ensure a good 134 ohmic contact between the ITO and the HTM layers. For the fabrication of the p-i-n 135 architectures in this work, the perovskite film was deposited by vacuum techniques. Thus, 136 poly(3,4-ethylenedioxythiophene:polystyrene sulfonate) (PEDOT:PSS) was not selected as the 137 standard HTM because it does not block the electrons and may cause losses in built-in potential 138 of the devices.⁴⁷ Instead of using PEDOT:PSS, TaTm was chosen as the standard HTM to do 139 the comparison with two new materials. The aim of this work is to investigate the effect of the 140 different substitutions (2,7 vs. 3,6-positions) in the FLTPA cores on their electrochemical, 141 optical and thermal properties. Moreover, the device performance and stability's comparison 142 among these new pristine HTMs with the conventional TaTm based devices under similar 143 conditions were carried out.

145 **RESULTS AND DISCUSSIONS**

146 Molecular Design and Synthesis

147 In this work, the rational design of these new HTMs is based on the symmetrical donor $-\pi$ linker – donor (D- π -D) structures. In this geometry, 9,9-bis(4-diphenylaminophenyl)fluorene 148 149 (FLTPA) unit is chosen as the π linker because it is a well-known bulky skeleton which is 150 beneficial for hole injection ability and high thermal stability on account of the presence of 151 electron-rich TPA and electron-deficient fluorenone (FL) groups.^{33, 48-51} Meanwhile, the other 152 TPA units are selected to be donors. In consequence of its outstanding features (such as strong 153 electron-donating and high hole transporting ability, amorphous structure forming ability, 3D propeller structure),^{52, 53} they have been employed intensively in solar cells⁵⁴⁻⁵⁶ and organic 154 light emitting diodes (OLEDs).^{17, 52, 53} These TPA groups were introduced at the 2 and 7 155 156 positions or at the 3 and 6 positions on the FLTPA core. While the 2,7-substitution makes the 157 linear structure of the HTM, the twisted one is created by the 3.6-substitution. Although there 158 are several reports related to the substitution at the 2,7-position in the FLTPA group, the 3,6-159 derivatives remain unexplored. Furthermore, there are few earlier studies reporting the effect 160 of the different position substitution of small molecular HTMs on the PSCs' performance.^{57, 58}

161 The synthesis strategy of TPA-2,7-FLTPA-TPA and TPA-3,6-FLTPA-TPA is 162 illustrated in Scheme 1, and a detailed synthesis procedure can be found in the Experimental 163 section. Briefly, 4,4'-(2,7-dibromo-9*H*-fluorene-9,9-diyl)bis(*N*,*N*-diphenylaniline) (compound 164 2) was made from commercial 2,7-dibromo-9H-fluoren-9-one (compound 1) with an excessive 165 triphenylamine in methanesulfonic acid at 140 °C for 48 h. Meanwhile, in order to synthesize 166 4,4'-(3,6-dibromo-9H-fluorene-9,9-diyl)bis(N,N-diphenylaniline) (compound 5), 3,6-dibromo-167 9H-fluoren-9-one (compound 4) was prepared by using commercially available 3,6-168 dibromophenanthrene-9,10-dione (compound 3) under the presence of potassium hydroxide 169 (KOH) and potassium permanganate (KMnO₄) at 130 °C for 72 h. Afterwards, compound 4 170 was used as the starting material to synthesize compound 5 under similar reaction condition 171 mentioned above. The use of a large excess of triphenylamine in two cases, producing 172 compounds 2 and 5, aims to protect the reaction of the free para-positions with more fluorenone 173 to give a bridged species.³³ Simultaneously, the precursor 4-methoxy-N-(4-methoxyphenyl)-174 N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (TPA-BE) was prepared as 175 described previously.^{7,16} Finally, the synthesis of the new target HTMs TPA-2,7-FLTPA-TPA 176 and TPA-3,6-FLTPA-TPA was conducted by using the classical Suzuki coupling reaction

177 between compound 2 with TPA-BE or compound 5 with TPA-BE, respectively. In Suzuki 178 reaction, while 2 M potassium carbonate (K₂CO₃) was used as a base, tetrakis 179 (triphenylphosphine)palladium (0) played the role of a catalyst. The reaction was stirred in 180 anhydrous toluene solvent at 120 °C for 48 h. Upon purification, the yields of these reactions 181 were found to be of 31% for TPA-2,7-FLTPA-TPA and 26% for TPA-3,6-FLTPA-TPA. The 182 purity and chemical structures of both compounds were confirmed by proton and C13 nuclear 183 magnetic resonance (NMR) spectroscopy, which are shown in Figures S1 and S2 (Supporting 184 Information). These materials exhibit good solubility in most common organic solvents, 185 including chloroform, dichloromethane and chlorobenzene.



