Thienylvinylenethienyl and Naphthalene Core Substituted with Triphenylamines -
Highly Efficient Hole Transporting Materials and their Comparative Study for
Inverted Perovskite Solar Cells

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Organic-inorganic halide perovskite materials have recently been employed in several types of optoelectronic devices, including thin-film transistors\(^1\) lasing\(^2\) solar cells\(^3\) light-emitting diodes\(^4\) and flexible memory\(^5\) devices, due to their outstanding properties. These properties include long charge carrier diffusion length, highly efficient ambipolar charge transport ability, wide optical absorption, and large absorption coefficients\(^6, 7\) The research on perovskite solar cells (PSCs) has gained a huge attention in scientific community mainly due to their ability to reach the performance close to that of the existing high performance silicon and other inorganic material based solar cell technologies. The world record power conversion efficiency (PCE) of PSCs has now exceeded 22% - a significant progress since the first PSC were reported with PCE values as low as 3.8% in 2009\(^8\) This rapid development clearly shows the potential of the PSC technology to become commercially viable as a solar energy harvesting tool and to contribute in a significant way to meeting future energy demand in a sustainable fashion. The obtained PSC performance is comparable to the traditional second generation thin film devices, such as the copper indium gallium selenide (CIGS) and cadmium telluride (CdTe) devices, and first generation silicon-based high performance solar energy technologies.

The device geometry and structure of PSCs can be classified into two main architectures. The first architecture is the conventional type where the main layers consist of a compact or mesoporous metal oxides electron transporting layer (ETL, n-type) followed by the perovskite active layer (i) and then a hole transporting layer (HTL, p-type). Devices with this architecture are also known as the n-i-p type devices. Although the PCE of this particular type of device architecture has been able to reach 20%\(^9\) this device geometry has some significant shortcomings. Firstly, the deposition of n-type metal oxides such as titanium dioxide (TiO\(_2\)) compact layer requires high temperature processing (over 450 °C), which increases the cost of production of these devices. Secondly, these devices suffer from high
instability and large hysteresis issues, which hamper their practical deployment.\textsuperscript{[10]} This second type of architecture, known as the inverted structure, alleviates these limitations. In an inverted structure, a p-type HTL is deposited first followed by the active perovskite layer (i) and then the n-type ETL layer (n). This is also known as the p-i-n structure. To date, the highest PCE of such inverted PSCs has been reported to be 19.4\% without any hysteresis issue,\textsuperscript{[11]} and hence this may be a more feasible approach for practical cells. Moreover, inverted devices can be easily made using low-temperature solution-processing techniques and thus can be easily employed on flexible substrates, which is very promising for large-area production of these devices.\textsuperscript{[7, 12]} These key aspects and advantages make the p-i-n device architecture one of the most promising strategies for the future of perovskite solar cells.

Development of optimal materials for the HTL is one of the key directions to further improve the PCE of these cells. The HTL not only transports the holes after exciton dissociation but also protects the active perovskite layer from moisture/oxygen ingress and electrode penetration.\textsuperscript{[13, 14]} In addition to the above benefits, the HTL suppresses charge recombination, which is critical for achieving higher PCE.\textsuperscript{[13]} The HTL is essential to achieve higher open circuit voltage ($V_{oc}$) and PCE in the inverted PSCs.\textsuperscript{[15]}

Organic hole transporting materials (HTMs) can be classified into two main categories: monodispersed small molecules and polydispersed polymers. Polymeric HTMs have been successfully employed and achieved some promising results in p-i-n devices. Currently, the highest PCE obtained with inverted PSCs was around 19.4\% using poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) as the HTM.\textsuperscript{[11]} In addition to PTAA polymer, poly(3,4-ethylenedioxythiophene : polystyrene sulfonate) (PEDOT : PSS) has been also successfully used as the HTM in p-i-n devices and was able to achieve a high PCE of 18.1\%.\textsuperscript{[16]} Using these polymeric HTMs, it has been shown that it is possible for p-i-n devices to obtain PCE values that are comparable to those of conventional n-i-p structures. However,
these most successful polymeric HTMs have some limitations when it comes to practical applications in the PSC technology. PTAA polymers is extremely expensive and costs about 50 times the price of gold and PEDOT:PSS is hydrophilic and of a strong acidic nature which compromises the device long-term stability.\textsuperscript{[7, 17]} The tediousness of synthesis and the requirement of high purity of monomers may add to the cost of the polymers. Moreover, molecular weight of polymers can vary batch-to-batch and this may further affect the performance of PSC. Compared to polymeric semiconductors as HTMs, small molecules can provide enormous benefits including good yield,\textsuperscript{[18]} defined molecular structure,\textsuperscript{[19]} tunable energetics,\textsuperscript{[20]} and good batch-to-batch reproducibility.\textsuperscript{[18, 19]} Thus, small molecular HTMs could be a better choice of materials compared to polymeric ones. To date, there are very few reports in the literature on small molecular HTMs specifically for the p-i-n device architecture. Amongst the few reported small molecular HTMs, 3,8,13-tri(di-4-methoxylphenylamino)-5,5,10,15,15-Hex(1-hexyl)10,15-dihydro-5H-diindeno[1,2-\alpha;1',2'-c]fluorene (Trux-OMeTAD) has been shown to be one of the most promising candidates and using this HTM, a PCE of 18.6% has been achieved.\textsuperscript{[21]} Using conventional 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spiro-bifluorene (Spiro-OMeTAD) HTM, a PCE of 16.3% was achieved under similar conditions. Trux-OMeTAD and Spiro-OMeTAD have clearly shown that small molecular HTMs have the potential to achieve comparable performance to that of polymeric ones. When considering the design of small molecular HTMs, it is seen that triphenylamine (TPA) is one of the most common efficient and successful end capping groups due to its strong electron-donating and excellent hole transporting nature.\textsuperscript{[19]} In addition, due to the three distorted phenyl groups substituted on the central nitrogen of TPA, there can be an additional benefit of protecting perovskite layer which is sandwiched between HTL and ETL. Electron coupling and reduction of charge recombination \textbf{in electronic devices such as solar cells} are also two very important
characteristics of TPA that make it a good choice \[ ^{[22]} \] Other major advantages of molecular design based on TPA include simple synthesis, low cost, easy scalability, and easy processability. Thus all these characteristics make this end group attractive in the design of high performance HTMs. To date, even though a number of novel HTMs have been reported recently using a \( \pi \)-conjugated core and TPA and subsequently applied in n-i-p perovskite device structures, there are very few reports on using such HTMs for the inverted or p-i-n layouts.

Herein, we have synthesized two explicitly simple HTMs namely (E)-4,4’-(ethene-1,2-diylbis(thiophene-5,2-diyl))bis(N,N-bis(4-methoxyphenyl)aniline) (TPA-TV-TPA) and 4,4’-(naphthalene-2,6-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (TPA-NAP-TPA) based on naphthalene (NAP) and thiophene-vinylene-thiophene (TVT) linear planar \( \pi \)-conjugated cores with common TPA end capping groups, respectively (Scheme 1). TPA-TV-TPA and TPA-NAP-TPA were successfully employed as HTMs in inverted p-i-n PSCs and their structure-property relationship will be discussed in detail. While working on this manuscript, TPA-NAP-TPA was reported by other group and used as HTL in inverted perovskite devices,\[ ^{[23]} \] but its performance is lower (13\%) than that of this study (14.63\%). The second molecule TPA-TV-TPA is a completely new material and has been not reported before in the literature. The rationale for the choice of TVT is discussed below. Inverted perovskite photovoltaic devices using TPA-TV-TPA and TPA-NAP-TPA as HTMs were fabricated using the following device architecture: glass/ITO/HTL/perovskite/PCPM/BCP/Ag. In these devices, indium tin oxide (ITO) on glass and silver (Ag) act as a transparent conducting cathode and anode, respectively. Our newly developed materials are used as HTMs, CH\(_3\)NH\(_3\)PbI\(_3\) perovskite as the active layer, fullerene derivative [6,6]-phenyl C61 butyric acid methyl ester (PCBM) as an electron transporting compact layer and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as an electron extracting and hole blocking layer.\[ ^{[24]} \] The
fabrication procedure is described in detail in the Supporting Information. Under standard illumination (AM 1.5G and 100 mW cm\(^{-2}\)), the PCE of these HTMs based devices was found to be of 16.32\% for TPA-TVT-TPA and 14.63\% for TPA-NAP-TPA.

The selection of electron donating thienylenevinylethenyl (TVT) and naphthalene (NAP) as the central conjugated core is based on the previous reports using these comonomers in the copolymer synthesis and their use as high hole mobility materials in the p-channel organic thin film transistor (OTFT). The TVT and NAP based copolymers with diketopyrrolopyrrole (DPP) have been shown to be some of the most promising hole transporting materials, with hole mobilities of more than 0.2 cm\(^2\)/Vs reported in OTFT devices\.[25, 26] Additionally, TVT and NAP based copolymers have also been shown as a promising choice of electron donating component with PCBM as the active layer in organic photovoltaics\.[25, 27] Since both cores, TVT and NAP, have been shown to be one of the best candidates for obtaining high hole mobility, it would be an obvious choice to use them as cores in the design of new hole transporting materials\.[28] For the naphthalene core unit, there are three possibilities to functionalize the conjugated backbone - via 1, 4-, 1, 5- or 2, 6-positions\.[29, 30] Among these options, the 2,6-postion of naphthalene will result in the most planar conformation to achieve highly extended π-conjugation\.[29] Compounds comprising of a planar naphthalene donor unit with other acceptor blocks also exhibited high hole mobility in organic electronic devices\.[31] All of these above explained features make the synthesized molecules promising candidates for future large area cost effective perovskite solar cell technology.
Synthesis routes of \textit{TPA-TV{T}TPA} and \textit{TPA-NAP-TPA}. Reagent and conditions: (a) 1-iodo-4-methoxybenzene, KOH, CuCl, 1,10-phenanthroline monohydrate, toluene, 120 °C, overnight; (b) trans-1,2-di(2-thienyl)ethylene, n-butyllithium, tetramethylethylenediamine, trimethyltin chloride, tetrahydrofuran, RT, overnight; (c) DMF, Pd(PPh$_3$)$_4$, 110 °C, 48 h; (d) 2M K$_2$CO$_3$, toluene, Pd(PPh$_3$)$_4$, 120 °C, 48 h.

Scheme 1. Synthesis of \textit{TPA-TV{T}TPA} and \textit{TPA-NAP-TPA}.

