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Facile Synthesis of Hole Transporting Material with Silafluorene Core for Efficient Mesoscopic $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Solar Cells

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A novel electron-rich small-molecule, 4,4'-(5,5-dihexyl-5H-dibenzo[b,d]silole-3,7-diyl)bis(N,N-bis(4-methoxyphenyl)aniline (S101), containing silafluorene as core with arylamine side groups, has been synthesized via a short efficient route. When incorporated into a $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cell as a hole transporting material (HTM), a short circuit photocurrent density (J_{sc}) of 18.9 mA cm^{-2} , an open circuit voltage (V_{oc}) of 0.92 V, a fill factor (FF) of 0.65 contributing to an overall power conversion efficiency (PCE) of ~11% was obtained which is comparable to the PCE obtained using the current state-of-the-art HTM 2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) ($\eta=12.3\%$). S101 is thus a promising HTM with the potential to replace the expensive spiro-OMeTAD due to its comparable performance and much simpler and less expensive synthesis route.

In recent years, organic–inorganic metal halide perovskites, in particular methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) have emerged as very promising light harvesting materials for high performance and low cost photovoltaic technology [1–3]. The methylammonium lead halide perovskites have properties such as excellent ambipolar mobility, large exciton diffusion lengths, high extinction coefficients, direct bandgap and excellent absorption throughout the UV-Vis-NIR spectrum which makes them excellent light harvesting materials [4–7]. Since the reports of an efficient solid state photovoltaic device using a perovskite as light absorber by Grätzel, Park et al. [2] and

Snaith et al. [1], the growth in efficiencies has been unprecedentedly rapid so that a certified PCE of 20.1% has recently been reported [8–10]. A typical solid state perovskite solar cell comprises a nanocrystalline mesoporous TiO_2 anode, a perovskite absorbing layer, a hole transporting layer and a metallic counter electrode. In addition to the quality of the perovskite film, the performance of perovskite solar cells is also strongly affected by the use of charge transporting layers, with high efficiencies only being obtained when using an HTM. In spite of the high price of spiro-OMeTAD, which is due to its multistep low yielding synthesis and difficult and expensive purification process, it is the most widely used HTM for perovskite based solar cells, as it has produced the highest device efficiencies to date. However, there has been a concerted research effort to design and synthesize alternative HTMs, which are more economical and show device performance comparable to spiro-OMeTAD [4,11]. Several solution processable conjugated polymers including P3HT, and poly(triarylamine) (PTAA) have been employed as HTMs, however their device results to date have been markedly inferior to that of spiro-OMeTAD [12]. A number of small molecule HTMs based on ethylenedioxythiophene [13], cruciform oligothiophenes [14], pyrene [15], triptycene [16], triazines [17], conjugated quinolizino acridine [18], carbazole [19], planar triphenylamine [20] furan [21], silolothiophene [22], methoxydiphenylamine-substituted carbazole [23], tetrathiafulvalene [24], phenoxazine [25], po-spiro-OMeTAD [26], spiro-thiophene [27], [2,2] paracyclophane [28] and ethene-tetraarylamine [29] cores have also been reported. The best performing HTMs show similar or superior performance to spiro-OMeTAD in some aspects but no material has yet emerged clearly superior in all aspects of device performance, particularly in terms of cost, device efficiency and stability. Hence it remains a key challenge to make simple, cost effective and high performing HTMs.

