Advances in hole transport materials engineering for stable and efficient perovskite solar cells

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ABSTRACT

This article reviews the various hole transporting materials (HTMs) used in perovskite solar cells (PSCs) in achieving high photo conversion efficiency (PCE) and operational stability. The PSCs are the latest development in solution processable solar cells offering PCE (~22%) on a par with that of practically deployed silicon and thin film solar cells. HTMs and electron transporting materials (ETMs) are important constituents in PSCs as they selectively transport charges within the device, influence photovoltaic parameters, determine device stability and also influence its cost. This article critically approaches role of structure, electrochemistry, and physical properties of varied choice of HTMs categorized diversely as small and long polymers, organometallic, and inorganic on the photovoltaic parameters of PSCs conceived in various device configurations. Achievements in tailoring the properties of HTMs to best fit for PSCs are detailed; a well designed HTM suppresses carrier recombination by facilitating the passage of holes but blocking electrons at the HTM/perovskite interface. Moreover, in many PSCs the HTM acts as the first line of defense to external degrading factors such as humidity, oxygen and photon dose, the extent of which depends on its hydrophobicity, permeability, and density.

1. Introduction

Organic inorganic halide perovskites have attracted worldwide attention due to their impressive electrical and optical properties leading to remarkable performance in solar cells and light emitting devices [1–5]. These materials can be represented by a general formula ABX_3 , where A is an organic methylammonium (CH_3NH_3) ion [6] or formamidinium ($NH=CHNH_3$) ion [7–9], B is Pb, Sn, Cs, or Cd ion, and X can be a halogen ion, I, Br, or Cl [10]. The remarkable performance of these perovskites in solar cells is attributed to their broad light absorption throughout the visible and near infrared spectrum, low exciton binding energy (~2 meV), and direct band gap [11]. In addition to high absorption coefficients, these materials demonstrated (i) long carrier lifetime (~270 ns) resulting in diffusion lengths of few microns (~1 μ m in its thin films [12] and up to ~175 μ m in single crystals [13]) so that the carriers can be transported safely across a 300 nm thick perovskite absorber without recombination

[12,14–17], (ii) high dielectric constant (~18–70) [11,18], and (iii) high charge carrier mobility (~10–2320 $cm^2 V^{-1} s^{-1}$) [16,19] thereby making them ideal photovoltaic materials [16,18,20]. Owing to these unique characteristics, a certified power conversion efficiency (PCE) of 22.1% is reported so far [21,22].

Fig. 1 gives a broad overview of the various configurations of PSCs. In a typical device, PSCs employ a thin perovskite absorber layer (~300 nm) between an electron transport layer (ETL) and a HTM. Based on whether electrons or holes are collected at the bottom conducting substrate (usually a transparent conducting oxide, TCO), the PSCs are classified as n-i-p or p-i-n device, respectively. The former is also often termed as conventional and the latter as inverted architectures in the literature, depending on whether an ETL or HTM is deposited over the TCO (Fig. 1). The n-i-p architecture can be further divided into (i) mesoporous PSC, employing a metal oxide semiconductor (MOS) layer (~200–600 nm thick) as ETL with an additional n-type compact layer (CL) over it [4], (ii) meso super

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Fig. 1. The various common device designs employed for PSCs. The designs employ both ETL and HTM (a, c, and d), an insulating scaffold that replaces conducting ETL (b), and PSCs that employ only one of the two selective contacts, such as ETL-free (e) and HTM-free (f). Figures (c and d) refer to conventional (n-i-p) and inverted (p-i-n) architectures that represents if the electron or holes are to be collected at the conducting substrate, respectively. Figure adapted with permission from Ref. [32]. Copy right of AIP Publishing.

structured PSCs, employing an insulating scaffold (Al_2O_3 or ZrO_2) which does not take part in charge collection [23,24], (iii) planar devices without a mesoporous layer but employ only a CL (thickness < 50 nm) [25], (iv) ETL free PSCs where the perovskite layer is deposited directly over the surface modified FTO [26,27], and (v) HTM free PSCs which do not employ an HTM [28]. In architectures (i) and (ii), the ETL may take part in charge collection, whereas in architectures (iii) and (iv), the perovskite works as an absorber as well as the only electron transporter. A particular type of n i p architecture without a back contact is the monolithic one consisting of a compact layer and a triple stack of screen printed mesoporous ETL, a mesoporous spacer and a ~10–15 μm thick conductive carbon layer, all of which are subsequently infiltrated with the perovskite [29]. Alternatively, in p i n devices, holes are collected at the TCO and electrons at the metal back contact. This architecture could also be mesoporous (vi) or a planar (vii) depending on whether the p type layer is a mesoporous or compact only [30,31].