The synthetic routes of \textit{TPA-TV{T}TPA} and \textit{TPA-NAP-TPA} are displayed in Scheme 1. Firstly, the precursor 4-bromo-$N,N$-bis(4-methoxyphenyl)aniline (2) was produced in a good yield from 4-bromoaniline (1) and 1-iodo-4-methoxybenzene in presence of strong base potassium hydroxide (KOH), copper chloride (CuCl), and 1,10-phenanthroline monohydrate reagent refluxing in anhydrous toluene overnight. Meanwhile, (E)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (4) and 2,6-bis(4,4,5,5-tetramethyl-1,3,2-
dioxaborolan-2-yl)naphthalene (5) were prepared from commercially available trans-1,2-di(2-thienyl)ethylene and 2, 6-dirbromo naphthalene starting materials accordingly to a previously reported procedure. The target HTM TPA-TV-TPA was synthesized by Stille coupling reaction between compound 2 and 4 using tetrakis triphenylphosphine palladium [Pd(PPh$_3$)$_4$] catalyst at 110 °C for 48 h in dimethyl formamide (DMF) solvent. TPA-NAP-TPA was prepared via classical Suzuki coupling reaction between compound 2 and 5 using tetrakis triphenylphosphine palladium [Pd(PPh$_3$)$_4$] catalyst, 2M K$_2$CO$_3$ base, at 120 °C for 48 h in toluene solvent. The yields of reactions were found to be of 55% for TPA-TV-TPA and 50% for TPA-NAP-TPA after purification by column chromatography. The purity was confirmed by proton and C13 NMR spectroscopy, which are shown in Figure S1 – S4 (Supporting Information). Both materials exhibited good solubility in most of the common organic solvents such as chloroform, dichloromethane and chlorobenzene.
Figure 1. The geometrical configuration ("side" view and "front" view) and isosurfaces of electron density of HOMO and LUMO of TPA-TVT-TPA and TPA-NAP-TPA.

In order to understand electronic properties of these molecules, density functional theory (DFT) calculations were performed at the B3LYP level of theory using the basis set 6-31g*(d,p). The resulting highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the molecular structures are shown in Figure 1. Both molecules exhibit similarities in the electron distributions of the HOMO and the LUMO in that the electron density of the LUMO is primarily localized on thienylenevinylene and...
naphthalene cores, whereas the HOMO is fully delocalized over the entire molecules including the electron rich TPA moieties, as expected. According to the DFT calculations, the HOMO energies of TPA-TV-TPA and TPA-NAP-TPA are -4.49 eV and -4.64 eV, respectively. The LUMO energies are -1.86 eV, and -1.31 eV, respectively. Even though the HOMO-LUMO values from the theoretical calculations may not match exactly the values estimated from the experiments due to approximations used and the single-molecule nature of the simulation, they provide the energy level trends based on molecular design. The computed visible peak maxima for TPA-TV-TPA and TPA-NAP-TPA are 544 and 425 nm, respectively, confirming that a significant redshift has been observed in case of TPA-TV-TPA (as shown in Figure 2). This theoretical optical red shift of 119 nm is due to the more extended conjugation of TPA-TV-TPA backbone than in TPA-NAP-TPA one. The transition intensity with TPA-TV-TPA is also noticeably higher with the oscillator strength of 2.18 compared to 1.22 for TPA-NAP-TPA. The absolute absorption peak maxima are red shifted vs. experiment, as is expected with B3LYP for transitions with charge transfer character.[33]

The thermal properties of both newly synthesized small molecule TPA-TV-TPA and TPA-NAP-TPA HTMs were measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques and the data is shown in Figure S6 and S7 (Supporting Information) respectively. In TGA, the 5% weight loss at high temperature above 390 °C was considered as the onset point of decomposition (T_d). TPA-TV-TPA and TPA-NAP-TPA were found to have extremely good thermal stability, with 5% weight loss at 390 and 405 °C, respectively, which were higher than that of common HTMs such as Spiro-OMeTAD (approximately 125 °C)[34] and PEDOT:PSS (below 200 °C).[35] This is a good indication that these small molecules could be thermally stable hole transporting materials for perovskite solar cells. From the DSC thermogram, it has been clearly seen that TPA-TV-T-TPA
TPA and TPA-NAP-TPA molecules exhibit glass transition temperature \( (T_g) \) at 87 °C and 85 °C, respectively, after two heating-cooling cycles. Moreover, the crystallization temperature does not appear during the two-cycle analysis because the non-planar conformation of TPA units leads to a lower degree of crystallinity.\[^{36}\] From the first heating – cooling cycle, TPA-TVT-TPA and TPA-NAP-TPA exhibit strong endothermic peaks at 170°C and 160 °C, respectively, which are ascribed to the melting transition. From the thermal analysis data, it follows that TPA-NAP-TPA and TPA-TVT-TPA have a comparable thermal stability due to only slight disparity in chemical structure.

The normalized UV-Vis absorption and emission spectra of TPA-TVT-TPA and TPA-NAP-TPA in solution (chloroform) and in solid state (thin film on glass) were measured and shown in Figure 2a and Figure S5 (Supporting Information). The relevant data is listed in Table 1. TPA-TVT-TPA shows a broad absorption bands ranging from 300 to 520 nm, which the peak extends to 550 nm as shown in Figure 2a. Meanwhile, TPA-NAP-TPA has an absorption range from 300 to 430 nm. The absorption maxima of TPA-TVT-TPA and TPA-NAP-TPA exhibits two absorption peaks in the lower and higher wavelength region which is arising from n-\( \pi^* \) and \( \pi-\pi^* \) transitions. The solution peak for TPA-NAP-TPA is found to be at 375 nm whereas solid-state peak was at 380 nm. In the case of TPA-TVT-TPA, the solution peak is found to be at 450 nm whereas thin film peak is measured at 460 nm. The optical absorption spectrum of TPA-TVT-TPA in solution and solid state are red-shifted noticeably compared to TPA-NAP-TPA, which is related to the more extended conjugation of the backbone of TPA-TVT-TPA than in TPA-NAP-TPA. Indeed, the optical band gap from the intersection of absorption spectra of the TPA-TVT-TPA and TPA-NAP-TPA in thin film is assessed to be 2.30 and 2.86 eV, respectively.
Figure 2. a) UV-Vis absorption spectra in chloroform solutions (dash line) and films (solid line), b) Photoelectron spectroscopy in air (PESA) spectra of TPA-TVT-TPA and TPA-NAP-TPA and c) Energy level diagram of each layer in the device.

As shown in Figure S5, the emission maxima of TPA-TVT-TPA and TPA-NAP-TPA are peaked at 524 nm and 466 nm, respectively. Stokes shifts are estimated from the gap between the maximum of absorption and emission spectra. These materials possess a large Stokes shift of about 72 nm for TPA-TVT-TPA and 89 nm for TPA-NAP-TPA, which indicates a non-rigid nature of the molecular structure.
Table 1. Thermal, optical and electrochemical properties of TPA-TV-TPA and TPA-NAP-TPA.

<table>
<thead>
<tr>
<th>HTMs</th>
<th>$\lambda_{abs}^{\text{max}}$ (nm)</th>
<th>$\lambda_{PL}^{(c)}$ (nm)</th>
<th>$E_g^{\text{opt}}^{(d)}$ (eV)</th>
<th>$E_{\text{HOMO}}^{(e)}$ (eV)</th>
<th>$E_{\text{LUMO}}^{(f)}$ (eV)</th>
<th>$T_d$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_g$ (°C)</th>
</tr>
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<tbody>
<tr>
<td>TPA-TV-TPA</td>
<td>450</td>
<td>524</td>
<td>2.30</td>
<td>-5.37</td>
<td>-3.07</td>
<td>390</td>
<td>170</td>
<td>87</td>
</tr>
<tr>
<td>TPA-NAP-TPA</td>
<td>375</td>
<td>466</td>
<td>2.86</td>
<td>-5.38</td>
<td>-2.52</td>
<td>405</td>
<td>160</td>
<td>85</td>
</tr>
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</table>

a) Absorption spectrum was measured in CF solution and b) in film; c) Emission spectrum was analysed in CF solution; d) Optical band gap was calculated from the formula of $1240/\lambda_{\text{onset}}$; e) The HOMO value determined by PESA; f) $E_{\text{LUMO}} = E_{\text{HOMO}}^{\text{PESA}} + E_g^{\text{opt}}$.

To evaluate the band-alignment of these two novel molecules with the perovskite, their HOMO levels were determined from photoelectron spectroscopy in air (PESA) and shown in Figure 2b. The respective LUMO levels of these two materials were obtained by subtracting the optical bandgap from HOMO levels. These energy levels were plotted together with the energy levels of perovskite and all the other layers employed in the device. The HOMO values of TPA-TV-TPA and TPA-NAP-TPA are estimated to be -5.37 eV and -5.38 eV, respectively. The energy gaps ($\Delta E$) between these two HOMOs with the valence band (VB) of perovskite are within 0.1 eV, which are good values for efficient extraction of holes without a significant voltage drop. As a comparison, the PEDOT:PSS possesses a $\Delta E$ as large as 0.34 eV with respect to the VB of perovskite [the value is 0.34 eV based on the data in Figure 2(c)]. The large mismatch between these two materials can cause severe photovoltage drop and thereby reduce the device performance. At the same time, the LUMO values of the new molecules remain significantly above the conduction band minimum (CBM) of the perovskite and can effectively block undesired electron back diffusion. The hole mobility of these two molecules, estimated from space charge-limited current (SCLC) measurement (Figure S8), was $5.1 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $2.1 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ for TPA-NAP-TPA.
TPA and TPA-TV-TPA respectively, which is slightly lower than spiro-OMeTAD (8.09×10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) and PEDOT:PSS (9.8×10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})^{[37]}

![Cross-sectional scanning electron microscopy image of the device](image)

Figure 3. a) Cross-sectional scanning electron microscopy image of the device, b) Current density–voltage curves (J-V) of PSCs with different HTMs, and c) their external quantum efficiency (EQE) spectra (lines with open symbols indicate the integrated $J_{sc}$ from EQE and solar spectrum).

The device performance based on these HTMs was investigated in inverted device architecture. Figure 3a shows a cross-sectional scanning electron microscopy (SEM) image of a complete device. A thin layer of HTM was first spin-coated on top of indium tin-oxide (ITO) coated glass, followed by the deposition of perovskite layer, electron transport layer and back electrode (Ag). Both TPA-TV-TPA and TPA-NAP-TPA illustrate smooth and compact surfaces with small roughness (RMS) of 3.9 nm and 7.8 nm, respectively, as determined by atomic force microscopy (Figure S9). The morphologies of perovskite layers
on top of each HTL are shown in Figure S10. The average grain sizes of perovskite layers formed on top of TPA-TV-T-TPA and TPA-NAP-TPA are larger than the one on PEDOT: PSS, implying the formation of high quality films of perovskite with fewer grain boundaries in the case of TPA-TV-T-TPA and TPA-NAP-TPA based devices.\(^{[38]}\) The perovskite films exemplify distinctive pure phase without PbI\(_2\) residue as manifested on the x-ray diffraction patterns in Figure S11. The larger grain size of perovskite layer on these two HTMs is likely due to the lower wetting of perovskite solution on top as shown in the contact angle measurement (Figure S12), which facilitates the extensive growth of perovskite grains as demonstrated in the earlier report.\(^{[39]}\)

Table 2. J-V parameters of PSCs with PEDOT:PSS, TPA-NAP-TPA and TPA-TV-T-TPA as HTLs.