The present study reports a novel HTM S101 (Fig. 1) based on an electron rich silafluorene core. Silole and its derivatives have been widely used in organic electronics because of their excellent properties including good redox stability in air, and

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Electronic Supplementary Information (ESI) available: Experimental details, spectra, results of crystal packing simulations and analysis of manufacturing costs for S101 and spiro-OMeTAD. See DOI: 10.1039/c000000x

high charge carrier mobilities [30–32]. In this work an electron rich silafluorene is used as core, to which are linked hole-accepting triphenylamine moieties while hexyl chains are attached to the silicon atom to produce high solubility in organic solvents and so improve processability. The S101 molecule has planar structure which is desirable for promoting intramolecular π -delocalization and intermolecular π - π stacking, which favour both, charge carrier mobility and lifetime, boosting device efficiency [33]. Silafluorene core based materials also has been used in organic light emitting diodes [34]. S101 was synthesized from a relatively inexpensive commercially available Silafluorene derivative in a single step with an acceptable yield (45%). In addition to extensive investigation of its material properties, we have also investigated the performance of S101 in mesoscopic perovskite solar cells in terms of I-V characteristics and charge carrier dynamics. The devices fabricated using S101 demonstrated efficiency $\sim 11\%$ which is comparable to the values obtained using the state-of-the-art HTM spiro-OMeTAD.

Scheme 1. Synthetic route for S101.

Fig. 1 shows the chemical structure of the S101 and spiro-OMeTAD together with the electronic density distribution of their frontier orbitals calculated by density functional theory (DFT). For S101, the highest occupied molecular orbital (HOMO) level shows π -bonding character, spreading over the whole molecule; while the lowest unoccupied molecular orbital (LUMO) shows π^* -antibonding character being predominately localized on the central silafluorene and two benzene units. The calculated HOMO energy of S101 (-4.49 eV) is quite close to that of spiro-OMeTAD (-4.48 eV), which would promote effective hole transfer from perovskite to S101.

The hole transfer rate of hole-transporting materials can be described by the Marcus-Hush equation which is dominated by two important parameters, namely, (1) reorganization energy and (2) electronic coupling, which can be obtained from DFT calculations (see the Computational Methods in Supporting Information). Fig. S1 (supporting information) demonstrates the predicted crystal structures of S101 and spiro-OMeTAD with all possible hole-hopping pathways. The molecular structure of S101, with a planar silafluorene core, has much smaller intermolecular distances, resulting in larger electronic coupling between HOMO levels of neighbouring molecules, which can improve the hole transporting mobility (see Table S1 and S2 in ESI). S101 shows smaller hole reorganization energy (0.13 eV) than spiro-OMeTAD (0.15 eV) and predicted hole mobilities for the simulated charge transport pathways (0.215 , 0.141 , and 0.049 $\text{cm}^2/\text{V}\cdot\text{s}$) which are one order of magnitude higher than those of spiro-OMeTAD (0.0058 , 0.0046 , and 0.0532 $\text{cm}^2/\text{V}\cdot\text{s}$). These values are comparable with our previously synthesized high performing furan-based HTM F101 [21], showing

that S101 is also a promising HTM with potentially relatively high hole mobility.

Together with its predicted material properties, the short relatively efficient synthesis route of S101 makes it an attractive HTM for any potential perovskite solar cell industry. The synthesis route of S101 (Scheme 1) is shorter and less expensive as compared to spiro-OMeTAD (see Scheme S1 and Table S4 in ESI for analysis of relative synthesis costs). The commercially available relatively inexpensive 3,7-dibromo-5,5-dihexyl-5H-dibenzo[b,d]silole was Suzuki coupled with a triphenylamine boronic acid derivative [35] to give S101 in 45% yield from an unoptimised reaction. NMR spectroscopy and MALDI-TOF mass spectrometry confirmed the molecular structure of S101.

Fig. 1(a) Chemical structure of S101, electronic density distribution of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) for S101; (b) chemical structure of spiro-OMeTAD, electronic density distribution of LUMO and HOMO for spiro-OMeTAD.