The HTM serves various purposes in PSCs: (i) it is a physical/energetic barrier between anode and perovskite layer that blocks the electron transfer to anode [33], (ii) it improves the hole transfer efficiency [34], (iii) influences the open voltage circuit (V_{oc}) by determining the splitting of the quasi Fermi energy levels of the perovskite [35–38], as will be discussed in detail in Section 3.2 and (iv) avoids the degradation at the metal (Au) perovskite interface which would take place in the absence of a HTM [39,40]. In fact, screening of suitable HTMs and a perovskite led to a V_{oc} as high as 1.5–1.61 V in PSCs [41,42]. Similarly, the presence of an HTM layer has shown to improve surface coverage compared to that of a perovskite layer only

[43] (Fig. 2) and consequently suppress charge recombination by fully separating the top contact from the bottom transport or contact layers leading to improved performance. Apart from benefits on the PCE, the choice of HTM has shown to increase the stability of PSCs. For example, NiO_x as an inorganic HTM layer in inverted PSCs not only showed a PCE > 16% but also 90% stable performance for over 60 days of storage in air [44]. Similarly, the champion HTM in inverted PSCs, 3,4 ethylenedioxythiophene): poly(styrene sulfonic) acid (PEDOT: PSS), is humidity sensitive and also known to cause degradation at conducting substrates due to its acidic nature. Removal of PEDOT: PSS with inorganic counterparts have shown remarkably stable performance in PSCs. Furthermore, when it comes to commercialization of PSCs, their manufacturing cost will play a significant role [45]. Currently, HTM is arguably the most expensive material component in PSCs (see Table 1 for cost comparison of various common HTMs).

Inspired from the crucial role that the HTM plays in improving the device performance as well as in the stability of PSCs, this review aims to provide in depth analysis of various HTMs employed so far. We first define selection criteria to choose an efficient HTM (Section 2) and then explain its role towards charge extraction at the HTM perovskite interface and also in determining the photovoltaic (PV) parameters in PSCs (Section 3). We then detail the wide range of HTMs employed such as organic (small molecules and polymers) and inorganic HTMs in Section 4 and discuss their performance in PSCs. The influence of the HTM on the stability of PSCs is outlined in Section 5 of this manuscript. Finally, we conclude our observations and provide an outlook to developing highly stable and efficient PSCs.

Fig. 2. Top view of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film with (a) and without (b) poly(3-hexylthiophene) P3HT. Figure reproduced with permission from Ref. [43]. Copy right of Elsevier.

2. Selection criteria for hole transport materials in PSCs

The photovoltaic process in PSCs, similar to any other PV technology, takes place in two steps: light absorption by an absorber material (the perovskite in PSCs) followed by selective charge collection at the respective contacts. Towards the latter, the HTM is one important active material in PSCs as it enables efficient hole extraction at the perovskite HTM interface. For efficient device operation, it should offer (i) high hole mobility to reduce losses during hole transport to the hole collecting contact, (ii) compatible ionization potential with that of the perovskite (i.e. highest occupied molecular orbital (HOMO) or valence band maximum (VB) almost matching that of the perovskite absorber so as to minimize injection losses), (iii) high thermal stability and resistance to external degradation factors such as moisture and oxygen for a long term durable PV operation, and (iv) low cost. Furthermore, a low electron affinity will also endow the HTM with beneficial electron blocking properties.

The mobility of the HTM has a significant bearing on the efficiency of the solar cell. Firstly, low mobilities lead to significant Ohmic losses across the HTM lowering the fill factor (FF). A recent computational study [46] shows that the FF improves by a wide margin (from 22% to 80% when the mobility changes from 10^{-6} to $10^{-4} \text{ cm}^2/\text{V s}$). The short

circuit photocurrent (J_{SC}) is also strongly affected (improving two fold w an order of magnitude change in mobility). Thus it is important to utilize HTMs which are as thin as possible (guaranteeing uniform coverage) as well as with high mobilities.

HTMs employed in PSCs can be categorized as inorganic (NiO, CuSCN, CuI, Cu_xO , and Graphene oxide (GO)) or organic (Table 1). The organic HTMs can further be divided into three types as (i) small molecules such as (2,2',7,7' tetrakis(N,N di *p* methoxyphenyl)amine) 9,9' spirobifluorene Spiro OMeTAD, DOR3T TBDT, and Fused F etc. (Please refer to [supplementary material](#) for the chemical name of all HTM materials) or (ii) polymers such as P3HT, PEDOT: PSS and poly(triarylamine) PTAA [47,48] or (iii) Oligomers such as S197 (full name not given). The Energy level diagram of common HTMs and their alignment with perovskite absorbers is shown in Fig. 3.

3. Hole transporting materials and photovoltaic parameters in PSCs

3.1. Charge transport/transfer at HTM perovskite interface

Although initially the role of perovskite was conceived to be only an absorber layer, the subsequent reports on its ambipolar charge trans

Table 1

An account of various common hole transporting materials in perovskite solar cells.