<table>
<thead>
<tr>
<th>HTL</th>
<th>PCE (%)</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mAcm(^{-2}))</th>
<th>FF</th>
<th>(R_s) ((\Omega \text{ cm}^2))</th>
<th>(R_{sh}) (k(\Omega \text{ cm}^2))</th>
<th>Cal. (J_{sc}) (mA cm(^{-2}))</th>
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<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>11.59</td>
<td>0.85</td>
<td>18.66</td>
<td>0.73</td>
<td>3.02</td>
<td>1.2</td>
<td>18.36</td>
</tr>
<tr>
<td>TPA-NAP-TPA</td>
<td>14.63</td>
<td>0.96</td>
<td>21.55</td>
<td>0.71</td>
<td>4.51</td>
<td>2.68</td>
<td>21.01</td>
</tr>
<tr>
<td>TPA-TV-T-TPA</td>
<td>16.32</td>
<td>1.07</td>
<td>21.49</td>
<td>0.71</td>
<td>6.45</td>
<td>15.6</td>
<td>21.15</td>
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</table>

Current–voltage (J–V) performance of PSC with different HTMs (Figure 3b) were measured under simulated sun illumination (AM 1.5 G, 100 mWcm\(^{-2}\)) and their respective parameters are summarized in Table 2. The TPA-NAP-TPA and TPA-TV-T-TPA based devices yield much improved PCE of 14.63% and 16.32%, respectively, compared with the PCE of PEDOT:PSS based device (11.59%). All the devices show little hysteresis when measured at different scan directions and good reproducibility as shown in Figure S13 and Figure S14, respectively. It is worth to note that our preliminary stability study shows much improved stability for the TPA-NAP-TPA and TPA-TV-T-TPA based devices than PEDOT:PSS due
to their hydrophobic nature that repels moisture from the degradation of perovskite layer (Figure S15).

The devices with **TPA-NAP-TPA** and **TPA-TV-T-TPA** as the HTMs exhibit higher open-circuit voltage ($V_{oc}$) than PEDOT:PSS, indicating the better band alignment of these two HTMs with perovskite. The $V_{oc}$ of **TPA-TV-T-TPA** based device achieved 1.07 V, one of the highest value for inverted structure devices, suggesting its excellent hole extraction property in PSCs. Furthermore, the short-circuit current ($J_{sc}$) for both **TPA-NAP-TPA** and **TPA-TV-T-TPA** based device has exceeded 21 mA cm$^{-2}$. The improved $J_{sc}$ compared with PEDOT:PSS is likely due to the better perovskite quality with less recombination at both the grain boundaries and the interface with HTMs. These results are also manifested on the corresponding external quantum efficiency (EQE) spectra in Figure 3c. The integrated $J_{sc}$ from EQE matches well with the values obtained on $J$-$V$ curves. The slightly dropped $FF$ for **TPA-NAP-TPA** and **TPA-TV-T-TPA** based devices (0.71 for both) could be originated from the relatively lower hole mobility for these two HTMs as manifested on the increased series resistance ($R_s$) for both.$^{[40]}$ Nevertheless, these two small molecules based devices show greater shunt resistance ($R_{sh}$) than that of PEDOT:PSS. The calculated $R_{sh}$ values are to be found of 15.6, 2.68 and 1.2 kΩ cm$^{-2}$ for **TPA-TV-T-TPA**, **TPA-NAP-TPA** and PEDOT:PSS, respectively. The large $R_{sh}$ for **TPA-TV-T-TPA** and **TPA-NAP-TPA** HTLs suggests their better electron blocking role, leading to less recombination at the HTM/perovskite interface. This trend is consistent with their improved $V_{oc}$.$^{[41]}$ This also elucidates the higher $V_{oc}$ value of **TPA-TV-T-TPA** than that of **TPA-NAP-TPA** even though their HOMO values are similar.
To study the hole extraction property of different HTMs, steady-state photoluminescence (PL) was performed on perovskite thin film with the HTMs. As shown in Figure 4a, the PL shows a remarkable quenching for perovskites fabricated a top of the three HTMs. In particular, the peak PL intensity for pristine perovskite dropped 75%, 84% and 87% for TPA-NAP-TPA, TPA-TVT-TPA and PEDOT:PSS, respectively. The higher quenching efficiency for the latter two can be ascribed by more efficient hole transfer from perovskite to HTMs. It is brought about by the interaction between sulfur atoms in thiophene of HTMs with iodine and lead ions in perovskite. Further study to reveal how molecular structure of HTMs interacts mainly with perovskite is currently being pursued.
To further investigate the mechanism behind the different device performance of three HTMs, a forward bias was applied to the PSCs in the dark and the \( J-V \) curves are shown in Figure 4b. The current increases with the applied voltage firstly governed by the shunt resistance followed by an exponential region dominated by recombination. Ideality factor \( (n) \) and saturation current \( (J_0) \) were derived from the exponential slope by fitting the data. The ideality factors for the three HTMs based devices are close to 2, indicating the recombination is dominated by defects as in the Shockley-Read-Hall (SRH) mechanism.\(^{[43]}\) The \( J_0 \) for TPA-NAP-TPA, TPA-TVT-TPA and PEDOT:PSS based devices are 2.9×10\(^{-6}\), 1.8×10\(^{-7}\) and 2.3×10\(^{-5}\) mA cm\(^{-2}\), respectively. The improvement of \( V_{oc} \) for TPA-NAP-TPA and TPA-TVT-TPA based devices can be explained by the reduced \( J_0 \) by the Shockley equation, \( V_{oc} = \frac{n k_B T \ln(J_{ph}/J_0) + 1}{q} \), where \( J_{ph} \) equals to \( J_{sc} \); \( n \), \( k_B \), \( T \) and \( q \) are ideality factor, Boltzmann constant, temperature and electron charge, respectively.\(^{[44]}\) Therefore, the decreased \( J_0 \) for TPA-NAP-TPA and TPA-TVT-TPA based devices implies less recombination loss, resulting in larger \( V_{oc} \) and better photovoltaic performance than PEDOT:PSS based device.

The light intensity dependence of \( J_{sc} \) and \( V_{oc} \) was investigated to further elucidate the recombination process inside the PSCs. Figure 4c shows the double logarithmic plot of \( J_{sc} \) with light intensity (\( I \)), where \( \alpha \) was derived from the slope as \( J_{sc} \propto I^\alpha \). Both TPA-NAP-TPA and TPA-TVT-TPA based devices show close to unity values for \( \alpha \), indicating highly efficient charge collections at short circuit condition. Meanwhile, the reduced slope for PEDOT:PSS based device \( (\alpha = 0.98) \) indicates a substantial recombination loss at the interface between HTM and perovskite. This is also manifested on the dependence of \( V_{oc} \) on light intensity (Figure 4d) when all the photo-generated charges recombine within the device under open-circuit condition. The slopes for PEDOT:PSS, TPA-NAP-TPA and TPA-TVT-TPA based PSCs are 1.3, 1.11, and 1.19 \( k_B T/q \) respectively. In principle, the slope equal to \( k_B T/q \) indicates bimolecular recombination as dominant process, while a higher value
suggests the involvement of trap-assisted SRH recombination.\cite{43, 45} The lower slope for TPA-NAP-TPA and TPA-TVT-TPA based PSCs suggests these two HTMs can alleviate the trap-assisted recombination and contributes to a higher $V_{oc}$, consistent with the results shown in $J$-$V$ curves.

A list of recently reported dopant-free organic small molecular HTMs employed successfully in inverted perovskite solar cells have been summarised and compared with PEDOT:PSS in Table 3. As it can be seen from the Table, the photovoltaic performance of TPA-TVT-TPA based devices is on the top in comparison with other recently reported new HTMs in inverted perovskite solar cell devices due to its high photovoltaic performance parameters. In all of these inverted p-i-n perovskite solar cell devices, CH$_3$NH$_3$PbI$_3$ has been used as the active layer. Among the listed HTM in Table 3, HTM namely Trux-OMeTAD exhibits highest PCE of 18.02\% compared to our TPA-TVT-TPA based device (16.32\%) but Trux-OMeTAD based devices exhibits lower $V_{oc}$ (1.02V) than our devices (1.07V). Notably, the novel TPA-TVT-TPA possesses outstanding $V_{oc}$ and highest PCE in comparison with other HTMs. In spite of the similar exceptional $V_{oc}$ of 1.07 (V) of DFTAB HTM, the $J_{sc}$ and PCE are far less than that of our study. The efficiency of Spiro-OMeTAD is as good as that of TPA-TVT-TPA, however it suffers from lower $V_{oc}$. The commercial cost of Spiro-OMeTAD is very high (300 USD per g) due to multistep synthesis \cite{7, 14} and lower yield (\~45\%)\cite{46}. In comparison with Spiro-OMeTAD and PEDOT:PSS widely used HTMs, the synthesis of TPA-TVT-TPA and TPA-NAP-TPA is straightforward and its cost is very low, which makes it a suitable choice of alternative HTM for perovskite solar cells. Based on the tabular comparison, our newly reported two simple HTMs exhibit comparable PCE to that of recently reported HTMs. Particularly, TPA-TVT-TPA can be a worthy candidate for PEDOT:PSS and Spiro-OMeTAD replacement.
In summary, we have reported **TPA-TVTT**-**TPA** and **TPA-NAP-TPA**, two highly promising novel, simple and low cost TPA-based small molecular HTMs and their successful use in high performance p-i-n PSCs devices. Between these two molecules, **TPA-TVTT**-**TPA** based devices unveiled a higher PCE of 16.32% with an impressive $V_{oc}$ of 1.07 V, which is better than that of PEDOT: PSS (11.5%) under the same condition (AM 1.5G illumination at an intensity of 100 mW cm$^{-2}$). In spite of high performance of the inverted devices using new HTMs, the lower fill factor of these devices should be taken into an account; it can however be further optimized either by new molecular material design or device engineering. Generally, the appropriate combination between linear $\pi$-conjugated cores and TPA end capping moieties can result a straightforward, low cost and high efficient HTMs not only for