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187 Scheme 1. Synthesis routes of TPA-2,7-FLTPA-TPA and TPA-3,6-FLTPA-TPA. Reagent
188 and conditions: (a) triphenylamine, MeSO₃H, 140 °C, 48 h; (b) 2M K₂CO₃, toluene, Pd(PPh₃)₄,
120 °C, 48 h; (c) KOH, KMnO₄, 130 °C, 72 h; (d) triphenylamine, MeSO₃H, 140 °C, 48 h; (e)
190 2M K₂CO₃, toluene, Pd(PPh₃)₄, 120 °C, 48 h.

191

192 Ab initio Calculations.



Figure 1. Calculated energy levels and orbital isosurfaces of HOMO and LUMO of TPA-2,7 FLTPA-TPA (left) and TPA-3,6-FLTPA-TPA (right)

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197 With the aim of understanding the frontier orbital electron density distributions of TPA-2,7-198 FLTPA-TPA and TPA-3,6-FLTPA-TPA, density functional theory (DFT) calculations were 199 performed by using the B3LYP/LANL2DZ level with a polarizable continuum model (PCM) 200 of the chloroform solvent.⁵⁹⁻⁶¹ Optical absorption spectra were computed with TD-DFT.⁶² The 201 resulting lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital 202 (HOMO) are illustrated in **Figure 1**. The relevant data are summarized in Table S1 (Supporting 203 Information). Generally, the electron distribution of the LUMO and HOMO of both materials 204exhibits the same trend. In terms of the LUMO, the electron density is primarily localized on 205 fluorene core and its adjacent phenyl groups. Meanwhile, that of the HOMO is mainly 206 delocalized on fluorene core and TPA end-capping units. The HOMO values of TPA-2,7-207 FLTPA-TPA and TPA-3,6-FLTPA-TPA are calculated to be -4.85 and -4.92 eV, 208 respectively; the LUMO values are -1.56 and -1.29 eV, respectively. As the result, the band 209 gap of each material is estimated to be 3.29 eV for TPA-2,7-FLTPA-TPA and 3.63 eV for 210 **TPA-3,6-FLTPA-TPA.** For comparison, the HOMO and LUMO values of TaTm computed 211 at the same level of theory are -5.02 and -1.57 eV, respectively. The obtained theoretical



215 userul to compute the electronic properties of the molecules. For quantitative analysis, th

214 frontier energy levels are measured in relevant aggregate state a photoelectron spectroscopy

215 measurement technique, as described below

The high LUMO positions of both molecules are beneficial for their use as HTMs, as are the relatively deep HOMO energies comparable to the valence band maximum of the perovskite. The computed lowest-energy absorption peaks are at 431 nm for **TPA-2,7-FLTPA-TPA** and 384 nm for **TPA-3,6-FLTPA-TPA** and are due to HOMO-to-LUMO transitions (Table S1, Supporting Information). The redshift of the **TPA-2,7-FLTPA-TPA** vs **TPA-3,6-FLTPA-TPA** observed experimentally is thus confirmed (the redshift of the absolute positions of the computed peaks vs experiment is expected for transitions with some charge transfer character).

223

224 **Optical Properties**



Figure 2. (a) UV-Vis absorption spectra in CF solutions (SL, solid line) and films (TF, dash
line) and (b) Normalised absorption (solid line) and emission spectra (dash line) in CF solutions
of TPA-2,7-FLTPA-TPA and TPA-3,6-FLTPA-TPA.

229

The UV absorption spectroscopy of **TPA-2,7-FLTPA-TPA** and **TPA-3,6-FLTPA-TPA** in chloroform solutions (SL) and solid state thin films (TF) were carried out and the normalized spectra are illustrated in **Figure 2a**. The corresponding data are displayed in **Table 1**. Overall, both compounds exhibit the absorption band at low wavelength (under 400 nm). Also, the UVvis spectra in SL and TF have similar peaks, indicating there is no significant aggregation or crystallization happening in solid films⁶³ and there is also poor π - π intermolecular interaction

occurring in solid states.⁶⁴ In case of TPA-3,6-FLTPA-TPA one maximum absorption peak
was observed whereas for the TPA-2,7-FLTPA-TPA, there are two absorption peaks.