HTM	Hole mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Cost/g (\$)	Perovskite material	Perovskite deposition	Device structure	Dopants	PCE	V _{oc}	Ref.
Spiro-OMeTAD	$10^{-3} - 10^{-4}$ [49,50],	500 [22]	$\text{CH}_3\text{NH}_3\text{PbI}_3$	OSSD	Mesoscopic	Li-TFSI, TBP	19.71	1.08	[51]
FDT		60 [22]	$\text{FAPbI}_3/\text{MAPbBr}_3$	OSSD	Mesoscopic	Li-TFSI, TBP, FK209	20.2%	1.14	[22]
P3HT	< 0.1 [52],	400 - 450*	$\text{CH}_3\text{NH}_3\text{PbI}_3$	OSSD	meso-superstructured	Li-TFSI, TBP, PMMA	15.3	1.02	[53]
PTAA	$10^{-2} - 10^{-3}$ [2],	2500 - 3000*	$(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$	TSSD	Mesoscopic	Li-TFSI, TBP,	20.2	1.06	[54]
PEDOT: PSS	$10^{-2} - 10^{-3}$ [55],	200 - 250*	$\text{CH}_3\text{NH}_3\text{PbI}_3$	OSSD	Inverted planar	Li-TFSI, TBP	18.1	1.1	[56]
CuI	9.3 [57],	10 - 15*	$\text{CH}_3\text{NH}_3\text{PbI}_3$	GSC	Inverted planar		13.58	1.04	[58]
CuSCN	25 [59],	2 - 5*	$\text{CH}_3\text{NH}_3\text{PbI}_3$	OSSD	Inverted planar		16.6	1.00	[60]
NiO	0.141 [61],	10 - 15*	$\text{CH}_3\text{NH}_3\text{PbI}_3$	SET	Inverted planar		17.3	1.06	[62]
Cu_2O	100 [63],	2 - 12.5*	$\text{CH}_3\text{NH}_3\text{PbI}_3$	OSSD	Inverted planar		16.52	1.07	[64]
GO		150 - 400*	$\text{CH}_3\text{NH}_3\text{PbI}_3$	SD	Mesoscopic		15.1	1.04	[65]

SD: Sequential deposition, **OSSD:** One step spin coating deposition, **GSC:** Gas solid crystallization process.

TSSD: Two step spin coating deposition, **SET:** solvent engineering technique, **DSVD:** Dual source vapor deposition.

FDT: 2,7-bis(4-methoxyphenyl)amino) spiro[cyclopenta [2,1-b:3,4-b']dithiophene-4,9-fluorene.

TBP: 4-*tert*-butylpyridine, **Li-TFSI:** lithium bis(trifluoromethylsulfonyl) imide.

FK209: Tris(2-(1H-pyrazol-1-yl)-4-*tert*-butylpyridine)-Tris(bis(trifluoromethylsulfonyl)imide).

PMMA: poly(methyl methacrylate).

* The price is taken from Sigma Aldrich website (<https://www.sigmaaldrich.com/germany.html> on September 2016).

Fig. 3. Energy levels of various common HTMs together with iodide and bromide based halide-perovskites. It is important to note that the energy levels are those of isolated materials and that upon formation of the multilayer device, changes in the energy scheme and alignment may occur due to interfacial dipoles, band bending, trap states and impurities. The minus () sign corresponding to the energy levels is omitted for simplicity. The Figure is drawn for free of scale for illustration only.

port characteristics showed that it carries both electrons and holes to their selective contacts [17]. An Electron Beam Induced Current (EBIC) analysis further showed $\text{CH}_3\text{NH}_3\text{PbI}_3$ exhibiting a slightly more p type behaviour with a better hole extraction ability than electrons whereas the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ shows characteristics similar to an intrinsic semiconductor [66]. This led to research in HTM free PSCs where a metal back contact was deposited directly on top of perovskite layer (PCE 10.85%) [28,67]. It is important to note that the monolithic PSCs [29,68,69] (employing a thick carbon layer as back contact with best PCE of 13.5%) [70,71] although are often termed as HTM free PSCs are not in fact HTM free. This is due to the fact that carbon layer acts as a p type selective contact and has shown to improve charge extraction efficiency at the carbon perovskite interface [72,73].

The crucial role of HTMs towards efficient charge extraction is also reported in literature [74,75] where a notable difference in both charge recombination resistance (R_{REC}) and series resistance (R_s) was observed in devices with and without an HTM. Impedance spectroscopy investigations (Fig. 4a and b) of complete PSCs (in an EPH configuration, employing both ETL and HTM, where E, P, and H represent ETL, perovskite and HTM layers, respectively) with those employing only one or no selective contact revealed that a device without HTM (labeled as EP) showed a larger R_s compared to PSCs employing one (labeled as EPH). Similarly, a lower contact resistance (R_{CON}) was also noted for EPH PSCs demonstrating that the presence of the HTM helps to form a smoother interface between the perovskite and the metal back contact. Furthermore, a lower R_{REC} was observed in PSCs without an HTM (Fig. 4c and d). As R_{REC} is inversely proportional to recombination kinetics in the film [76,77], it is evident that inclusion of HTM improves the charge collection characteristics of PSCs. However, one must note that a thicker HTM layer will also add to R_s of the film which would reduce the fill factor (FF) of the device. For best performance, a compromise between the thickness and also compactness of HTM layer must be made. In general, the R_{REC} for these devices showed the following trend: EPH > PH > EP > P. The lower recombination (or higher R_{REC}) in PH than EP can be understood from the better hole extraction ability of the perovskite film compared to its electron extraction ability [66].