The optoelectronic properties of S101 have been systematically investigated and compared with those of spiro-OMeTAD. In the UV-Vis absorption spectra (shown in Fig. 2a), absorption peaks of S101 and spiro-OMeTAD were observed at 381 nm and 384 nm, respectively. The absorption onset wavelengths of S101 and spiro-OMeTAD are 434 nm and 420 nm, respectively which correspond to band gaps of 2.86 eV and 2.95 eV, respectively. The onset of absorption in S101 is slightly red shifted with respect to spiro-OMeTAD which can be attributed to the more extended conjugation in the backbone of S101 due to the presence of two extra phenyl rings between the nitrogens. From the cyclic voltammograms of S101 and spiro-OMeTAD, shown in Fig. 2b, the pair of redox peaks for S101 is observed to be highly reversible, showing that it has excellent electrochemical stability. The HOMO energy level was calculated from the CV data using the following equation: $E_{\text{HOMO}} = -5.1 - (E_{\text{ox,HTM}} \text{ vs. } \text{Fc}/\text{Fc}^+)$ (eV), where $E_{\text{ox,HTM}} \text{ vs. } \text{Fc}/\text{Fc}^+$ is the onset of oxidation potential of ferrocene, which is used as reference and -5.1 eV is the redox potential of ferrocene [36]. The HOMO levels of S101 and spiro-OMeTAD as calculated from CV are

5.32 eV and 5.15 eV, respectively while the reported HOMO energy level of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is 5.44 eV [2] which indicates that S101 has favourable energetics for the hole transfer (Fig. 2c). The energetics of the system employing S101/spiro-OMeTAD are represented in Fig. 2d and Table 1 summarizes the optical and electrochemical properties of the two HTMs. Differential scanning calorimetry (DSC) showed S101 has a weak glass transition (T_g) at 45 °C and a melting point (T_m) of 143 °C (see Figure S5 in ESI); cf. $T_g = 124$ °C, $T_m = 245$ °C for spiro-OMeTAD. The cross-sectional scanning electron microscopy (SEM) images shown in Figure 3d displays the various interfaces of the S101 HTM based $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cell indicating we have achieved formation of a well-defined hybrid structure with clear interfaces. From the FE-SEM image the thicknesses of the TiO_2 , perovskite and the HTM layers can be estimated to be ~350, 550 and 200 nm, respectively. To investigate the charge-carrier mobility of S101 and spiro-OMeTAD, Field effect transistors were fabricated. To determine the charge carrier mobility, field effect transistors (FET) were fabricated using spiro-OMeTAD and S101. Hole mobilities evaluated from FET transfer characteristics (shown in Figure S6 in ESI) are $1.2 \times 10^{-4} \text{ cm}^2/\text{Vs}$ (at $V_d = -50 \text{ V}$; $V_g = -40 \text{ V}$) for spiro-OMeTAD, and $7.2 \times 10^{-5} \text{ cm}^2/\text{Vs}$ (at $V_d = -50 \text{ V}$; $V_g = -40 \text{ V}$) for S101. Contrary to the predictions, Spiro-OMeTAD thus has slightly higher field-effect mobility than S101, which suggests that spiro-OMeTAD based devices should show slightly higher fill factors.

Fig 2(a) Absorption spectra for spiro-OMeTAD and S101, (b) cyclic voltammograms for spiro-OMeTAD and S101, (c) band diagram for the device with new HTM S101 and spiro-OMeTAD, and (d) cross-sectional SEM image of device fabricated with S101.

Table 1. Optical and electrochemical properties of S101 and spiro-OMeTAD.

HTM	λ_{max} (nm)	λ_{onset} (nm)	$^a E_g$ (eV)	E_{HOMO} (eV)	$^b E_{\text{LUMO}}$ (eV)
S101	381	434	2.86	-5.32	-2.46
Spiro-OMeTAD	384	420	2.95	-5.15	-2.2

[a] Optical band gap (E_g) obtained from the onset value of absorption (λ_{onset}). [b] LUMO calculated by $\text{LUMO} = \text{HOMO} + E_g$.

Fig. 3 Current density vs. voltage curve under AM 1.5G illuminations (100 mWcm^{-2}).