<table>
<thead>
<tr>
<th>HTM</th>
<th>Device Structure</th>
<th>HOMO (eV)</th>
<th>Active area (mm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>PCE$^a$ (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPA-TVTT-TPA</td>
<td>ITO/HTM/CH$_3$NH$_3$PbI$<em>3$/PC$</em>{60}$BM/BCP/Ag</td>
<td>5.37</td>
<td>7</td>
<td>1.07</td>
<td>21.49</td>
<td>0.71</td>
<td>16.32 (11.59)</td>
<td>This study</td>
</tr>
<tr>
<td>TPA-NAP-TPA</td>
<td>ITO/HTM/CH$_3$NH$_3$PbI$<em>3$/PC$</em>{60}$BM/BCP/Ag</td>
<td>5.38</td>
<td>7</td>
<td>0.96</td>
<td>21.55</td>
<td>0.71</td>
<td>14.63 (11.59)</td>
<td>This study</td>
</tr>
<tr>
<td>NTPA</td>
<td>ITO/HTM/CH$_3$NH$_3$PbI$<em>3$/PC$</em>{60}$M/Ag</td>
<td>5.27</td>
<td>10</td>
<td>1.02</td>
<td>17.4</td>
<td>0.733</td>
<td>12.2 (10.9)</td>
<td>[23]</td>
</tr>
<tr>
<td>BTPA</td>
<td>ITO/HTM/CH$_3$NH$_3$PbI$<em>3$/PC$</em>{60}$M/Ag</td>
<td>5.20</td>
<td>10</td>
<td>0.98</td>
<td>17.4</td>
<td>0.708</td>
<td>11.45 (10.9)</td>
<td>[23]</td>
</tr>
<tr>
<td>Trux-OMeTAD</td>
<td>ITO/HTM/CH$_3$NH$_3$PbI$<em>3$/PC$</em>{61}$BM/ZnO/Al</td>
<td>5.28</td>
<td>5.5</td>
<td>1.02</td>
<td>23.3</td>
<td>0.765</td>
<td>18.05 (16.1)</td>
<td>[21]</td>
</tr>
<tr>
<td>Spiro-OMeTAD</td>
<td>ITO/HTM/CH$_3$NH$_3$PbI$<em>3$/PC$</em>{61}$BM/ZnO/Al</td>
<td>5.10</td>
<td>5.5</td>
<td>0.99</td>
<td>23.0</td>
<td>0.72</td>
<td>16.3 (16.1)</td>
<td>[21]</td>
</tr>
<tr>
<td>TPASBP</td>
<td>ITO/HTM/CH$_3$NH$_3$PbI$<em>3$/PC$</em>{61}$BM/Al</td>
<td>5.00</td>
<td>4</td>
<td>1.04</td>
<td>20.7</td>
<td>0.80</td>
<td>15.7 (12.1)</td>
<td>[47]</td>
</tr>
<tr>
<td>TPASB</td>
<td>ITO/HTM/CH$_3$NH$_3$PbI$<em>3$/PC$</em>{61}$BM/Al</td>
<td>5.49</td>
<td>4</td>
<td>1.05</td>
<td>20.8</td>
<td>0.80</td>
<td>16.2 (12.1)</td>
<td>[47]</td>
</tr>
<tr>
<td>TPAC3M</td>
<td>ITO/HTM/CH$_3$NH$_3$PbI$<em>3$/PC$</em>{61}$BM/Al</td>
<td>4.96</td>
<td>4</td>
<td>0.99</td>
<td>22.11</td>
<td>0.75</td>
<td>16.58 (11.44)</td>
<td>[48]</td>
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<tr>
<td>DFTAB</td>
<td>ITO/HTM/CH$_3$NH$_3$PbI$<em>3$/PC$</em>{60}$M/Ag</td>
<td>5.2</td>
<td>10</td>
<td>1.07</td>
<td>17.5</td>
<td>0.69</td>
<td>11.8 (11.1)</td>
<td>[49]</td>
</tr>
</tbody>
</table>

$^a$Average PCE |

$^b$PCE of PEDOT: PSS based devices
conventional but also for inverted perovskite devices. The new class of materials based on this design paves the way for the development and commercialization of perovskite solar cells in the future.

Supporting Information

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

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Reference


Thienylvinlenethienyl and Naphthalene Core Substituted with Triphenylamines -

Highly Efficient Hole Transporting Materials and their Comparative Study for

Inverted Perovskite Solar Cells

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Organic-inorganic halide perovskite materials have recently been employed in several types of optoelectronic devices, including thin-film transistors,[1] lasing,[2] solar cells,[3] light-emitting diodes[4] and flexible memory[5] devices, due to their outstanding properties. These properties include long charge carrier diffusion length, highly efficient ambipolar charge transport ability, wide optical absorption, and large absorption coefficients.[6, 7] The research on perovskite solar cells (PSCs) has gained a huge attention in scientific community mainly due to their ability to reach the performance close to that of the existing high performance silicon and other inorganic material based solar cell technologies. The world record power conversion efficiency (PCE) of PSCs has now exceeded 22% - a significant progress since the first PSC were reported with PCE values as low as 3.8% in 2009.[8] This rapid development clearly shows the potential of the PSC technology to become commercially viable as a solar energy harvesting tool and to contribute in a significant way to meeting future energy demand in a sustainable fashion. The obtained PSC performance is comparable to the traditional second generation thin film devices, such as the copper indium gallium selenide (CIGS) and cadmium telluride (CdTe) devices, and first generation silicon-based high performance solar energy technologies.

The device geometry and structure of PSCs can be classified into two main architectures. The first architecture is the conventional type where the main layers consist of a compact or mesoporous metal oxides electron transporting layer (ETL, n-type) followed by the perovskite active layer (i) and then a hole transporting layer (HTL, p-type). Devices with this architecture are also known as the n-i-p type devices. Although the PCE of this particular type of device architecture has been able to reach 20%,[9] this device geometry has some significant shortcomings. Firstly, the deposition of n-type metal oxides such as titanium dioxide (TiO₂) compact layer requires high temperature processing (over 450 °C), which increases the cost of production of these devices. Secondly, these devices suffer from high
instability and large hysteresis issues, which hamper their practical deployment. This second type of architecture, known as the inverted structure, alleviates these limitations. In an inverted structure, a p-type HTL is deposited first followed by the active perovskite layer (i) and then the n-type ETL layer (n). This is also known as the p-i-n structure. To date, the highest PCE of such inverted PSCs has been reported to be 19.4% without any hysteresis issue, and hence this may be a more feasible approach for practical cells. Moreover, inverted devices can be easily made using low-temperature solution-processing techniques and thus can be easily employed on flexible substrates, which is very promising for large-area production of these devices. These key aspects and advantages make the p-i-n device architecture one of the most promising strategies for the future of perovskite solar cells.

Development of optimal materials for the HTL is one of the key directions to further improve the PCE of these cells. The HTL not only transports the holes after exciton dissociation but also protects the active perovskite layer from moisture/oxygen ingress and electrode penetration. In addition to the above benefits, the HTL suppresses charge recombination, which is critical for achieving higher PCE. The HTL is essential to achieve higher open circuit voltage \(V_{oc}\) and PCE in the inverted PSCs.

Organic hole transporting materials (HTMs) can be classified into two main categories: monodispersed small molecules and polydispersed polymers. Polymeric HTMs have been successfully employed and achieved some promising results in p-i-n devices. Currently, the highest PCE obtained with inverted PSCs was around 19.4% using poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) as the HTM. In addition to PTAA polymer, poly(3,4-ethylenedioxythiophene : polystyrene sulfonate) (PEDOT : PSS) has been also successfully used as the HTM in p-i-n devices and was able to achieve a high PCE of 18.1%. Using these polymeric HTMs, it has been shown that it is possible for p-i-n devices to obtain PCE values that are comparable to those of conventional n-i-p structures. However,
these most successful polymeric HTMs have some limitations when it comes to practical applications in the PSC technology. PTAA polymers is extremely expensive and costs about 50 times the price of gold and PEDOT:PSS is hydrophilic and of a strong acidic nature which compromises the device long-term stability.\cite{7, 17} The tediousness of synthesis and the requirement of high purity of monomers may add to the cost of the polymers. Moreover, molecular weight of polymers can vary batch-to-batch and this may further affect the performance of PSC. Compared to polymeric semiconductors as HTMs, small molecules can provide enormous benefits including good yield,\cite{18} defined molecular structure,\cite{19} tunable energetics,\cite{20} and good batch-to-batch reproducibility.\cite{18, 19} Thus, small molecular HTMs could be a better choice of materials compared to polymeric ones. To date, there are very few reports in the literature on small molecular HTMs specifically for the p-i-n device architecture. Amongst the few reported small molecular HTMs, 3,8,13-tri(di-4-methoxylphenylamino)-5,5,10,15-Hex(1-hexyl)10,15-dihydro-5H-diinden[1,2-α;1′,2′-c]fluorene (Trux-OMeTAD) has been shown to be one of the most promising candidates and using this HTM, a PCE of 18.6% has been achieved.\cite{21} Using conventional 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spiro-bifluorene (Spiro-OMeTAD) HTM, a PCE of 16.3% was achieved under similar conditions. Trux-OMeTAD and Spiro-OMeTAD have clearly shown that small molecular HTMs have the potential to achieve comparable performance to that of polymeric ones. When considering the design of small molecular HTMs, it is seen that triphenylamine (TPA) is one of the most common efficient and successful end capping groups due to its strong electron-donating and excellent hole transporting nature.\cite{19} In addition, due to the three distorted phenyl groups substituted on the central nitrogen of TPA, there can be an additional benefit of protecting perovskite layer which is sandwiched between HTL and ETL. Electron coupling and reduction of charge recombination in electronic devices such as solar cells are also two very important
characteristics of TPA that make it a good choice.[22] Other major advantages of molecular design based on TPA include simple synthesis, low cost, easy scalability, and easy processibility. Thus all these characteristics make this end group attractive in the design of high performance HTMs. To date, even though a number of novel HTMs have been reported recently using a $\pi$-conjugated core and TPA and subsequently applied in n-i-p perovskite device structures, there are very few reports on using such HTMs for the inverted or p-i-n layouts.