Choice of selective contacts also affect the PV performance of the device. Whereas a device with both ETL and HTM selective contacts showed a PCE~9.1%, PSCs employing either an ETL or HTM only showed a PCE of 1.8% and 5%, respectively [75]. On the other hand, devices employing perovskite layer only (labeled as P, without any

selective contact) showed a PCE of only 0.1%. This would also affirm that the PSCs require at least one of the selective contacts to be present to function. Also, interestingly, the PH devices showed a similar V_{OC} (0.95 V) to that of EPH cells (0.97 V); however, the short circuit current density (J_{SC}) and FF dropped significantly. The FF for EPH, PH, EP and P cells was 0.60, 0.44, 0.35, and 0.25, respectively, which can be correlated with the increasing R_s upon removing the selective contacts.

An improved hole extraction efficiency at HTM/perovskite interface is directly reflected in improvement in PV performance, particularly, the V_{OC} and the FF [78–81]. For example, Choi et al. [78] employed poly[2,6 (4,4 bis potassiumbutanysulfonate 4H cyclopenta [2,1 b;3, 4 b'] dithiophene) alt 4,7 (2,1,3 benzothiadiazole)] (CPE K) in inverted planar PSCs and compared its performance with PEDOT: PSS. Whereas the steady state photoluminescence (PL) experiments showed that 71% and 99% of the photogenerated charges are quenched for PEDOT: PSS and CPE K, respectively, time resolved PL showed a carrier extraction time of 91 ns for glass/PEDOT: PSS/perovskite and 1.41 ns for glass/CPE K/perovskite. The improved charge extraction resulted in FF~0.77 (PCE~10.8%) for CPE K, higher than a PEDOT: PSS alternative (FF~0.66, PCE~10.8%), which is attributed to superior hole selectivity of the former.

3.2. Hole transport materials and open circuit voltage in PSCs

One of the remarkable feature of PSCs is their high output voltage; the V_{OC} is ~1.1 V and ~1.61 V for $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$, respectively, which accounts for $E_G - qV_{\text{OC}}$ ~0.45 V and ~0.7 V respectively (Table 2). It has been recently predicted, using Shockley Queisser limits, that theoretical maximum V_{OC} for a perovskite material with bandgap ~1.6 V is 1.33 ± 0.02 V [82]. However, one must consider the fact that the practically obtainable V_{OC} is always lower than its theoretical maximum, considering the losses during charge transport and transfer/collection. This is where selective contacts, particularly, play an important role. In PSCs, the V_{OC} is significantly influenced by non radiative recombination which can be quantified by the emission yield (EQE) of electroluminescence (EL) spectra. The external electroluminescence yield (EQE_{EL}) is higher if the charge injection from perovskite to an interfacing material is higher. In a recent work, Tress et al. [82] compared the EQE_{EL} for PSCs with and without an HTM. Whereas the PSCs with HTM showed EQE_{EL} ~ 10^{-5} – 10^{-6} (labeled as TiO_2 and Al_2O_3 in Fig. 5), the HTM free device showed an order of

Fig. 4. (a and b): Nyquist plot of PSCs with and without selective contacts at DC bias of $V=0.1$ V under 1 sun illumination. Herein, EPH and EP show PSCs made with and with hole transport layer, PH shows PSCs with no electron-selective contact and P is a device without any selective contact (perovskite layer only). (a) Complete range and (b) zoom at high-frequency region, (c) Series resistance of the same devices and (d) recombination resistance, RREC obtained from impedance spectroscopy data. Figure are reproduced with permission from Ref. [75]. Copy right of American Chemical Society.

magnitude lower value. Although the authors of the study point out the intrinsic losses of perovskite film to be the primary limiting factor to the V_{OC} , a report by Chen et al. [35] suggest otherwise. They report that the V_{OC} in PSCs is primarily limited by charge losses at the interfaces during extraction rather than the bulk losses within perovskite film. In their experiments employing $CH_3NH_3PbBr_3$ as perovskite absorber, $V_{OC} \sim 1.5$ V is obtained which is lower than the limiting V_{OC} ($V_{OC, rad} \sim 1.95$ V), i.e., $\Delta V_{OC} \sim 0.45$ V.