238 In case of **TPA-2,7-FLTPA-TPA**, the absorption spectra in SL shows one strong peak at 305 239 nm and this is attributed to the π - π * local electron transition of the TPA end-capping units, and the other lower peak at 382 nm contributed to the π - π * electron transition between fluorene 240 241 core and two adjacent phenyl conjugated moieties. Meanwhile, TPA-2,7-FLTPA-TPA thin 242 films exhibited a strong absorption observed at 298 nm and a weaker feature detected at 384 243 nm. For TPA-3,6-FLTPA-TPA, the absorption maxima are observed at 313 nm in SL and 315 244 nm in TF. The slightly red-shifted and broaden absorption in TF compared to in SL indicates 245 very weak intermolecular interactions in the solid-state in TPA-2,7-FLTPA-TPA while in 246 **TPA-3,6-FLTPA-TPA**, the broad spectral feature at low wavelength appearing in TF but not 247 in SL is indicative of intermolecular transitions.⁶⁵ The optical band gap of TPA-2,7-FLTPA-**TPA** and **TPA-3,6-FLTPA-TPA** in thin film is estimated to be 2.95 and 2.88 eV, respectively. 248 249 The wide band gap nature of these molecules is obvious due to the non-planar conjugated 250 backbone and weak electron donor nature of phenylene moiety. According to the HOMO-to-251 LUMO nature of the peaks (as confirmed by TD-DFT calculations), the high optical band gap 252 is an indicator of a high LUMO energy (in agreement with ab initio calculations) which is 253 beneficial for an HTM.

254 Furthermore, the photoluminescence (PL) in chloroform solutions was characterized and 255 illustrated in Figure 2b. The response data is listed in Table 1. The maxima peak of TPA-2,7-256 FLTPA-TPA is located at 463 nm, whereas for TPA-3,6-FLTPA-TPA, the maxima peak is 257 observed at 446 nm. The Stoke shift, which is estimated by the gap between the maximum 258 peaks of absorption and emission, of two compounds is found to be 157 nm for TPA-2,7-259 FLTPA-TPA and 133 nm for TPA-3,6-FLTPA-TPA. The large Stoke shift of both 260 compounds is clearly beneficial for high pore filling capability and this is attributed with high 261 hole-transport ability materials.63,66-68

262

263 Thermal Properties

The thermal behavior of **TPA-2,7-FLTPA-TPA** and **TPA-3,6-FLTPA-TPA** was characterized by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. As shown in Figure S3 (Supporting Information), the 5% weight loss is recorded at 434 °C for **TPA-2,7-FLTPA-TPA** and 456 °C for **TPA-3,6-FLTPA**- 268 **TPA** in TGA experiments. The observed decomposition temperature is one of the highest 269 values in reported HTMs and this clearly demonstrate the outstanding thermal stability of these 270 compounds. The outstanding thermal stability of both compounds is attributed to their rigid 271 aromatic backbone and higher Stoke shift. During second scan of DSC investigations (shown 272 in Figure S4, Supporting Information), TPA-2,7-FLTPA-TPA and TPA-3,6-FLTPA-TPA 273 shows amorphous phases with the higher glass transition temperatures (T_{α}) at 162 and 167 °C. 274 respectively. This indicates more stable amorphous state of two new materials, being quite 275 indispensable to the optoelectronic devices since their operating temperature is higher than 276 room temperature. The measured glass transition temperature is higher than the conventional 277 classical HTM Spiro-OMeTAD (124 °C). From the industrial perspective, higher T_g is 278 absolutely critical measure for the commercialization of perovskite solar cells using new HTM 279 material. Overall, the introduction of TPA terminal substituents at different positions (2,7 vs. 280 3,6) of the 9,9-bis(4-diphenylaminophenyl)fluorene groups has little impact on the thermal 281 stability of both compounds and this is obvious since most of the molecular building blocks 282 are same and only their substitution patterns are alerted.

283

284 Electrochemical Properties

285 To achieve higher-performance PSCs, the well alignment of energy levels between HTL and 286 perovskite layer is very crucial. In this work, the HOMO values of both materials are measured 287 by photoelectron spectroscopy in air (PESA) (Figure 3a, b) technique. Meanwhile, the LUMO 288 values of materials are estimated through the equation of $E_{\text{LUMO}}^{\text{PESA}} = E_{\text{HOMO}}^{\text{PESA}} + E_{q}^{opt}$. The 289 corresponding HOMO and LUMO data are presented in Table 1. The energy values calculated 290 using PESA technique are used further to evaluate new HTMs in actual device design because 291 PESA gives more appropriate and realistic values since the measurement are performed in thin 292 film form. The HOMO value calculated by PESA are found to be -5.57 eV and -5.45 eV for 293 TPA-3,6-FLTPA-TPA and TPA-2,7-FLTPA-TPA HTMs respectively and the obtained 294 values are quite close the VBM value of main light absorbing perovskite active layer (-5.46 295 eV). The deeper (than VBM) HOMO of TPA-3,6-FLTPA-TPA compared to TPA-2,7-296 FLTPA-TPA is expected to provide lower performance. ^{63, 69} Furthermore, the LUMO of both 297 materials is higher than the CBM of perovskite layer (-3.93 eV), which confirms the electron blocking ability of the two new HTMs. The TaTm's HOMO (-5.4 eV)²⁹ is similar to the HOMO 298 299 value of **TPA-2,7-FLTPA-TPA**, hence we expect to achieve at least as good efficiencies as 300 the TaTm devices.