Herein, we have synthesized two explicitly simple HTMs namely (E)-4,4’-(ethene-1,2-diylbis(thiophene-5,2-diyl))bis(N,N-bis(4-methoxyphenyl)aniline) (TPA-TV T-TPA) and 4,4’-(naphthalene-2,6-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (TPA-NAP-TPA) based on naphthalene (NAP) and thiophene-vinylene-thiophene (TVT) linear planar $\pi$-conjugated cores with common TPA end capping groups, respectively (Scheme 1). TPA-TV T-TPA and TPA-NAP-TPA were successfully employed as HTMs in inverted p-i-n PSCs and their structure-property relationship will be discussed in detail. While working on this manuscript, TPA-NAP-TPA was reported by other group and used as HTL in inverted perovskite devices,[23] but its performance is lower (13%) than that of this study (14.63%). The second molecule TPA-TV T-TPA is a completely new material and has been not reported before in the literature. The rationale for the choice of TVT is discussed below. Inverted perovskite photovoltaic devices using TPA-TV T-TPA and TPA-NAP-TPA as HTMs were fabricated using the following device architecture: glass/ITO/HTL/perovskite/PCPM/BCP/Ag. In these devices, indium tin oxide (ITO) on glass and silver (Ag) act as a transparent conducting cathode and anode, respectively. Our newly developed materials are used as HTMs, CH$_3$NH$_3$PbI$_3$ perovskite as the active layer, fullerene derivative [6,6]-phenyl C61 butyric acid methyl ester (PCBM) as an electron transporting compact layer and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as an electron extracting and hole blocking layer.[24] The
fabrication procedure is described in detail in the Supporting Information. Under standard illumination (AM 1.5G and 100 mW cm\(^{-2}\)), the PCE of these HTMs based devices was found to be of 16.32\% for TPA-TVT-TPA and 14.63\% for TPA-NAP-TPA.

The selection of electron donating thienylenevinylene-thienyl (TVT) and naphthalene (NAP) as the central conjugated core is based on the previous reports using these comonomers in the copolymer synthesis and their use as high hole mobility materials in the p-channel organic thin film transistor (OTFT). The TVT and NAP based copolymers with diketopyrrolopyrrole (DPP) have been shown to be some of the most promising hole transporting materials, with hole mobilities of more than 0.2 cm\(^2\)/Vs reported in OTFT devices\(^{25, 26}\). Additionally, TVT and NAP based copolymers have also been shown as a promising choice of electron donating component with PCBM as the active layer in organic photovoltaics\(^{25, 27}\). Since both cores, TVT and NAP, have been shown to be one of the best candidates for obtaining high hole mobility, it would be an obvious choice to use them as cores in the design of new hole transporting materials\(^{28}\). For the naphthalene core unit, there are three possibilities to functionalize the conjugated backbone - via 1, 4-, 1, 5- or 2, 6-positions\(^{29, 30}\). Among these options, the 2,6-position of naphthalene will result in the most planar conformation to achieve highly extended \(\pi\)-conjugation\(^{29}\). Compounds comprising of a planar naphthalene donor unit with other acceptor blocks also exhibited high hole mobility in organic electronic devices\(^{31}\).

All of these above explained features make the synthesized molecules promising candidates for future large area cost effective perovskite solar cell technology.
Synthesis routes of **TPA-TVT-TPA** and **TPA-NAP-TPA**. Reagent and conditions: (a) 1-iodo-4-methoxybenzene, KOH, CuCl, 1,10-phenanthroline monohydrate, toluene, 120 °C, overnight; (b) trans-1,2-di(2-thienyl)ethylene, n-butyllithium, tetramethylethylenediamine, trimethyltin chloride, tetrahydrofuran, RT, overnight; (c) DMF, Pd(PPh₃)₄, 110 °C, 48 h; (d) 2M K₂CO₃, toluene, Pd(PPh₃)₄, 120 °C, 48 h.

**Scheme 1.** Synthesis of **TPA-TVT-TPA** and **TPA-NAP-TPA**.

The synthetic routes of **TPA-TVT-TPA** and **TPA-NAP-TPA** are displayed in Scheme 1. Firstly, the precursor 4-bromo-\(N,N\)-bis(4-methoxyphenyl)aniline (2) was produced in a good yield from 4-bromoaniline (1) and 1-iodo-4-methoxybenzene in presence of strong base potassium hydroxide (KOH), copper chloride (CuCl), and 1,10-phenanthroline monohydrate reagent refluxing in anhydrous toluene overnight. Meanwhile, \((E)\)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (4) and 2,6-bis(4,4,5,5-tetramethyl-1,3,2-
dioxaborolan-2-yl)naphthalene (5) were prepared from commercially available trans-1,2-di(2-thienyl)ethylene and 2, 6-dirbromo naphthalene starting materials accordingly to a previously reported procedure.\textsuperscript{[25, 29]} The target HTM TPA-TV-TPA was synthesized by Stille coupling reaction between compound 2 and 4 using tetrakis triphenylphosphine palladium [Pd(PPh\textsubscript{3})\textsubscript{4}] catalyst at 110 °C for 48 h in dimethyl formamide (DMF) solvent. TPA-NAP-TPA was prepared via classical Suzuki coupling reaction between compound 2 and 5 using tetrakis triphenylphosphine palladium [Pd(PPh\textsubscript{3})\textsubscript{4}] catalyst, 2M K\textsubscript{2}CO\textsubscript{3} base, at 120 °C for 48 h in toluene solvent. The yields of reactions were found to be of 55% for TPA-TV-TPA and 50% for TPA-NAP-TPA after purification by column chromatography. The purity was confirmed by proton and C13 NMR spectroscopy, which are shown in Figure S1 – S4 (Supporting Information). Both materials exhibited good solubility in most of the common organic solvents such as chloroform, dichloromethane and chlorobenzene.
In order to understand electronic properties of these molecules, density functional theory (DFT) calculations were performed at the B3LYP level of theory using the basis set 6-31g+(d,p).\textsuperscript{[32]} The resulting highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the molecular structures are shown in Figure 1. Both molecules exhibit similarities in the electron distributions of the HOMO and the LUMO in that the electron density of the LUMO is primarily localized on thienylenevinylene and
naphthalene cores, whereas the HOMO is fully delocalized over the entire molecules including the electron rich TPA moieties, as expected. According to the DFT calculations, the HOMO energies of TPA-TV-TPA and TPA-NAP-TPA are -4.49 eV and -4.64 eV, respectively. The LUMO energies are -1.86 eV, and -1.31 eV, respectively. Even though the HOMO-LUMO values from the theoretical calculations may not match exactly the values estimated from the experiments due to approximations used and the single-molecule nature of the simulation, they provide the energy level trends based on molecular design. The computed visible peak maxima for TPA-TV-TPA and TPA-NAP-TPA are 544 and 425 nm, respectively, confirming that a significant redshift has been observed in case of TPA-TV-TPA (as shown in Figure 2). This theoretical optical red shift of 119 nm is due to the more extended conjugation of TPA-TV-TPA backbone than in TPA-NAP-TPA one. The transition intensity with TPA-TV-TPA is also noticeably higher with the oscillator strength of 2.18 compared to 1.22 for TPA-NAP-TPA. The absolute absorption peak maxima are red shifted vs. experiment, as is expected with B3LYP for transitions with charge transfer character.\[33\]

The thermal properties of both newly synthesized small molecule TPA-TV-TPA and TPA-NAP-TPA HTMs were measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques and the data is shown in Figure S6 and S7 (Supporting Information) respectively. In TGA, the 5% weight loss at high temperature above 390 °C was considered as the onset point of decomposition (T_d). TPA-TV-TPA and TPA-NAP-TPA were found to have extremely good thermal stability, with 5% weight loss at 390 and 405 °C, respectively, which were higher than that of common HTMs such as Spiro-OMeTAD (approximately 125 °C)\[34\] and PEDOT:PSS (below 200 °C)\[35\]. This is a good indication that these small molecules could be thermally stable hole transporting materials for perovskite solar cells. From the DSC thermogram, it has been clearly seen that TPA-TV-TP
TPA and TPA-NAP-TPA molecules exhibit glass transition temperature ($T_g$) at 87 °C and 85 °C, respectively, after two heating-cooling cycles. Moreover, the crystallization temperature does not appear during the two-cycle analysis because the non-planar conformation of TPA units leads to a lower degree of crystallinity.[36] From the first heating – cooling cycle, TPA-TVT-TPA and TPA-NAP-TPA exhibit strong endothermic peaks at 170°C and 160 °C, respectively, which are ascribed to the melting transition. From the thermal analysis data, it follows that TPA-NAP-TPA and TPA-TVT-TPA have a comparable thermal stability due to only slight disparity in chemical structure.

The normalized UV-Vis absorption and emission spectra of TPA-TVT-TPA and TPA-NAP-TPA in solution (chloroform) and in solid state (thin film on glass) were measured and shown in Figure 2a and Figure S5 (Supporting Information). The relevant data is listed in Table 1. TPA-TVT-TPA shows a broad absorption bands ranging from 300 to 520 nm, which the peak extends to 550 nm as shown in Figure 2a. Meanwhile, TPA-NAP-TPA has an absorption range from 300 to 430 nm. The absorption maxima of TPA-TVT-TPA and TPA-NAP-TPA exhibits two absorption peaks in the lower and higher wavelength region which is arising from n-$\pi^*$ and $\pi$-$\pi^*$ transitions. The solution peak for TPA-NAP-TPA is found to be at 375 nm whereas solid-state peak was at 380 nm. In the case of TPA-TVT-TPA, the solution peak is found to be at 450 nm whereas thin film peak is measured at 460 nm. The optical absorption spectrum of TPA-TVT-TPA in solution and solid state are red-shifted noticeably compared to TPA-NAP-TPA, which is related to the more extended conjugation of the backbone of TPA-TVT-TPA than in TPA-NAP-TPA. Indeed, the optical band gap from the intersection of absorption spectra of the TPA-TVT-TPA and TPA-NAP-TPA in thin film is assessed to be 2.30 and 2.86 eV, respectively.
Figure 2. a) UV-Vis absorption spectra in chloroform solutions (dash line) and films (solid line), b) Photoelectron spectroscopy in air (PESA) spectra of TPA-TVTTVA and TPA-NAP-TPA and c) Energy level diagram of each layer in the device.

As shown in Figure S5, the emission maxima of TPA-TVTTVA and TPA-NAP-TPA are peaked at 524 nm and 466 nm, respectively. Stokes shifts are estimated from the gap between the maximum of absorption and emission spectra. These materials possess a large Stokes shift of about 72 nm for TPA-TVTTVA and 89 nm for TPA-NAP-TPA, which indicates a non-rigid nature of the molecular structure.
Table 1. Thermal, optical and electrochemical properties of TPA-TV-TPA and TPA-NAP-TPA.