The current–voltage (J–V) characteristics of perovskite solar cells employing S101 and spiro-OMeTAD as HTMs, together with devices without HTM are shown in **Fig. 3** and summarized in Table 2. The PCEs of the best performing device with S101 and spiro-OMeTAD as HTM are 11% and 12.3% respectively. Our study also showed that the device fabricated without the HTM had a PCE of only around 4.7 %, which confirmed that a HTM must be an integral component of the high efficiency perovskite solar cells. The short circuit current densities (J_{sc}) of the cells fabricated using spiro-OMeTAD and S101 are 19.7 mA/cm^2 and 18.9 mA/cm^2 , respectively. The slightly higher current using spiro-OMeTAD can be attributed to its higher HOMO level as compared to S101, which gives spiro-OMeTAD a higher driving force for charge transfer from the perovskite to the HTM. The devices fabricated from both HTMs exhibit similar fill factors. The devices with S101 showed a slightly lower open circuit voltage ($V_{\text{oc}} = 0.92\text{V}$) than devices employing spiro-OMeTAD ($V_{\text{oc}} = 0.975\text{V}$). However, from our CV data, it is observed that HOMO energy level for S101 is deeper than spiro-OMeTAD which should result in higher V_{oc} . As the V_{oc} depends on (1) the splitting of the Fermi levels for photogenerated charges, (2) the recombination, and (3) the energetics of the devices [15, 16, 21], the slightly lower voltage in devices fabricated with S101 as HTM might be due to high recombination which suggests S101 has slightly inferior charge extraction capability as compared to spiro-OMeTAD.

Table 2. Summary of device parameters; open circuit voltage (V_{oc}), current density (J_{sc}), fill factor (FF) and efficiency (η). Area= 0.2 cm^2 .

HTM	$J_{\text{sc}} (\text{mA/cm}^2)$	$V_{\text{oc}} (\text{V})$	FF(%)	$\eta_{\text{max}} (\%)$	$^a \eta_{\text{avg}} (\%)$
S101	18.9	0.92	65	11	10.6
Spiro-OMeTAD	19.7	0.975	64.2	12.3	12.0
W/O HTM	8.54	0.76	72	4.7	4.3

[a] Average PCE is based on six cells in a single batch.

To further elucidate the low V_{oc} obtained from S101 devices, the charge-carrier dynamics at the perovskite/ HTM interface and hole

extraction ability were investigated using steady-state and time-resolved photoluminescence (PL) measurements, in which the efficient quenching of the steady-state PL and the reduction of the PL lifetime are indicators of efficient charge extraction at the perovskite/HTM interface. From the PL spectra (Fig. 4a), it is evident that both HTMs significantly quench perovskite emission signal, with HTM spiro-OMeTAD having a slightly better PL quenching efficiency (ca. 93%) relative to S101 (ca. 89%). Time-resolved PL measurements were carried out with excitation at 404 nm and monitoring the entire emission spectral range (Fig. 4b). The pristine perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) exhibited a radiative life time of about 2.7 ns, whereas this was shorter in $\text{CH}_3\text{NH}_3\text{PbI}_3$ /HTM samples. $\text{CH}_3\text{NH}_3\text{PbI}_3$ /spiro-OMeTAD samples showed a decay time of 0.8 ns whereas $\text{CH}_3\text{NH}_3\text{PbI}_3$ /S101 samples showed a longer decay life time of 1.1 ns. This indicates that spiro-OMeTAD has slightly better hole extraction ability as compared to S101. As a result it is unlikely that further device optimization will enable the device performance of S101 to exceed that from spiro-OMeTAD-based devices. The values of 11% and 12.3% obtained from our devices are below the current state-of-the-art values of over 20% but those result from extensive optimization of the perovskite preparation and device fabrication. We believe that with similar optimization efficiency values close to 20% might be attainable using S101. In that case, the much lower cost of S101, due to its simpler synthesis and comparable device performance might offer a potentially lower cost/power ratio which is the ultimate economic criterion for photovoltaic systems.