301

302 **Table 1.** Thermal, optical and electrochemical properties of new organic materials.

HTMs	λ_{\max} [[nm]	m] λ_{PL}^{c} Stoke $E_g^{opt_d} E_{HOMO}^{e} E_{LUMO}$		$E_{\rm LUMO}^{\rm f}$	T _d	Tg		
1111015	Solution ^{a)}	Film ^{b)}	[nm]	[nm]	[eV]	[eV]	[eV]	[°C]	[°C]
TPA-2,7-FLTPA -TPA	305, 382	298, 384	463	157	2.95	-5.45	-2.50	434	162
TPA-3,6-FLTPA -TPA	313	315	446	133	2.88	-5.57	-2.69	456	167

^{a)}Absorption spectrum was measured in chloroform (CF) solution; ^{b)} Film was prepared by spin-coating CF solution containing the sample onto glass substrate at a spin speed of 1000 rpm at room temperature; ^{c)}Emission spectrum was analysed in CF solution; ^{d)}Optical bandgap was calculated from the formula of 1240/ λ_{onset} ; ^{e)}The oxidation potential was also measured by photoelectron spectroscopy in air (PESA); ^{b)} $E_{LUMO}^{PESA} = E_{HOMO}^{PESA} + E_g^{opt}$.

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309 Perovskite Solar Cells



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312 (b) **TPA-3,6-FLTPA-TPA**; (c) Diagram of the device structure and energy levels.

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314 The photovoltaic performances of PSCs based on these newly reported HTMs are evaluated 315 using ITO/MoO₃/HTM/CH₃NH₃PbI₃/C₆₀/BCP/Ag device configurations. In these layouts, 316 indium tin oxide (ITO) on glass is used as a transparent conducting cathode whereas silver (Ag) 317 act as a transparent conducting anode. The MoO₃ plays as an assisting hole transporting layer, 318 whereas commercially available TaTm and our novel organic materials are employed as HTMs. 319 Subsequently, a CH₃NH₃PbI₃ perovskite layer is deposited as the active layer followed by 320 fullerene C₆₀ as an electron transporting compact layer. The 2,9-dimethyl-4,7-diphenyl-1,10-321 phenanthroline (BCP) is used as an electron extracting and hole blocking layer as per our 322 previous study.²⁹ The chemical structures of all these charge transporting layers are presented 323 in Figure S5 (Supporting Information). The energy diagram of each layer in the device 324 architecture is shown in Figure 3c, whereas the device fabrication and measurement can be 325 found in Experimental section.

326 Current-voltage (J-V) performance of PSC with different HTMs (Figure 4a) was measured 327 under simulated sun parameters (AM 1.5G, 100 mW cm⁻²). Their respective parameters are 328 summarized in Table 2. Devices with TPA-2,7-FLTPA-TPA HTM yielded the highest 329 efficiency of up to 17.1%. While the PCE of TPA-3.6-FLTPA-TPA based devices is found 330 around 13.9% and the standard ones with TaTm HTM displayed a PCE of 15.9%. From the J-331 V curves and the forward reverse scan, it is clear that there is no hysteresis observed in any of 332 the fabricated devices (Figure S6, Supporting Information) and this is a good indication of lack 333 of charge trapping. The outstanding PCE of **TPA-2,7-FLTPA-TPA** can be attributed to the 334 higher Voc, Jsc and FF values compared to those of other HTMs-based devices. The obtained 335 V_{oc} of FLTPA derivates-based devices are measured close to 1.05 V and this is closure to the 336 devices based on the commercial TaTm (1.037 V). Generally, the higher V_{oc} is ascribed to 337 deeper HOMO energy levels of HTLs, leading to better PCE. In this work, the Voc of TPA-338 **2,7-FLTPA-TPA-**based devices is higher than that of TaTm ones. The variation of V_{oc} might 339 be attributed to the band bending at the interlayer interfaces. The slightly higher HOMO of 340 TPA-2,7-FLTPA-TPA might be helpful for better hole extraction vs TaTm (which is supported by a better FF). In addition to V_{oc}, the short circuit current (J_{sc}) for the TPA-2,7-341 342 FLTPA-TPA is close to 21 mAcm⁻² whereas those of TPA-3,6-FLTPA-TPA and TaTm are