<table>
<thead>
<tr>
<th>HTMs</th>
<th>$\lambda_{abs}^{max}$ (nm)</th>
<th>$\lambda_{PL}$ (nm)</th>
<th>$E_{g}^{opt}$ (eV)</th>
<th>$E_{HOMO}$ (eV)</th>
<th>$E_{LUMO}$ (eV)</th>
<th>$T_d$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPA-TV-TPA</td>
<td>450</td>
<td>524</td>
<td>2.30</td>
<td>-5.37</td>
<td>-3.07</td>
<td>390</td>
<td>170</td>
<td>87</td>
</tr>
<tr>
<td>TPA-NAP-TPA</td>
<td>375</td>
<td>466</td>
<td>2.86</td>
<td>-5.38</td>
<td>-2.52</td>
<td>405</td>
<td>160</td>
<td>85</td>
</tr>
</tbody>
</table>

a) Absorption spectrum was measured in CF solution and b) in film; c) Emission spectrum was analysed in CF solution; d) Optical band gap was calculated from the formula of $1240/\lambda_{onset}$; e) The HOMO value determined by PESA; f) $E_{LUMO}=E_{HOMO}^{PESA}+E_{g}^{opt}$.

To evaluate the band-alignment of these two novel molecules with the perovskite, their HOMO levels were determined from photoelectron spectroscopy in air (PESA) and shown in Figure 2b. The respective LUMO levels of these two materials were obtained by subtracting the optical bandgap from HOMO levels. These energy levels were plotted in Figure 2c together with the energy levels of perovskite and all the other layers employed in the device. The HOMO values of TPA-TV-TPA and TPA-NAP-TPA are estimated to be -5.37 eV and -5.38 eV, respectively. The energy gaps ($\Delta E$) between these two HOMOs with the valence band (VB) of perovskite are within 0.1 eV, which are good values for efficient extraction of holes without a significant voltage drop. As a comparison, the PEDOT:PSS possesses a $\Delta E$ as large as 0.34 eV with respect to the VB of perovskite [the value is 0.34 eV based on the data in Figure 2(c)]. The large mismatch between these two materials can cause severe photovoltage drop and thereby reduce the device performance. At the same time, the LUMO values of the new molecules remain significantly above the conduction band minimum (CBM) of the perovskite and can effectively block undesired electron back diffusion. The hole mobility of these two molecules, estimated from space charge-limited current (SCLC) measurement (Figure S8), was $5.1 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $2.1 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ for TPA-NAP-
TPA and TPA-TV-TPA respectively, which is slightly lower than spiro-OMeTAD (8.09×10⁴ cm² V⁻¹ s⁻¹) and PEDOT:PSS (9.8×10⁵ cm² V⁻¹ s⁻¹).[37]

![Cross-sectional scanning electron microscopy image of the device](image)

**Figure 3.** a) Cross-sectional scanning electron microscopy image of the device, b) Current density–voltage curves (J-V) of PSCs with different HTMs, and c) their external quantum efficiency (EQE) spectra (lines with open symbols indicate the integrated J_sc from EQE and solar spectrum).

The device performance based on these HTMs was investigated in inverted device architecture. Figure 3a shows a cross-sectional scanning electron microscopy (SEM) image of a complete device. A thin layer of HTM was first spin-coated on top of indium tin-oxide (ITO) coated glass, followed by the deposition of perovskite layer, electron transport layer and back electrode (Ag). Both TPA-TV-TPA and TPA-NAP-TPA illustrate smooth and compact surfaces with small roughness (RMS) of 3.9 nm and 7.8 nm, respectively, as determined by atomic force microscopy (Figure S9). The morphologies of perovskite layers
on top of each HTL are shown in Figure S10. The average grain sizes of perovskite layers formed on top of \textbf{TPA-TV-T-TPA} and \textbf{TPA-NAP-TPA} are larger than the one on PEDOT:PSS, implying the formation of high quality films of perovskite with fewer grain boundaries in the case of \textbf{TPA-TV-T-TPA} and \textbf{TPA-NAP-TPA} based devices.\cite{38} The perovskite films exemplify distinctive pure phase without PbI$_2$ residue as manifested on the x-ray diffraction patterns in Figure S11. The larger grain size of perovskite layer on these two HTMs is likely due to the lower wetting of perovskite solution on top as shown in the contact angle measurement (Figure S12), which facilitates the extensive growth of perovskite grains as demonstrated in the earlier report.\cite{39}

\begin{table}[h]
\centering
\caption{\textit{J–V} parameters of PSCs with PEDOT:PSS, \textbf{TPA-NAP-TPA} and \textbf{TPA-TV-T-TPA} as HTLs.}
\begin{tabular}{|l|c|c|c|c|c|c|c|}
\hline
HTL & PCE (\%) & $V_{oc}$ (V) & $J_{sc}$ (mA cm$^{-2}$) & FF & $R_s$ ($\Omega$ cm$^2$) & $R_{sh}$ (k$\Omega$ cm$^2$) & Cal. $J_{sc}$ (mA cm$^{-2}$) \\
\hline
PEDOT:PSS & 11.59 & 0.85 & 18.66 & 0.73 & 3.02 & 1.2 & 18.36 \\
TPA-NAP-TPA & 14.63 & 0.96 & 21.55 & 0.71 & 4.51 & 2.68 & 21.01 \\
TPA-TV-T-TPA & 16.32 & 1.07 & 21.49 & 0.71 & 6.45 & 15.6 & 21.15 \\
\hline
\end{tabular}
\end{table}

Current–voltage (\textit{J–V}) performance of PSC with different HTMs (Figure 3b) were measured under simulated sun illumination (AM 1.5 G, 100 mWcm$^{-2}$) and their respective parameters are summarized in Table 2. The \textbf{TPA-NAP-TPA} and \textbf{TPA-TV-T-TPA} based devices yield much improved PCE of 14.63\% and 16.32\%, respectively, compared with the PCE of PEDOT:PSS based device (11.59\%). All the devices show little hysteresis when measured at different scan directions and good reproducitivy as shown in Figure S13 and Figure S14, respectively. It is worth to note that our preliminary stability study shows much improved stability for the \textbf{TPA-NAP-TPA} and \textbf{TPA-TV-T-TPA} based devices than PEDOT:PSS due
to their hydrophobic nature that repels moisture from the degradation of perovskite layer (Figure S15).

The devices with TPA-NAP-TPA and TPA-TV-TTPA as the HTMs exhibit higher open-circuit voltage (Voc) than PEDOT:PSS, indicating the better band alignment of these two HTMs with perovskite. The Voc of TPA-TV-TTPA based device achieved 1.07 V, one of the highest value for inverted structure devices, suggesting its excellent hole extraction property in PSCs. Furthermore, the short-circuit current (Jsc) for both TPA-NAP-TPA and TPA-TV-TTPA based device has exceeded 21 mA cm⁻². The improved Jsc compared with PEDOT:PSS is likely due to the better perovskite quality with less recombination at both the grain boundaries and the interface with HTMs. These results are also manifested on the corresponding external quantum efficiency (EQE) spectra in Figure 3c. The integrated Jsc from EQE matches well with the values obtained on J-V curves. The slightly dropped FF for TPA-NAP-TPA and TPA-TV-TTPA based devices (0.71 for both) could be originated from the relatively lower hole mobility for these two HTMs as manifested on the increased series resistance (Rs) for both. Nevertheless, these two small molecules based devices show greater shunt resistance (Rsh) than that of PEDOT:PSS. The calculated Rsh values are to be found of 15.6, 2.68 and 1.2 kΩ cm⁻² for TPA-TV-TTPA, TPA-NAP-TPA and PEDOT:PSS, respectively. The large Rsh for TPA-TV-TTPA and TPA-NAP-TPA HTLs suggests their better electron blocking role, leading to less recombination at the HTM/perovskite interface. This trend is consistent with their improved Voc. This also elucidates the higher Voc value of TPA-TV-TTPA than that of TPA-NAP-TPA even though their HOMO values are similar.
Figure 4. a) Steady-state photoluminescence spectra of perovskite films on glass slide, TPA-NAP-TPA, TPA-TV-TTPA and PEDOT:PSS, b) J-V curves of PSCs measured under darkness, and the dependence of $J_{sc}$ (c) and $V_{oc}$ (d) on light intensity. Symbols and solid lines represent experimental data and fittings respectively.

To study the hole extraction property of different HTMs, steady-state photoluminescence (PL) was performed on perovskite thin film with the HTMs. As shown in Figure 4a, the PL shows a remarkable quenching for perovskites fabricated a top of the three HTMs. In particular, the peak PL intensity for pristine perovskite dropped 75%, 84% and 87% for TPA-NAP-TPA, TPA-TV-TTPA and PEDOT:PSS, respectively. The higher quenching efficiency for the latter two can be ascribed by more efficient hole transfer from perovskite to HTMs. It is brought about by the interaction between sulfur atoms in thiophene of HTMs with iodine$^{[9]}$ and lead$^{[43]}$ ions in perovskite. Further study to reveal how molecular structure of HTMs interacts mainly with perovskite is currently being pursued.
To further investigate the mechanism behind the different device performance of three HTMs, a forward bias was applied to the PSCs in the dark and the $J$-$V$ curves are shown in Figure 4b. The current increases with the applied voltage firstly governed by the shunt resistance followed by an exponential region dominated by recombination. Ideality factor (n) and saturation current ($J_0$) were derived from the exponential slope by fitting the data. The ideality factors for the three HTMs based devices are close to 2, indicating the recombination is dominated by defects as in the Shockley-Read-Hall (SRH) mechanism.\[43\] The $J_0$ for TPA-NAP-TPA, TPA-TVT-TPA and PEDOT:PSS based devices are $2.9 \times 10^{-6}$, $1.8 \times 10^{-7}$ and $2.3 \times 10^{-5}$ mA cm$^{-2}$, respectively. The improvement of $V_{oc}$ for TPA-NAP-TPA and TPA-TVT-TPA based devices can be explained by the reduced $J_0$ by the Shockley equation, $V_{nc} = n k_B T (\ln(J_{ph}/J_0) + 1)/q$, where $J_{ph}$ equals to $J_{sc}$; n, $k_B$, T and q are ideality factor, Boltzmann constant, temperature and electron charge, respectively.\[44\] Therefore, the decreased $J_0$ for TPA-NAP-TPA and TPA-TVT-TPA based devices implies less recombination loss, resulting in larger $V_{oc}$ and better photovoltaic performance than PEDOT:PSS based device.