Fig. 4(a) The steady-state photoluminescence (PL) spectra and (b) time-resolved PL spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbI}_3$ /S101 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ /spiro-OMeTAD.

Conclusions

A novel HTM S101 based Silafluorene core has been synthesized via a short, low cost route and employed in perovskite as hole transporting layer. The devices fabricated with HTM S101 shows a PCE of $\sim 11\%$ which is comparable to that ($\eta = 12.3\%$) obtained with the state of the HTM spiro-OMeTAD. We firmly believe that with further optimization and fine tuning of various device parameters and by developing more understanding of interfacial characteristics, there can be further significant enhancement in the device performance. The short, efficient synthesis and good device performance

means S101 has potential to replace the more expensive spiro-OMeTAD. This work also lays out a strategy for the design and development of new cost effective and efficient HTMs for PSCs.

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Facile Synthesis of Hole Transporting Material with Silafluorene Core for Efficient Mesoscopic CH₃NH₃PbI₃ Perovskite Solar Cells

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1. EXPERIMENTAL SECTION

(a) *Synthesis of 4,4'-(5,5-dihexyl-5H-dibenzo[b,d]silole-3,7-diyl)bis(N,N-bis(4-methoxyphenyl)aniline (S101).* 3,7-Dibromo-5,5-dihexyl-5H-dibenzo-[b,d]-silole (0.8 g, 1.58 mmol), {4-[bis(4-methoxyphenyl)amino]phenyl} boronic-acid [28] (1.16g g, 3.3 mmol), Pd(0)(PPh₃)₄ (0.13 g, 0.1 mmol), K₂CO₃ (5 mL) and degassed toluene (20 ml) were transferred in to a 50 mL RBF. This reaction mixture in RBF was then stirred at 90 °C under nitrogen for 48 h. The reaction mixture was cooled down to r.t. and poured into water, extracted with dichloromethane (DCM) and the extract was washed with water. The DCM layer was dried over MgSO₄, concentrated and the residue mixture was purified by column chromatography on silica gel eluting with DCM/hexane=1/1 (v/v) to obtain the product as a white solid (0.68 g, 45 %). ¹H-NMR (CDCl₃, 400MHz): δ(ppm): 7.86 (d, 2H, J=8Hz), 7.80(d, 2H, J=1.6Hz), 7.63 (dd, 2H, J=8.2 Hz), 7.50 (d, 4H, J=8Hz), 7.12 (d, 8H, J=8Hz), 7.04 (d, 4H, J=8Hz), 6.87 (d, 8H, J=8Hz), 3.82 (s, 12H), 1.42 (m, 4H), 1.29 (m, 4H), 1.22 (m, 8H), 0.99 (m, 4H), 0.83 (t, 6H, J=6.8Hz). ¹³C-NMR (CDCl₃, 400MHz): δ (ppm): 155.99, 148.16, 146.79, 141.13, 139.42, 138.71, 133.44, 131.34, 128.46, 127.55, 126.66, 121.17, 121.08, 114.86, 55.65, 33.23, 31.49, 24.08, 22.70, 14.20, 12.56. HRMS (MALDITOF): m/z calcd for C₆₄H₆₈N₂O₄Si, 957.34; found, 957.

(b) Device Fabrication

Fluorine doped tin oxide (FTO, <14 ohm/square, 2.2 mm thick) substrates were laser etched to form the desired pattern, which was subsequently cleaned by sonication in decon soap solution and ethanol respectively. A thin compact layer of TiO₂ acting as a blocking layer, is about 80 - 100 nm, was deposited by aerosol spray-pyrolysis, using titanium diisopropoxide bis(acetylacetonate) (75 wt. % in isopropanol) and absolute ethanol in the ratio 1:9 by volume