343 19.85 and 20.42 mAcm⁻², respectively. The lower J_{sc} of TPA-3,6-FLTPA-TPA HTM in 344 comparison with other HTMs may be attributed to the mismatched energy level between the 345 HOMO of the HTM and the valence band of the perovskite, resulting in a negative impact on 346 the efficient hole-transport ability between the hole transporting layer and perovskite one. 347 Furthermore, the FF values of these HTMs are in order: TPA-2,7-FLTPA-TPA (78%) > TaTm 348 (75%) > **TPA-3,6-FLTPA-TPA** (67%). The worse FF of **TPA-3,6-FLTPA-TPA-based** 349 devices could be ascribed to their higher series resistance (R_s).^{16, 17} From all above observations, 350 it is clear that the **TPA-2,7-FLTPA-TPA** exhibits higher performance and this might be 351 attributed to a more linear conjugated structure arising from the attachment of TPA group at 352 the 2,7 position than the twisted molecular structure of **TPA-3,6-FLTPA-TPA**. The devices 353 were characterized by measuring the EQE as a function of the incident light wavelength 354 (Figure 4b). The perovskite solar cells with different HTMs show a similar photocurrent 355 response of about 75-85% over the whole visible spectrum. To ensure sufficient statistics, at 356 least two different devices each containing four cells were evaluated for both HTMs tested 357 (Figure S7, Supporting Information).



Figure 4. a) J-V characteristics under 100 mW cm⁻² illumination, b) EQE spectra, c) Maximum
 power point tracking over 40 min for an unencapsulated device, measured in inert atmosphere.

[%]

17.1

13.9

78

67

20.82

19.85

HTLs	Additives	$V_{\rm oc}$ [V]	$J_{\rm sc} [{\rm mA} {\rm cm}^2]$	FF	PCE ^{b)} [
TaTm	None	1.037	20.42	75	15.9

362 **Table 2.** J–V parameters of PSCs with different hole transporting layers.^{a)}

None

None

TPA-2,7-FLTPA -TPA

TPA-3,6-FLTPA -TPA

363	^{a)} Cell size (active area): 1 mm ² . Photovoltaic performance at 1000 wm ⁻² (AM1.5G) and
364	constant scan speed of 30 mV/s inverted CH ₃ NH ₃ PbI ₃ devices; ^{b)} An average device efficiency
365	of total 8 cells.

1.052

1.051

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A forward bias was applied to the perovskite solar cells in the dark (Figure S8, Supporting Information). In all the HTMs based devices, we could observe the typical diode behaviour. The leakage current is low, indicating the high quality of the diodes independent on the HTM employed. A low leakage current density is beneficial for maximum open circuit voltages as the recombination due to leakage is diminished.

Finally, the stability was measured on the **TPA-2,7-FLTPA-TPA** and TaTm HTMs based devices. The maximum power point tracking of a representative cell with **TPA-2,7-FLTPA-TPA** HTL at 25°C and without UV filter is reported in **Figure 4c**, showing no signs of degradation after 40 min under continuous illumination. We can claim the stability of this new HTM is comparable to that of devices using TaTm as an HTL.

A list of recently reported small molecular fluorene based hole transporting materials is summarized in Table S2 and their chemical structures are revealed in the Figure S9 (Supporting Information). While there are several fluorene derivatives developed for perovskite solar cells, almost these materials are fabricated in conventional/regular (n-i-p) layouts. Particularly, they required additives to enhance the device performance, which impede the long-term stability of the devices and increase the production cost of PSCs. Meanwhile, our new materials do not rely on additives and are employed in inverted devices.

A cost evaluation of our two newly developed materials and commercially used TaTm standard material are compared in Table 3. The synthesis cost of two new hole transporting compounds is estimated by following the same procedure reported in earlier published papers^{63, 70, 71} by taking Australian chemical suppliers cost into an account. Based on the low cost reported Journal of Materials Chemistry A Accepted Manuscript

388 HTMs, negligible cost-per-peak-Watt contribution of 0.004 \$ W-11 has been calculated for 389 EDOT-OMeTPA HTM.⁷¹ Additionally, the high synthetic accessibility of this compound 390 greatly imparts reduction of toxic chemical waste and this is a great green synthesis 391 methodology with lower cost HTM for generating environment friendly materials. The price 392 of the reference materials used in this study TaTm was provided by TCI America Research 393 Chemicals, a commercial chemical supplier company. The flowchart clearly demonstrates the 394 synthesis of 1 g of TPA-3,6-FLTPA -TPA and 1 g of TPA-2,7-FLTPA -TPA and both are 395 illustrated in Figure S10 and S11 respectively (Supporting Information). The cost of our newly 396 developed high-performance TPA-2,7-FLTPA-TPA HTM (taking both efficiency and 397 stability data into consideration) is a half cheaper than that of commercial TaTm. We believe 398 that the synthesis cost of our new materials will be reduced when the synthesis in large-scale 399 production is carried out.