The light intensity dependence of $J_{sc}$ and $V_{oc}$ was investigated to further elucidate the recombination process inside the PSCs. Figure 4c shows the double logarithmic plot of $J_{sc}$ with light intensity ($I$), where $\alpha$ was derived from the slope as $J_{sc} \propto I^{\alpha}$. Both TPA-NAP-TPA and TPA-TVT-TPA based devices show close to unity values for $\alpha$, indicating highly efficient charge collections at short circuit condition. Meanwhile, the reduced slope for PEDOT:PSS based device ($\alpha = 0.98$) indicates a substantial recombination loss at the interface between HTM and perovskite. This is also manifested on the dependence of $V_{oc}$ on light intensity (Figure 4d) when all the photo-generated charges recombine within the device under open-circuit condition. The slopes for PEDOT:PSS, TPA-NAP-TPA and TPA-TVT-TPA based PSCs are 1.3, 1.11, and 1.19 $k_B T/q$ respectively. In principle, the slope equal to $k_B T/q$ indicates bimolecular recombination as dominant process, while a higher value
suggests the involvement of trap-assisted SRH recombination.[43, 45] The lower slope for TPA-NAP-TPA and TPA-TV-TPA based PSCs suggests these two HTMs can alleviate the trap-assisted recombination and contributes to a higher $V_{oc}$, consistent with the results shown in $J-V$ curves.

A list of recently reported dopant-free organic small molecular HTMs employed successfully in inverted perovskite solar cells have been summarised and compared with PEDOT:PSS in Table 3. As it can be seen from the Table, the photovoltaic performance of TPA-TV-TPA based devices is on the top in comparison with other recently reported new HTMs in inverted perovskite solar cell devices due to its high photovoltaic performance parameters. In all of these inverted p-i-n perovskite solar cell devices, CH$_3$NH$_3$PbI$_3$ has been used as the active layer. Among the listed HTM in Table 3, HTM namely Trux-OMeTAD exhibits highest PCE of 18.02% compared to our TPA-TV-TPA based device (16.32%) but Trux-OMeTAD based devices exhibits lower $V_{oc}$ (1.02V) than our devices (1.07V). Notably, the novel TPA-TV-TPA possesses outstanding $V_{oc}$ and highest PCE in comparison with other HTMs. In spite of the similar exceptional $V_{oc}$ of 1.07 (V) of DFTAB HTM, the $J_{sc}$ and PCE are far less than that of our study. The efficiency of Spiro-OMeTAD is as good as that of TPA-TV-TPA, however it suffers from lower $V_{oc}$. The commercial cost of Spiro-OMeTAD is very high (300 USD per g) due to multistep synthesis [7, 14] and lower yield (~45%)[46]. In comparison with Spiro-OMeTAD and PEDOT:PSS widely used HTMs, the synthesis of TPA-TV-TPA and TPA-NAP-TPA is straightforward and its cost is very low, which makes it a suitable choice of alternative HTM for perovskite solar cells. Based on the tabular comparison, our newly reported two simple HTMs exhibit comparable PCE to that of recently reported HTMs. Particularly, TPA-TV-TPA can be a worthy candidate for PEDOT:PSS and Spiro-OMeTAD replacement.
Table 1. The comparison among promising small molecular HTMs.

<table>
<thead>
<tr>
<th>HTM</th>
<th>Device Structure</th>
<th>HOMO (eV)</th>
<th>Active area (mm²)</th>
<th>Voc (V)</th>
<th>Jsc (mA cm⁻²)</th>
<th>FF</th>
<th>PCEa (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPA-TVT-TPA</td>
<td>ITO/HTM/CH₃NH₃Pbi₃/PC₆₀BM/BCP/Ag</td>
<td>-5.37</td>
<td>7</td>
<td>1.07</td>
<td>21.49</td>
<td>0.71</td>
<td>16.32 (11.59)b</td>
<td>This study</td>
</tr>
<tr>
<td>TPA-NAP-TPA</td>
<td>ITO/HTM/CH₃NH₃Pbi₃/PC₆₀BM/BCP/Ag</td>
<td>-5.38</td>
<td>7</td>
<td>0.96</td>
<td>21.55</td>
<td>0.71</td>
<td>14.63 (11.59)</td>
<td>This study</td>
</tr>
<tr>
<td>NTPA</td>
<td>ITO/HTM/CH₃NH₃Pbi₃/PC₆₀P M/Ag</td>
<td>-5.27</td>
<td>10</td>
<td>1.02</td>
<td>17.4</td>
<td>0.733</td>
<td>12.2 (10.9)</td>
<td>[23]</td>
</tr>
<tr>
<td>BTPA</td>
<td>ITO/HTM/CH₃NH₃Pbi₃/PC₆₀P M/Ag</td>
<td>-5.20</td>
<td>10</td>
<td>0.98</td>
<td>17.4</td>
<td>0.708</td>
<td>11.45 (10.9)</td>
<td>[23]</td>
</tr>
<tr>
<td>Trux-OMeTAD</td>
<td>ITO/HTM/CH₃NH₃Pbi₃/PC₆₁P M/Ag</td>
<td>-5.28</td>
<td>5.5</td>
<td>1.02</td>
<td>23.3</td>
<td>0.765</td>
<td>18.05 (16.1)</td>
<td>[21]</td>
</tr>
<tr>
<td>Spiro-OMeTAD</td>
<td>ITO/HTM/CH₃NH₃Pbi₃/PC₆₁P M/ZnO/Al</td>
<td>-5.10</td>
<td>5.5</td>
<td>0.99</td>
<td>23.0</td>
<td>0.72</td>
<td>16.3 (16.1)</td>
<td>[21]</td>
</tr>
<tr>
<td>TPASBP</td>
<td>ITO/HTM/CH₃NH₃Pbi₃/PC₆₁P M/Al</td>
<td>-5.00</td>
<td>4</td>
<td>1.04</td>
<td>20.7</td>
<td>0.80</td>
<td>15.7 (12.1)</td>
<td>[47]</td>
</tr>
<tr>
<td>TPASB</td>
<td>ITO/HTM/CH₃NH₃Pbi₃/PC₆₁P M/Al</td>
<td>-5.49</td>
<td>4</td>
<td>1.05</td>
<td>20.8</td>
<td>0.80</td>
<td>16.2 (12.1)</td>
<td>[47]</td>
</tr>
<tr>
<td>TPAC3M</td>
<td>ITO/HTM/CH₃NH₃Pbi₃/PC₆₁P M/ZnO/Al</td>
<td>-4.96</td>
<td>-</td>
<td>0.99</td>
<td>22.11</td>
<td>0.75</td>
<td>16.58 (11.44)</td>
<td>[48]</td>
</tr>
<tr>
<td>DFTAB</td>
<td>ITO/HTM/CH₃NH₃Pbi₃/PC₆₀P M/Ag</td>
<td>-5.2</td>
<td>10</td>
<td>1.07</td>
<td>17.5</td>
<td>0.69</td>
<td>11.8 (11.1)</td>
<td>[49]</td>
</tr>
</tbody>
</table>

*aAverage PCE
bPCE of PEDOT:PSS based devices

In summary, we have reported **TPA-TVT-TPA** and **TPA-NAP-TPA**, two highly promising novel, simple and low cost TPA-based small molecular HTMs and their successful use in high performance p-i-n PSCs devices. Between these two molecules, **TPA-TVT-TPA** based devices unveiled a higher PCE of 16.32% with an impressive Voc of 1.07 V, which is better than that of PEDOT: PSS (11.5%) under the same condition (AM 1.5G illumination at an intensity of 100 mW cm⁻²). In spite of high performance of the inverted devices using new HTMs, the lower fill factor of these devices should be taken into an account; it can however be further optimized either by new molecular material design or device engineering. Generally, the appropriate combination between linear π-conjugated cores and TPA end capping moieties can result a straightforward, low cost and high efficient HTMs not only for...
conventional but also for inverted perovskite devices. The new class of materials based on this design paves the way for the development and commercialization of perovskite solar cells in the future.

Supporting Information

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

Acknowledgements

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Reference


A simple and cost-effective hole-transporting materials have been synthesised and used successfully in inverted perovskite solar cells. The device with TPA-TVT-TPA exhibited a high power conversion energy of 16.32% and it is going to be the suitable replacement to the expensive PEDOT:PSS.
Supporting Information

Thienylvinlenethienyl and Naphthalene Core Substituted with Triphenylamines - Highly Efficient Hole Transporting Materials and their Comparative Study for Inverted Perovskite Solar Cells

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Experimental

Materials:
All chemicals and reagents were purchased from commercial vendors and used directly without any further purification. Reactions were monitored by thin layer chromatography (TLC) and were carried out under argon atmosphere.

Instrument and Measurements:
$^1$H and $^{13}$C NMR spectra were performed on a Bruker 600 MHz spectrometer. High-resolution mass spectra were acquired on an LTQ Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) equipped with an electrospray ionisation (ESI) source,
operating in the positive ion mode at a resolution of 120,000 (at \( m/z \) 400). Reserpine ([M+H]\(^+\), \( m/z \) 609.28066) was used as a lockmass calibrant to increase the measurement accuracy. UV-Vis spectra were recorded on a Shimadzu UV-1800 spectrometer. Differential-scanning-calorimetry (DSC) was performed using a Q100 DSC Chimaera equipped with a cooling apparatus. The thermogravimetric analysis (TGA) was performed using a Q500TGA Pegasus. Photoelectron spectroscopy in air (PESA) measurements was conducted using on an AC-2 photoelectron spectrometer (Riken-Keiki Co.).

**Synthesis**

![Synthesis Scheme 1](image)

**Scheme 1.** Synthesis of TVT and NAP. Synthesis routes of TPA-TV-TTPA and TPA-NAP-TPA. Reagent and conditions: (a) 1-iodo-4-methoxybenzene, KOH, CuCl, 1,10-phenanthroline monohydrate, toluene, 120 °C, overnight; (b) trans-1,2-di(2-thienyl)ethylene, n-butyllithium, tetramethylethylenediamine, trimethylin chloride, tetrahydrofuran, RT, overnight; (c) DMF, Pd(PPh3)4, 110 °C, 48 h; (d) 2M K2CO3, toluene, Pd(PPh3)4, 120 °C, 48 h.
Synthesis of 4-bromo-N,N-bis(4-methoxyphenyl)aniline (2):

Compound 3 (2 g, 11.6 mmol), 1-iodo-4-methoxybenzene (5.97 g, 25.5 mmol), KOH (5.1 g, 90.5 mmol), CuCl (0.05 g, 0.5 mmol) and 1,10-phenanthroline monohydrate (0.1 g, 0.5 mmol) were dissolved in anhydrous toluene. After being degassed by argon for 20 min, the reaction mixture was heated at 120 °C overnight. Then the mixture was cooled to room temperature (RT). Excessive potassium hydroxide (KOH) was neutralized by water. After that, the mixture was extracted by dichloromethane (DCM). The organic layer was dried over anhydrous sodium sulphate (Na$_2$SO$_4$) and concentrated by evaporation. The crude product was purified by silica gel chromatography using a mixture of hexane and DCM as eluent to obtain product as a white crystal (2.5 g, 56%). $^1$H NMR (600 MHz, CDCl$_3$, ppm): $\delta$ 7.16 (d, $J$ = 9.0 Hz, 2H), 6.95 (d, $J$ = 8.4 Hz, 4H), 6.75 (d, $J$ = 8.4 Hz, 4H), 6.72 (d, $J$ = 8.4 Hz, 2H), 3.72 (s, 6H). $^{13}$C NMR (120 MHz, CDCl$_3$, ppm): $\delta$ 156.23, 151.33, 140.35, 135.74, 127.18, 118.68, 114.69, 83.41, 55.48, 24.86.