and ambient air as the carrier gas. Then these substrates were annealed at 450 °C for 30 min and then were treated with 100 mM TiCl_4 solution for 60 min at 70 °C, followed by rinsing with deionized water and ethanol and subsequent annealing at 500 °C for an hour. The mesoporous TiO_2 layer composed of 30-nm-sized particles was deposited by spin coating at 5,000 r.p.m. for 30 s using a commercial TiO_2 paste (Dyesol DSL 30 NRD) diluted in ethanol (2:7, weight ratio). After drying at 125 °C, the TiO_2 films were gradually heated to 500 °C, baked at this temperature for 15 min and cooled to room temperature. An organic-inorganic perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ was deposited by the published sequential method [3]. Lead (II) iodide (1 M) was dissolved in N,N-dimethylformamide overnight under stirring conditions at 70 °C and was spincoated on the substrates at 6000 r.p.m for 5 s. These substrates were then dried for 30 min at 70 °C. Subsequently the films were dipped in 8 mg/mL solution of $\text{CH}_3\text{NH}_3\text{I}$ in 2-propanol for 20 min and were rinsed with 2-propanol and were spun at 4000 rpm for 30s for drying followed by annealing then at 100 °C for 30 min. The HTMs S101 and spiro-OMeTAD were dissolved in chlorobenzene (90 mg/ml and 100 mg/ml) respectively and spincoated on these substrates at 4000 rpm for 30s. Additives like Li $(\text{CF}_3\text{SO}_2)_2\text{N}$, tert-butylpyridine and tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(III) (FK 102) dopant were added to the above solution as per literature [3]. The masked substrates were placed in a thermal evaporator for gold (Au) deposition via shadow masking. Thickness of the Au electrode was about 100 nm and an active area of 0.2 cm^2 was defined by the overlap of TiO_2 and Au.

2. Materials and Equipment

Reactants and reagents, unless otherwise stated, were purchased either from Sigma-Aldrich or Lumtec (Taiwan), and used without further purification. The boronic acid was prepared by a literature route [33]. Both absorption and reflection TiO_2 pastes were purchased from Dyesol.

Column chromatography was carried out using Merck silica (230 – 400 mesh) while thin layer chromatography (TLC) was performed on Merck silica 60 Al-backed plates (20 cm x 20 cm). ^1H and ^{13}C NMR data were obtained on a Bruker DPX 400 MHz spectrometer with chemical shifts referenced to DMSO- d_6 . Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Shimadzu Biotech AXIMA-TOF. UV-Vis absorption spectra were recorded using Shimadzu UV-3600 Spectrometer. CV measurements were carried out on a CHI411 electrochemical workstation. All CV measurements were recorded in CH_2Cl_2 with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte (scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$) and the experiments were performed with a conventional three electrodes configuration consisting of a platinum wire working electrode, a gold counter electrode, and an Ag/AgCl in 3 M KCl reference electrode. Photovoltaic measurements utilized an AM 1.5G solar simulator equipped with a 450 W xenon lamp (model 81172, Oriel). Its power output was adjusted to match AM 1.5G sunlight (100 mWcm^{-2}) by using a reference Si photodiode. The I–V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2612A digital source meter. The readings were taken in reverse scan mode, with applied potential starting at V_{oc} and being reduced to 0 V. All devices were measured by masking the active area with a black tape mask. Steady-state PL spectra of pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{HTM}$ film samples were recorded using a spectrofluorometer (Fluorolog, HORIBA JobinYvon). For time resolved fluorescence spectroscopy, a time-correlated single photon counting (TCSPC) system was used. The samples were excited with a picosecond diode laser (Edinburgh Instruments, EPL405) at 404.6 nm (77.1 ps pulses, 5.5 μW , 1 MHz) and emission was detected after a long pass filter that cut out the scattered excitation light and

covered the entire perovskite emission spectral range. The counts were collected for a 10 min time interval. The TCSPC setup is described in detail in literature [1].