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401 **Table 3.** Comparison of lab synthesis costs of FLTPA derivatives and TaTm

HTLs	Synthesis cost [\$/g]	Commercial price [\$/g]
 TaTm	-	264
ТРА-2 7-FI ТРА -ТРА	92.89	
ТРА-3 6-FI ТРА -ТРА	105 56	_
IIA-5,0-FLIFA-IFA	105.50	-

402

403 CONCLUSIONS

404 In summary, we have reported two triphenylamine substituted fluorene based newly developed 405 organic hole transporting materials, namely TPA-2,7-FLTPA-TPA and TPA-3,6-FLTPA-406 **TPA** using low cost starting precursors via an elegant synthesis method. The newly synthesised 407 materials exhibit outstanding thermal stability with high glass transition temperature compared 408 to the conventional Spiro-OMeTAD and this is one of the important requirements for 409 commercialization as per industry demand concerns. To the best of out knowledge, for the first 410 time, dopant free fluorene based HTMs were integrated into the inverted perovskite solar cell 411 devices. After being fabricated into the devices, the TPA-2,7-FLTPA-TPA HTL exhibits an 412 outstanding power conversion efficiency of 17.1% with an impressive fill factor reaching to 413 78%. The obtained fill factor is one of the highest values among reported TPA derivatives-414 based HTMs using CH₃NH₃PbI₃ as an active layer in inverted devices. Interestingly, the 415 synthesis cost of our new materials is quite inexpensive. Our elegant molecular design clearly

indicates a good potential of these newly developed cost efficient HTM for fabricating stable

417 high-performance perovskite devices using the most appropriate inverted device geometry 418 required for industry applications. The obtained device performance suggests that the linear 419 molecular structure is better than a twisted one. Our obtained results will open up further 420 research avenues using FLTPA based low-cost and stable HTMs for the development of PSCs. 421 422 **EXPERIMENTAL SECTION** 423 Materials and instruments Published on 15 April 2019. Downloaded on 4/16/2019 1:49:12 AM.

416

424 All chemicals and reagents were purchased from commercial vendors could we be more 425 specific which company and used directly without any further purification. Synthesized 426 compounds were characterized by ¹H-NMR and ¹³C-NMR spectrum, which were obtained with 427 a Varian-400 spectrometer or a Bruker 600 MHz spectrometer. High-resolution mass spectra 428 were acquired on an LTQ Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, Bremen, 429 Germany) equipped with an electrospray ionisation (ESI) source, operating in the positive ion 430 mode at a resolution of 120,000 (at m/z 400). Reserpine ([M+H]⁺, m/z 609.28066) was used as 431 a lock mass calibrant to increase the measurement accuracy. Thermal analysis was performed 432 using a Pegasus Q500TGA thermogravimetric analyzer under nitrogen atmosphere at a heating 433 rate of 10 °C/min. Differential scanning calorimetry (DSC) was conducted under nitrogen using 434 a Chimaera instrument Q100 DSC. The sample was heated at 10 °C/min from 30 °C to 300 °C. 435 Absorption spectra were recorded on a Shimadzu UV-1800 spectrometer. Photoelectron 436 spectroscopy in air (PESA) measurements were conducted using on an AC-2 photoelectron 437 spectrometer (Riken-Keiki Co.).

438

439 **Synthesis**

- 440 The synthesis of TPA precursors was followed earlier published synthetic procedure.^{7, 16}
- 441 Synthesis of 4,4'-(2,7-dibromo-9*H*-fluorene-9,9-diyl)bis(*N*,*N*-diphenylaniline) (2):

The synthesis was followed an previous attempt³³: Initially, compound 1 (3 g, 8.93 mmol) was 442 443 mixed with triphenylamine (35 g, 0.143 mol) and methane sulfonic acid (1 g, 10.4 mmol). Then 444 the mixture was stirred and heated at 140 °C under argon gas for 8 h. After that, the mixture 445 was cooled to room temperature and extracted by using dichloromethane. Prior to be dried and 446 concentrated, the mixture was washed with saturated sodium carbonate solution. For

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purification, firstly the residue was loaded on silica using hexane-dichloromethane as the eluent.
Subsequently, tt was recrystallized by acetone to yield the desired compound as a white solid
(2) (4.69 g, 65%).