Synthesis of (E)-1,2-bis(5-trimethylstannyl)thiophen-2-yl-ethene (4)

In a 250-ml round bottom flask, trans-1,2-di(2-thienyl)ethylene (1.3 g, 6.76 mmol) and tetramethylethlenediamine (2.3 mL, 15.1 mmol) were mixed in anhydrous tetrahydrofuran (THF) (50 ml) at -78 °C. Afterwards, n-butyllithium (2.0M solution in cyclohexane, 8.2 mL, 16.1 mmol) was added dropwise at -78 °C. The mixture was heated at 100 °C. After 1 hr, the reaction solution was cooled to -78 °C in order to add trimethyltin chloride in THF (1.0M solution in THF, 16.5 mL, 16.1 mmol). The mixture was stirred overnight at room temperature. The crude component was extracted by water and diethyl ether. The organic layer was dried over anhydrous sodium sulfate and concentrated by evaporation. It was purified by doing recrystallization from ethanol to afford the desire product as gray.
crystalline solid (1.5 g, 43%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.04 (d, $J$ = 2.4 Hz, 2H), 7.02 (s, 2H), 7.00-6.99 (d, $J$ = 2.0 Hz, 2H), 0.30 (s, 18 H). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.04 (d, $J$ = 2.4 Hz, 2H), 7.02 (s, 2H), 7.00-6.99 (d, $J$ = 2.0 Hz, 2H), 0.30 (s, 18 H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 184.24, 137.53, 135.78, 127.05, 121.22.

**Synthesis of (E)-4,4'-(ethene-1,2-diylbis(thiophene-5,2-diyl))bis(N,N-bis(4-methoxyphenyl) aniline) (TPA-TV-T-TPA):**

(E)-1,2-bis(5-trimethylstannyl) thiophen-2-yl-ethene (200 mg, 0.386 mmol) and c (406 mg, 1.057 mmol) were vacuumed for 20 minutes prior to adding anhydrous DMF (20 ml). The solution was degassed with argon for 20 minutes and then tetrakis(triphenylphosphine)palladium (17 mg, 0.014 mmol) was added. The reaction was refluxed at 110 °C for 2 days. After cooling to room temperature, the reaction mixture was extracted with chloroform and water. The organic layer was dried over anhydrous sodium sulfate and concentrated by evaporation. After removing the solvent under reduced pressure, the residue was purified using silica gel column chromatography (eluent: Hx:CF:DCM 6:2:2 (v:v:v)). The crude product was recrystallized from hot methanol to yield an orange red solid (170 mg, 55%) like the desire compound. $^1$H NMR (600 MHz, CDCl$_3$, ppm): $\delta$ 7.32-7.30 (d, $J$ = 8.4 Hz, 4H), 7.00-6.98 (d, $J$ = 9 Hz, 10H), 6.87-6.82 (m, 8H), 6.77-6.75 (d, $J$ = 8.4 Hz, 8H), 3.72 (s, 12 H). $^{13}$C NMR (120 MHz, CDCl$_3$, ppm): $\delta$ 156.05, 148.30, 143.23, 140.72, 140.59, 127.29, 126.73, 126.31, 126.24, 122.19, 120.99, 120.42, 114.76, 55.52. ESI-MS: C$_{50}$H$_{42}$N$_2$O$_4$S$_2$$^{**}$ $m/z$ 798.50 (calculated $m/z$ 798.26).
Synthesis of 4,4’-(naphthalene-2,6-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (TPA-NAP-TPA):

In a round bottom flask 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (150 mg, 0.395 mmol), 4-bromo-N,N-bis(4-methoxyphenyl)aniline (455 mg, 1.184 mmol), and 2 M aqueous K$_2$CO$_3$ solution (12 mL) were dissolved in degassed toluene (18 mL). The solution was purged with argon for 15 minutes, then tetrakis(triphenylphosphine)palladium (16.18 mg, 0.014 mmol) was added. The reaction was stirred at 120 °C for 2 days. Then the reaction mixture was cooled to room temperature and extracted with chloroform and water. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated by evaporation. After removing the solvent under reduced pressure, the residue was purified using silica gel column chromatography (eluent: Hexane : Ethyl Acetate 10:1 v:v)). Then the crude product recrystallized from hot Methanol to yield the desired compound as a light brown solid (150 mg, 50%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.89 (s, 2H), 7.81-7.80 (d, $J = 8.4$ Hz, 2H), 7.65-7.63 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, 2H), 7.48-7.47 (d, $J = 8.4$ Hz, 4H), 7.03-6.96 (m, 12H), 6.79-6.77 (d, $J = 9.0$ Hz, 8H), 3.73 (s, 12 H). $^{13}$C NMR (120 MHz, CDCl$_3$): $\delta$ 155.93, 148.21, 140.88, 137.84, 132.92, 132.63, 128.45, 127.71, 126.65, 125.58, 124.39, 120.86, 114.74, 55.53. ESI-MS: C$_{50}$H$_{42}$N$_2$O$_4^{+}$ m/z 734.50 (calculated m/z 734.31).

Device fabrication and characterization:

Poly(3,4-ethylenedioxythiophene) polystyrene sulphonate (PEDOT:PSS, Al 4083) and bathocuproine (BCP) were purchased from Heraeous and Lumtec, respectively. PbI$_2$ was purchased from TCI (Tokyo Chemical Industry). Other chemicals were purchased from Sigma-Aldrich. PCBM (60) was purchased from Nano-C. Methylammonium iodide (MAI) was synthesized according to the reported method. Perovskite precursor solution (MAPbI$_3$)
was prepared by dissolving MAI and PbI$_2$ with stoichiometric ratio in gamma-butyrolactone/dimethyl sulfoxide (7:3 v/v, 1.1 M) at 80°C.

Perovskite solar cells were prepared on pre-cleaned patterned ITO substrate. Filtered PEDOT:PSS solution was spin-coated on ITO at 3000 rpm and annealed at 150°C for 10 min.

For TPA-NAP-TPA and TPA-TVT-TPA based devices, the molecules were dissolved in 1,2-dichlorobenzene at 5 mg/ml and spin-coated on ITO substrate. The film thickness was varied by changing the spin speed from 2000 rpm to 5000 rpm. The perovskite precursor solution (pre-heated at 80°C) was spin-coated onto these hole-transporting layers at 1000 rpm for 10 s and 4000 rpm for 30 s, 250 μL toluene was dripped on the sample surface at 15 s of the second step spin-coating. Subsequently, the perovskite layer was annealed at 80°C for 5 min, 100°C for 30 min. The PCBM solution was coated from chlorobenzene solution (20 mg/mL) at 1000 rpm for 60 s. The devices were completed by evaporating BCP (6 nm) and Ag (120 nm) sequentially under high vacuum (1× 10$^{-6}$ mbar). The active area was 7 mm$^2$ as defined by the overlapping between back electrode and ITO. Current density-voltage ($J$-$V$) characteristics was measured using a calibrated solar simulator (AAA, SAN-EI ELECTRIC CO., LTD.) coupled with Keithley 2400 Source meter. External quantum efficiency (EQE) was obtained by combining a monochromatic light source, a light chopper and a lock-in amplifier (SR830-DSP).
Figure S1. (a) \(^1\text{H} \) (400 MHz, CDCl\(_3\)) spectrum and (b) \(^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) spectrum of \((E)-1,2\)-bis(5-trimethylstannyl)thiophen-2-yl-ethene (2).
Figure S2. (a) $^1$H (600 MHz, CDCl$_3$) spectrum and (b) $^{13}$C NMR (120 MHz, CDCl$_3$) spectrum of 4-bromo-$N,N$-bis(4-methoxyphenyl)aniline (4).
Figure S3. (a) $^1$H (400 MHz, CDCl$_3$) spectrum and (b) $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of TPA-TV-T-TPA.
Figure S4. (a) $^1$H (400 MHz, CDCl$_3$) spectrum and (b) $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of TPA-NAP-TPA.
Figure S5. Normalised absorption and emission spectra of TPA-TVTTPA and TPA-NAP-TPA in chloroform (CF) solution.

Figure S6. Thermogravimetric analysis (TGA) curve of TPA-TVTTPA and TPA-NAP-TPA.
Figure S7. Differential scanning calorimetry (DSC) of (a) TPA-NAP-TPA and TPA-TVTT-TPA with scan rate of 10 °C/min under N₂ atmosphere.

Figure S8. Hole transport properties of various HTMs based on the device structure ITO/HTM/MoO₃/Au. The hole mobility ($\mu_h$) was obtained by fitting the data according Mott–Gurney law:

$$J = \frac{9\varepsilon \mu V_d^2}{8L^3}$$

where $\varepsilon$ is the relative permittivity, $L$ is the film thickness.
Figure S9. Atomic-force microscopy (AFM) of TPA-NAP-TPA (a) and TPA-TVT-TPA (b).

Figure S10. SEM images of perovskite films on top of PEDOT:PSS (a), TPA-NAP-TPA (b), and TPA-TVT-TPA (c); the corresponding grain size distribution was displayed in d, e and f.
Figure S11. X-ray diffraction patterns (XRD) of perovskite films on top of PEDOT:PSS, TPA-NAP-TPA and TPA-TV-T-TPA.

Figure S12. Contact angles of perovskite precursor solution on PEDOT:PSS (a), TPA-NAP-TPA (b), and TPA-TV-T-TPA (c).
Figure S13. a) Hysteresis measurements of PSCs at different scanning directions and the respective PCEs; b) Stabilized photocurrent measurement at maximum power point voltage of the PSCs.

Figure S14. Statistical analysis of PSCs based on different HTMs. Four photovoltaic parameters are listed: \(V_{oc}\) (a), \(J_{sc}\) (b), \(FF\) and PCE (d).
Figure S15. Stability measurement of the fabricated devices stored under ambient environment with 50% humidity without sealing. The PEDOT:PSS based PSC failed in 2 hrs while the TPA-NAP-TPA and TPA-TV-T-TPA based devices show a much longer lifetime.