3. COMPUTATIONAL METHODS

The hole transfer can be represented by Marcus-Hush equation of $k_h = \frac{V_h^2}{\hbar} \sqrt{\frac{\pi}{\lambda_h k_B T}} \exp\left(-\frac{\lambda_h}{4k_B T}\right)$, where V_h is the electronic coupling between HOMO levels of neighbouring molecules in the HTM crystals, T is the temperature, k_B and $\hbar$ refer to Boltzman and Planck constants. λ_h is the hole reorganization energy calculated by adiabatic potential energy surfaces method. Electronic coupling V_{ij} , defined as $\langle \phi_i | \hat{F} | \phi_j \rangle$, can be calculated by projecting the Fock Matrix of dimer onto molecular orbitals of respective donor (ϕ_i) and acceptor molecule (ϕ_j) with the subsequent symmetric orthogonalization, where $\hat{F}$ is the Kohn-Sham Fock operator for the dimer system.

Then the hole mobility can be well described by the Einstein relation $\mu = \frac{eD}{k_B T}$, where e is the electron charge and D is the charge diffusion coefficient of charge carriers, which can be approximately describe as $D = \frac{1}{2d} \sum_i r_i^2 k_i P_i$, where k_i and r_i are the charge-transfer rate and intermolecular distance of the dimer, and P_i is the probability for hole hopping along the i th pathway.

The density functional theory (DFT) calculations using CAM-B3LYP functional together with basis sets 6-31G(d, p) were performed to optimize the molecular structures of molecules S101 and spiro-OMeTAD and study their transporting properties. The crystal structures of S101 and spiro-OMeTAD were predicted by using the polymorph module in Material Studio 5.0. The PBE functional and Dreiding force field were combined to predict the crystal structures. Three possible stable crystal structures with space groups for S101 (C2/C, P/1, and P212121) and

Spiro-OMeTAD (C2/C, P21, and P212121) were considered in our study for calculating hole mobility. All the DFT calculations were performed using Gaussian09 program (Revision D.01).

Figure S1. (a) Hole transfer pathways for possible crystal structure (1) C2/C, (2) P/1 and (3) P212121 of S101 molecule; (b) hole transfer pathways for possible crystal structure (1) C2/C, (2) P21 and (3) P212121 of Spiro-OMeTAD molecule.

Table S1. Intermolecular electronic coupling, distance and transfer rate and hole mobility of S101 crystal (Fig 2a).

Crystals	Pathway	Electronic Coupling (meV)	Distance (Å)	Hole Transfer Rate (s^{-1})	Mobility ($cm^2/V \cdot s$)
C2/C	1	3.18	8.56750	1.05×10^{11}	0.215
	2	27.5	6.68700	7.81×10^{12}	
	3	5.85	10.86821	3.54×10^{11}	
P/1	1	26.2	5.73052	7.11×10^{12}	0.141
	2	4.91	6.34593	2.49×10^{11}	
	3	5.67	10.81330	3.33×10^{11}	
P212121	1	12.0	7.08085	1.49×10^{12}	0.049
	2	0.25	13.65105	6.50×10^8	
	3	0.51	10.72813	2.68×10^9	

Table S2. Intermolecular electronic coupling, distance and transfer rate and hole mobility of Spiro-OMeTAD crystal (Fig 2b).

Crystals	Pathway	Electronic Coupling (meV)	Distance (Å)	Hole Transfer Rate (s ⁻¹)	Mobility (cm ² /V·s)
C2/C	1	1.13	17.15	1.32×10 ¹⁰	0.0058
	2	1.99	15.24	4.10×10 ¹⁰	
	3	1.96	16.00	3.96×10 ¹⁰	
P21	1	0.95	16.02	9.38×10 ⁹	0.0046
	2	2.08	13.67	4.48×10 ¹⁰	
	3	0.45	16.30	2.14×10 ⁹	
P212121	1	2.67	15.52	7.36×10 ¹⁰	0.0532
	2	7.80	11.92	6.30×10 ¹¹	
	3	0.11	14.88	1.26×10 ⁸

Figure S2. ¹H NMR spectrum of S101.