450

451 <u>Synthesis of 4,4'-(2,7-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-9H-fluorene-9,9-</u> 452 <u>diyl)bis(N,N-diphenylaniline) (TPA-2,7-FLTPA-TPA)</u>:

453 In a round bottom flask, 4,4'-(2,7-dibrom -9H-fluorene -9,9-diyl)bis(N,N-diphenylaniline)454 (200 mg, 0.247 mmol), 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-455 dioxaborolan-2-yl)phenyl)aniline (TPA-BE, 300 mg, 0.693 mmol), and 2 M aqueous K₂CO₃ 456 solution (12 mL) were dissolved in anhydrous toluene (20 mL). The solution was degassed by 457 argon for 20 minutes, then tetrakis(triphenylphosphine)palladium (21 mg, 0.018 mmol) was 458 added. Subsequently, the mixture was degassed for 30 min before the reaction was stirred at 459 120 °C for 2 days. After the reaction mixture was cooled to room temperature and extracted 460 with chloroform and water. The organic layer was dried over anhydrous Na₂SO₄. After 461 removing the solvent under reduced pressure, the residue was purified using silica gel column 462 chromatography with a mixture of hexane and dichloromethane as eluent. Then the crude 463 product recrystallized from hot methanol to yield the desired compound as light yellow solid 464 (95 mg, 31%). ¹H NMR (600 MHz, CDCl₃): δ 7.69-7.68 (d, J = 7.8 Hz, 2H), 7.52 (s, 2H), 7.48-7.46 (dd, J = 1.2, 9 Hz, 2H), 7.33-7.31 (d, J = 9 Hz, 4H), 7.14-7.11 (m, 8H), 7.06-7.04 (d, 465 466 J = 9 Hz, 4H), 7.01-6.97 (m, 16H), 6.90-6.88 (m, 8H), 6.83-6.81 (d, J = 8.4 Hz, 4H), 6.77-6.75 467 (d, J = 9 Hz, 8H), 3.72 (s, 12H).¹³C NMR (120 MHz, CDCl₃): δ 155.90, 152.36, 148.11, 147.70, 468 146.16, 140.84, 140.09, 139.77, 138.77, 133.23, 129.16, 129.00, 127.54, 126.59, 125.92, 124.40, 124.24, 123.12, 122.70, 120.67, 120.23, 64.61, 55.52. ESI-MS: C₈₉H₇₀N₄O₄+• *m/z* 469 470 1258.73 (calculated *m/z* 1258.54).

471 <u>Synthesis of 3,6-dibromo-9*H*-fluoren-9-one (4)</u>:

The synthesis route of compound (4) was followed by earlier studies^{72, 73}: First of all, KOH (2 g) was stirred with 20 ml distilled water at 130 °C for 20 min in a two-neck round bottom flask. Later, 3,6-dibromophenanthrene-9,10-dione (compound 3) (1 g) was added into the KOH solution and the suspension was heated to reflux at 130 °C for 30 min. Then, KMnO4 (0.85 g) was added carefully within a period of 6 hours. Next, the mixture was stirred at 130 °C for 3 days. After being cooled to room temperature, the mixture was extracted with chloroform and water many times to neutralize the excessive KOH. Next, the crude product recrystallized from

- 480 used in the next step without any further purification.
- 481

482 <u>Synthesis of 4,4'-(3,6-dibromo-9*H*-fluorene-9,9-diyl)bis(*N*,*N*-diphenylaniline) (5):</u>

483 The synthesis was similar to that of 4,4'-(2,7-dibromo-9H-fluorene-9,9-diyl)bis(N,N-484 diphenylaniline) (2).

485 Synthesis of 4,4'-(3,6-bis(4-(bis(4-methoxyphenyl)amino)phenyl)-9H-fluorene-9,9-

486 <u>diyl)bis(*N*,*N*-diphenylaniline) (**TPA-3,6-FLTPA-TPA**):</u>

487 In a round bottom flask 4,4'-(3,6-dibromo-9*H*-fluorene-9,9-diyl)bis(*N*,*N*-diphenylaniline) (200 488 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-0.247 mmol). mg, 489 dioxaborolan-2-yl)phenyl)aniline (TPA-BE, 300 mg, 0.693 mmol), and 2 M aqueous K₂CO₃ 490 solution (12 mL) were dissolved in anhydrous toluene (20 mL). The solution was degassed by 491 argon for 20 minutes, then tetrakis(triphenylphosphine)palladium (21 mg, 0.018 mmol) was 492 added. Subsequently, the mixture was degassed for 30 min before the reaction was stirred at 493 120 °C for 2 days. After the reaction mixture was cooled to room temperature and extracted 494 with chloroform and water. The organic layer was dried over anhydrous Na₂SO₄. After 495 removing the solvent under reduced pressure, the residue was purified using silica gel column 496 chromatography with a mixture of hexane and dichloromethane as eluent. Then the crude 497 product recrystallized from hot methanol to yield the desired compound as light pink solid (110 498 mg, 26%). ¹H NMR (600 MHz, CDCl₃): δ 7.86 (s, 2H), 7.41-7.37 (m, 8H), 7.14-7.113 (m, 499 8H), 7.05-7.013 (m, 12H), 6.98-6.97 (dd, J = 1.2, 9 Hz, 8H), 6.94-6.88 (m, 8H), 6.85-6.82 (d, 500 J = 9 Hz, 4H), 6.78-6.76 (d, J = 9 Hz, 8H), 3.73 (s, 12H). ¹³C NMR (120 MHz, CDCl₃): δ 501 155.86, 150.17, 148.12, 146.15, 140.94, 140.54, 140.33, 139.87, 133.16, 129.16, 128.89, 502 127.64, 126.58, 126.38, 126.27, 124.34, 123.18, 122.70, 120.78, 118.11, 114.71, 64.02, 55.52. 503 ESI-MS: C₈₉H₇₀N₄O₄^{+•} *m/z* 1258.73 (calculated *m/z* 1258.54).