The above experiments make it hard to fully understand the origin of V_{OC} in PSCs, however, the selective contacts, particularly HTMs, contribute significantly to it. For example, in an early report on PSCs that compares two different polymers HTMs, viz, P3HT and poly[N 9 hepta decanyl 2,7 carbazole *alt* 3,6 bis (thiophen 5 yl) 2,5 dioctyl 2,5 di hydropyrrolo[3,4 [pyrrole 1,4 dione] (PCBTDP) a difference of ~ 0.66 V is observed in their V_{OC} [83]. Whereas the P3HT based PSCs resulted in $V_{OC} \sim 0.5$ V, the latter resulted in ~ 1.16 V, in a similar device design. Various factors accounted for the observed large difference in the V_{OC} : (i) the HOMO of PCBTDP (~ 5.4 eV) is deeper than P3HT (~ 5.2 eV). This also makes the former have a smaller energy offset with the valance band maximum of the perovskite employed $CH_3NH_3PbBr_3$ (~ 5.38 eV) and a higher obtainable voltage. However, the HOMO level difference between the two polymers is only ~ 0.2 eV which is only one third of the difference in their V_{OC} . This brings

into account other factors such as (ii) the different chemical structures of the two polymers, (iii) their different charge mobility (and conductivity of the polymer which would otherwise result in voltage drop), and (iv) light filtering effect. As shown in Fig. 6b, the PCBTDP has carbazole groups that would interact different with perovskite. Also, the hole mobility of PCBTDP is ~ 0.02 $cm^2 V^{-1} s^{-1}$ which is ~ 70 times higher [84] than that of P3HT. Towards (iv), the P3HT overlaps absorbance of perovskite thereby creating a light filtering effect which could limit the PV parameters.

Table 2 list few examples where the HOMO level of HTM and the hole mobility made significant effect on the V_{OC} . A systematic increase in V_{OC} is observed when HTMs with deeper HOMO levels are employed. For example, ~ 0.45 V increase in V_{OC} is observed when P3HT is replaced with PIF8 TAA (poly indenofluorene 8 triarylamine). It is noteworthy that this increase is nearly equal to the energy level difference of the two HTMs. Interestingly, the energy level difference is not solely the vital factor. For example, in a comparative study, PSCs made using Phenyl C_{61} butyric acid methyl ester (PCBM) (HOMO ~ 6.1 eV) showed ~ 0.24 V lesser V_{OC} than N,N'-dialkyl perylenediimide (PDI) (HOMO ~ 5.8 eV). This is because of the two orders of magnitude lower mobility of PCBM (10^{-2} 10^{-3} $cm^2 V^{-1} s^{-1}$) than PDI (~ 2.1 $cm^2 V^{-1} s^{-1}$). Therefore, to obtain high V_{OC} a high charge mobility as well as suitable energy level alignment are equally crucial.

Table 2

A comparison of state-of-the-art open circuit voltage obtained using various halide perovskites in conjunction with a diverse range of electron and hole selective contacts. The Conduction band (CB) and VB edges for MAPbI₃ and MAPbBr₃ are (3.9/ 5.4) eV and (3.4/ 5.6) eV, respectively. Table is reproduced with permission from Ref. [32]. Copy right of AIP Publishing.

V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF	PCE (%)	ETL	Device architecture	HTM	Band edges (CB/HOMO)	Hole mobility (cm ² V ⁻¹ s ⁻¹)	Device	qV _{OC} /E _G (%)	E _G -qV _{OC} (eV)	Reference
1.11	21.00	0.76	17.9	c,m-TiO ₂	Cs _x (MA _{0.17} FA _{0.83}) _(100x)	Spiro-OMeTAD	4.4■/-5.11▲	10 ⁻³ 10 ⁻⁴ [49]	Mesoporous PSC	72	0.44	Saliba et al. [85]
1.29	6.60	0.70	5.9	TiO ₂	Pb(I _{0.83} Br _{0.17}) ₃	P-TAA	5.14▲	> 0.1 [86]	Mesoporous PSC	56	1.01	Ryu et al. [87]
1.36	6.30	0.70	6.0	TiO ₂	MAPbBr ₃	PF8-TAA	5.44▲	4×10 ⁻³		59	0.94	
1.40	6.10	0.79	6.7	TiO ₂	MAPbBr ₃	PIF8-TAA	5.51▲	4×10 ⁻²		61	0.90	
1.04	21.3	0.73	16.2	TiO ₂	MAPbI ₃	P-TAA	5.14▲	> 0.1,		67	0.51	
0.92	8.90	0.56	4.6	TiO ₂	MAPbI ₃	PF8-TAA	5.44▲	4×10 ⁻³		59	0.63	
1.04	19.0	0.46	9.1	TiO ₂	MAPbI ₃	PIF8-TAA	5.51▲	4×10 ⁻²		67	0.51	
1.09	8.5	0.79	7.3	TiO ₂	MAPbBr ₃	P3HT	5.0▲	> 0.1 [86]	Mesoporous PSC	47	1.21	Heo et al. [88]
1.35	8.4	0.82	9.3	TiO ₂	MAPbBr ₃	P-TAA	5.14▲	4×10 ⁻³		59	0.95	
1.51	8.4	0.82	10.4	TiO ₂	MAPbBr ₃	PIF8-TAA	5.51▲	4×10 ⁻²		67	0.65	
1.38	5.2	0.78	5.6	PCBM	MAPbBr ₃	PEDOT:PSS	3.9■/5.3▲		p-i-n inverted	60	0.92	Wu et al. [42]
1.61	6.04	0.77	7.5	ICBA ^a	MAPbBr ₃	PEDOT:PSS	3.7■/5.3▲			70	0.69	Wu et al. [42]

^a ICBA: 1',1'',4',4''-tetrahydro-di [1,4] methanonaphthaleno[1,2:2',3',5,6,6':2'',3''] [5,6] fullerene-C60.