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Figure S3. ^{13}C NMR spectrum of S101.

Figure S4. MALDI-TOF mass spectra of S101.

Figure S5. Differential Scanning Calorimetry (DSC) curves for S101.

Figure S6. Transfer characteristics in the p-channel type FET of (a) spiro-OMeTAD and (b) S101. These characteristics are measured at $V_g = -40V$.

Table S3. Time resolved photoluminescence characterization of the $CH_3NH_3PbI_3$ perovskite.

	Fraction	τ_1 (ns)	Fraction	τ_2 (ns)	τ_{av} (ns)
$CH_3NH_3PbI_3$	0.65	3.5	0.35	1.2	2.7
$CH_3NH_3PbI_3$ /Spiro	0.64	0.78	0.36	0.71	0.8
$CH_3NH_3PbI_3$ /S101	0.62	1.02	0.38	1.1	1.1

Analysis of relative costs of manufacture of spiro-OMeTAD and S101

The detailed comparisons between the synthesis of Silole based HTM and spiro-OMeTAD are discussed here, in terms of number of steps, yields of each step, cost of starting materials and total reaction time. As shown in the **Scheme S1**, the comparisons are actually focused on the

synthesis of tetrabromo-spirofluorene core (compound **6**) and S101 core 3,7-(dibromo-5,5-diethyl-5H-dibenzo[b,d]silole) (compound **12**). The data is summarized in **Table S4**.

Scheme S1. Synthetic schemes to the core **6** and **12**, with reaction condition, duration of time and yield of each step indicated.

First of all, in both cases four steps are needed to achieve core molecules from readily available and cheap starting materials. Moreover, the equal number of steps makes the comparison easier. The prices were quoted from Alfa Aesar US website and Fluorochem UK with the largest

possible package size available for fair comparison. The costs of solvents and reagents used in both routes such as THF, DMF, acids, salts, etc. were assumed to be approximately the same - these are very common and inexpensive chemicals and there is an equal number of steps.

In order to make 10 g of (spiro) core **6**, the amount of compound **1** and **3** consumed, calculated from the yield of each step, is 9.0 g and 9.1 g, respectively. The unit price of compound **1** and **3**, is \$76.3/5g and \$580/2.5kg, respectively. As a result, the total cost of starting materials for making core **6** is \$139.5/10g. For comparison, the price of spiro-OMeTAD from Merck, one of the few licensed companies, is about \$850/g. In the same way, in order to make 10 g of (S101) core **12**, the amount of compound **7** and **11** consumed, calculated from the yield of each step, is 20.7 g and 9.3 g, respectively. The unit price of compound **7** and **11**, is \$135.9/100g and \$271/50g, respectively. As a result, the total cost of starting materials for making core **12** ~ \$76/10g. The difference will be rather considerable when scaled up.

The total duration time of the reactions from first step to the end is an important factor to estimate the timeline for production. As we can see from **Table S1** that the total reaction time for making core **12** is almost half of the amount of time for making core **6**. Since both have four steps, it can easily conclude that it is faster to make core **12** than core **6**, which not only saves the time but also saves the manpower which is much more expensive.

In short, we can confirm that making core **12** is cheaper than core **6**. In addition the purification of spiro-OMeTAD requires expensive sublimation, whereas S101 can be purified by cheaper methods such as column chromatography.

Table S4. Summarization of the comparisons, the better one is highlighted.

	total cost of starting materials	number of steps	total duration of reactions	estimated number of days to complete the process
Core 6	\$139.5/10g	4	59.5 hours	5 days
Core 12	\$76/10g	4	27 hours	3 days

References

1. A. El-Zohry, A. Orthaber and B. Zietz, *J. Phys. Chem. C*, 2012, **116** (50), 26144-26153.