504 **Perovskite Device Fabrication**

505 Materials: photo-lithographically patterned ITO covered glass substrates were purchased from

506 Naranjo Substrates (www.naranjosubstrates.com). MoO_3 , PbI_2 and C_{60} were purchased from

507 Aldrich and CH₃NH₃I and BCP from Lumtec. TaTm was provided by Novaled.

508 Devices were prepared on pre-cleaned ITO substrates subsequently cleaned with soap, water 509 and isopropanol in an ultrasonic bath, followed by UV-ozone treatment. The substrates were

510 then transferred to a vacuum chamber integrated into a nitrogen-filled glovebox (MBraun, H₂O 511 and $O_2 < 0.1$ ppm) and evacuated to a pressure of 3×10^{-6} mbar. For thickness calibration, we 512 individually sublimed the MoO_3 and TaTm materials and a calibration factor was obtained by 513 comparing the thickness inferred from the quartz crystal microbalance (QCM) sensors with 514 that measured with a mechanical profilometer (Ambios XP1). Once the materials were calibrated, a 5-nm thick MoO₃ film was deposited at 0.1 Å s^{-1} deposition rate. Following the 515 516 film deposition, the chamber was vented and the substrates were transferred to another vacuum 517 chamber integrated in the same glovebox and evacuated to 1×10^{-6} mbar. The vacuum chamber 518 is equipped with six temperature-controlled evaporation sources (Creaphys) fitted with ceramic 519 crucibles. The thermal sources were directed upwards with an angle of approximately 90° with respect to the bottom of the evaporator. The substrate holder to evaporation sources distance is 520 521 approximately 20 cm. Three QCM sensors were used, two monitoring the deposition rate of 522 each evaporation source while the third one close to the substrate holder monitoring the total 523 deposition rate. Then, 10 nm thick films of TaTm were deposited by heating the crucible at 524 250 °C with a deposition rate of 0.5 Å s⁻¹. The HTMs tested were deposited by solution process 525 using a 5 mg/ml toluene solution (3000rpm, 30s). After deposition, the films were annealed at 526 100°C 10 min. Once the hole transport layers were deposited, the perovskite was deposited by 527 co-evaporation of CH₃NH₃I and PbI₂. The use of clean QCM sensors for the perovskite 528 evaporations is important to avoid false readings due to perovskite formation on the sensor. 529 For a more accurate deposition the density of PbI_2 (6.16g/cm3) is set in the equipment. For 530 CH₃NH₃I the density is assumed to be 1 g/cm3. And the z factor for both materials is set to 1. 531 The calibration of the deposition rate for the CH₃NH₃I was found to be difficult due to non-532 uniform layers and the soft nature of the material impeded accurate thickness measurements. 533 Hence, the CH₃NH₃I was evaporated by keeping the temperature constant at 70 $^{\circ}$ C, while the 534 CH₃NH₃I:PbI₂ ratio was controlled off line using grazing incident X-ray diffraction by 535 adjusting the PbI_2 deposition temperature. The optimum deposition temperatures were found 536 to be 250 °C for the PbI₂ and 70 °C for the CH₃NH₃I. This was followed by deposition of the 537 electron selective contacts by thermal evaporation, C_{60} (25 nm) and BCP (8 nm). The devices were finished by the thermal evaporation of the metal electrode under a base pressure of 538 539 2×10^{-6} mbar to a thickness of 100 nm of Ag. 540

541 Device Characterization

542 The external quantum efficiency (EQE) was estimated using the cell response at different 543 wavelength (measured with a white light halogen lamp in combination with band-pass filters), 544 where the spectrum mismatch was corrected using a calibrated Si reference cell (MiniSun 545 simulator by ECN, the Netherlands). The un-encapsulated devices were measured in a N2-filled 546 glovebox. The J-V characteristics were collected in the dark and under illumination using a Keithey 2400 source measure unit. The device active area was 0.04 cm⁻² (defined as the 547 548 overlap between the ITO and the top metal contact) and measured through a shadow mask with 549 0.01 cm² aperture to prohibit lateral current collection from outside the active area.

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555	Author Contributions
556	The manuscript was written through contributions of all authors. All authors have given
557	approval to the final version of the manuscript.
558	
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