■ For CB/conduction band edge of ETM and ▲ for HOMO of HTM.

Fig. 5. External electroluminescence yield (EQE_{EL}) as a function of the injection current. Dashed lines show the calculated EQE_{EL} . The injection current as a function of applied voltage is shown in the inset (solid lines) including a fit to a shunt resistance (dashed), which is used to calculate the dashed lines in the main figure. Figure is reproduced with permission from Ref. [82]. Copyright of John Wiley and Sons.

3.3. Buffer layers to reduce interfacial recombination at perovskite/HTM interface

The HTM/perovskite interface is one of the possible recombination centers within the device as the electrons photogenerated near the HTM layer, if not efficiently extracted, may recombine with holes in HTM. Furthermore, if the HTM layer is not compact, the electrons might reach the metal contact thereby creating short circuit in the device. This often results in low FF in the devices. Buffer layer (also called interfacial layer) of thickness of few nanometer are employed to reduce interfacial recombination [89,90]. For example, an ultrathin Al₂O₃ layer between perovskite and HTM improved the PCE from 15% (J_{SC} 21.3 mA cm⁻², V_{OC} 1.03 V, FF 0.69) to 18% (J_{SC} 21.7 mA cm⁻², V_{OC} 1.08 V, FF 0.77) [90]. The devices also showed significantly less hysteresis upon addition of the buffer layer. Herein, not only the Al₂O₃ layer reduced the back recombination at interface, but also passivated defects on perovskite surface, leading to an improved contact and eventually effective charge transfer. In another report, incorporation of graphene oxide thin layer between HTM and perovskite demonstrated PCE 18.2% (J_{SC} 22.5 mA cm⁻², V_{OC} 1.08 V, FF

0.75), significantly higher than a reference device (m TiO₂/perovskite/spiroOMeTAD) without buffer layer (J_{SC} 20.9 mA cm⁻², V_{OC} 1.03 V, FF 0.71, PCE 15.3%). The buffer layer passivated perovskite surface and facilitated more efficient hole extraction at perovskite/HTM interface. Other similar examples include Molybdenum isopropoxide resulting in better valance band alignment of spiroOMeTAD with perovskite and resulted in PCE enhancement from 10.8% to 12% [91].

4. Hole Transporting materials in PSCs

4.1. Small molecules based hole transporting materials

4.1.1. Spiro OMeTAD

Spiro OMeTAD (Fig. 6a) has been one of the most commonly used and successful HTMs in solid state dye sensitized solar cells (s DSSCs). However, the PCE in the state of the art s DSSCs employing Spiro OMeTAD as a HTM has been limited to ~6–7.2% [92,93], which is far lower than the liquid electrolyte based counterparts ~14.3% in DSSC [94]. This is primarily due to low hole mobility of pristine Spiro OMeTAD (~10⁻⁴ cm² V⁻¹ s⁻¹) and its incomplete pore filling in relatively thick mesoporous TiO₂ (~1–3 μm in s DSSCs which is much higher than the ~300 nm thick TiO₂ employed in PSCs) [95]. On the other hand, the first report of PSCs in 2009, that employed a device architecture similar to that of a liquid electrolyte DSSC, was marked by significant device degradation. The perovskite absorber (CH₃NH₃PbI₃) started to dissolve in the polar liquid electrolyte due to hygroscopic nature of the organic component (MAI) which led to rapid degradation of performance after 10 min at 1 sun illumination [3]. Park et al. replaced the liquid electrolyte with the solid state counterpart, spiroOMeTAD, which not only increased the stability of the device but remarkably increased the PCE up to 9.7% from the ~3.9% of a liquid electrolyte analogue [4].

The low charge mobility and poor conductivity in pristine spiroOMeTAD arises from its inherent triangular pyramid configuration that leads to large intermolecular distances [92,96]. This results in inferior photovoltaic performance in PSCs due to high R_s and low R_{REC} . Dopants such as lithium bis(trifluoromethylsulfonyl) imide (Li TFSI) and 4 *tert* butylpyridine (TBP) are added to suppress charge recombination as well as improve the contact between absorber and HTM [97]. These additives and Co (III) complexes have shown to enhance hole mobility of the

spiroOMeTAD by an order of magnitude compared to the pure counterpart [98].

The spiroOMeTAD remains as one of the best performing HTMs in PSCs with PCEs as high as ~19–20% [51,99]. For example, Snaith and co workers reported PSCs employing a mixed halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) coated on a conducting scaffold of Al_2O_3 in conjunction with spiroOMeTAD and demonstrated a PCE of ~10.9% [24]. Subsequent efforts to optimize the morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on the TiO_2 scaffold via a sequential deposition method coupled with spiroOMeTAD as HTM yielded a PCE~15% [1]. The performance was further enhanced to ~15.4% in a planar structure, employing a compact layer of TiO_2 only, that allowed dense and pin hole free $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ deposition via dual source thermal evaporation [25]. A PCEs of ~19.3% was obtained using Li and Co doped spiroOMeTAD as HTM in planar PSCs via interface optimizations to reduce energy offset at the various device interfaces [99]. A similar high performance (PCE of ~19.7%) was also reported for mesoporous PSCs where spiroOMeTAD was used in conjunction with the perovskite prepared via Lewis Base Adduct of Lead(II) Iodide [51]. Moreover, a

reproducible and hysteresis free PSC with PCE of ~20.5% (certified PCE~19.6%) are also reported by Li et al. [100] prepared via vacuum flash solution processing method to obtain high electronic quality film over large area exceeding ~1 cm^2 . This spiroOMeTAD based PSC also corresponds to one of the highest performing PSCs. Table 3 summarizes high performing PSCs employing spiroOMeTAD as HTM.

4.1.2. Role of dopants in spiroOMeTAD and its derivatives

The role of OMe group in the spiroOMeTAD is to tune its electronic properties. Recently, Seok et al. [101] reported ortho substituted derivative in spiroOMeTAD and achieved a efficiency of ~16.7% compared to ~15.2% for conventional p OMe substituents. Similarly, Li et al. [102] employed three spiroacridine fluorene based HTMs and reported PCE~16.5% when tBP and Li TFSI are employed as dopant compared to ~14.3% for undoped spiroOMeTAD based device. A cost effective spiro type HTM 4,4',4'' (2 H,2H,4 H,4H 3,3' spiro bi[thieno[3,4 b] [1,4]dioxepine] 6,6',8,8'tetrayl)tetrakis(N, Nbis(4 methoxyphenyl)aniline) (PST1) was reported by Ganesan et al. [103] A PCE of ~12.7% was achieved without Co as dopant (~9.6% for Spiro OMeTAD based PSCs) which paves the way for develop

Fig. 6. (a): Chemical structures of most common small molecules based hole transport materials in perovskite solar cells. Chemical structures of the HTMs are reproduced with permission from references [47,48]. Copyright of John Wiley and Sons. (b): Chemical structures of most common polymers based hole transport materials in perovskite solar cells. Chemical structures of the HTMs are reproduced with permission from Refs. [47,48]. Copyright of John Wiley and Sons.

Fig. 6. (continued)

ing alternative hole transporting materials. The FDT is the most interesting deviation for Spiro OMeTAD which achieved the highest PCE~20.2% whilst it can be prepared by one fifth of the costs of Spiro OMeTAD, and is environmentally friendly as it can be dissolved in toluene instead of chlorobenzene which is the typical solvent for spiroOMeTAD [22].

An important aspect while using Spiro OMeTAD as HTM is its interaction with atmosphere, particularly, when doped with Li TFSI dopant. Hwash et al. reported a [104] a decrease in conductivity in pristine Spiro MeOTAD films when exposed to humidity due to incorporation of gas molecules in the film films possibly leading to hole traps. The Spiro MeOTAD films were prepared by vacuum evaporation and do not contain the typically employed dopants (Li TFSI and tBP). A downward shift in Fermi energy level is also noted. A similar effect is noted for pentacene films when exposed to different gases (N_2 , Ar and O_2) demonstrating that gas molecules creep into the film via grain boundaries [105]. The authors reported a decrease in conductivity and downwards shift of Fermi level

(closed to valance band) owing to a sharp rise in sub bandgap states density (from $\sim 10^{16}$ to $\sim 10^{18}$ states $eV^{-1} cm^{-3}$). In the case of Li TFSI doped Spiro OMTAD, Zafer et al. [106] studied the redistribution of Li TFSI dopant across the spiroMeOTAD under controlled environmental conditions (H_2O , O_2 and ambient air) and demonstrated that the conductivity of spiroMeOTAD increased remarkably when exposed to humidity. However, an access humidity exposure leads to creation of pinholes in the film [107]. These pinholes could provide a channel to Li TFSI migration across the film (bottom to top) and facilitate diffusion of gas molecules from ambient air (e.g., H_2O and O_2) causing degradation. This would require incorporation of alternative dopants or dopant free HTM.

Xu et al. [108] introduced a silver based organic salt, silver bis(trifluoromethanesulfonyl) imide (Ag TFSI), as an effective dopant for Spiro OMeTAD and reported higher PV performance (PCE~12% and FF~0.62) compared to a Li TFSI doped Spiro OMTAD rival (PCE~10.1% and FF~0.55). Another interesting p dopant is a, tris[2

Table 3

Photovoltaic parameters of several best performing PSCs using Spiro OMTAD as HTM and various dopants.

Device structure	Perovskite deposition method	Photovoltaic parameters				Dopants	Ref.
		V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF	PCE (%)		
Mesoporous PSCs							
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₃ /Spiro/Au	OSSD	0.88	17.6	0.62	9.7	Li-TFSL, TBP	[4]
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₃ /Spiro/Au	SD	0.99	20	0.73	15	Li-TFSL, FK209, TBP	[1]
CL(ZnO)/N-ZnO/CH ₃ NH ₃ PbI ₃ /Spiro/Ag	SD	0.96	21.3	0.7	16.05	Not mention	[111]
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₃ /Spiro/Au	TSSD	1.05	21.64	0.74	17.01	Li-TFSL, TBP	[112]
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₃ /Spiro/Ag	OSSD	1.08	23.83	0.76	19.71	Li-TFSL, TBP	[51]
CL/mp TiO ₂ /FA _{0.81} MA _{0.15} PbI _{2.51} Br _{0.45} /Spiro/Au	VASP	1.14	23.18	0.76	20.38	Li-TFSL, TBP	[100]
Planar PSCs							
CL/CH ₃ NH ₃ PbI _{3-x} Cl _x /Spiro/Ag	DSVD	1.07	21.5	0.67	15.4	Li-TFSL, TBP	[25]
CL-ZnO/CH ₃ NH ₃ PbI ₃ /Spiro/Ag	SD	1.03	20.4	0.74	15.7	Li-TFSL, TBP	[113]
CL-(TiO ₂ /ZnO)/CH ₃ NH ₃ PbI ₃ /Spiro/Au*	SET	1.08	21.08	0.75	17.17	not mention	[114]
SnO ₂ /CH ₃ NH ₃ PbI ₃ /Spiro/Au*	SD	1.11	23.27	0.67	17.21	Li-TFSL, TBP	[115]
SnO ₂ /(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /Spiro/Au	SET	1.13	21.2	0.75	18.1	Li-TFSL, FK209, TBP	[116]
CL(Y-TiO ₂)/CH ₃ NH ₃ PbI _{3-x} Cl _x /Spiro/Au	OSSD	1.13	22.75	0.75	19.3	Li-TFSL, FK209, TBP	[99]
Meso-superstructured PSCs							
CL/ZrO ₂ /CH ₃ NH ₃ PbI ₃ /Spiro/Ag	OSSD	1.07	17.3	0.59	10.8	Li-TFSL and TBP	[23]
CL/SiO ₂ /CH ₃ NH ₃ PbI ₃ /Spiro/Au	OSSD	1.05	16.4	0.66	11.45	Li-TFSL and TBP	[117]
CL/Al ₂ O ₃ /CH ₃ NH ₃ PbI _{3-x} Cl _x /Spiro/Ag	OSSD	1.02	21.5	0.71	15.9	Li-TFSL and TBP	[118]

SVD: Sequential Vacuum Deposition.

Spiro=Spiro-OMeTAD.

* J-V data obtained at reverse bias, VASP: Vacuum flash solution processing.

(1H pyrazol yl)pyrimidine] cobalt(III) tris[bis (trifluoromethylsulfonyl)imide] (MY11) which has the deepest redox potential among all cobalt based dopants used in solar cell applications [109]. In MY11, a pyrazolyl moiety is coupled with a pyrimidine moiety which is responsible to tune the redox potential of the dopant more positively. Koh et al. [109] reported MY11 as a new co dopant for Spiro OMTAD which increased the conductivity of pristine Spiro OMeTAD by two orders of magnitude, resulting in PCE~11.9%, V_{OC}~1.0 V, FF~0.71 compared to PCE~11%, V_{OC}~0.96 V and FF~0.68 for **FK102** doped Spiro OMTAD (**FK102**: Co dopant tris(2 (1H pyrazol 1 yl)pyridine) cobalt(III) tris(hexafluorophosphate)). Similarly, a new iridium complex, where Li is replaced with Ir (IrCp*Cl(PyPyz)(TFSL)) by Badia et al. [110] demonstrated higher PCE and V_{OC} (~10.8% and ~1.06 V) than pristine Spiro OMeTAD (PCE~9.2%, V_{OC}~1 V).

Despite the fact that Spiro OMeTAD demonstrated remarkable PCE~20% in PSCs owing to a good pore filling of the TiO₂ layer, it is characterized by low conductivity (~10⁻⁵ S cm⁻¹) [119] and a low hole mobility (~10⁻⁴ cm² V⁻¹ s⁻¹) in its pristine form. Although the dopants such as Li salt, TBP and Co (III) increased the transport properties of Spiro OMeTAD, they made Spiro OMeTAD sensitive to humidity, for example, Li TFSL which is extremely hygroscopic in nature acts as a humidity centre in HTM. This leads PSCs employing doped Spiro OMeTAD as HTM to degrade drastically when exposed to humid conditions. Moreover, currently, spiroOMeTAD is arguably one of the most expensive components in PSCs due to extensive synthetic processes involved in the preparation of the spirobifluorene core which might hamper the commercialization of PSCs. Alternative cost effective HTM materials are therefore extensively sought to overcome this issue.

4.1.3. Alternative small molecule based hole transport materials to spiroOMeTAD

In pursuit of cost effective and dopant free HTM materials, various research groups reported alternative small molecule based HTMs (listed in Table 4) which not only improved the PV parameters but also the stability of PSCs. Small molecules based HTMs can be mainly classified as: pyrenes derivatives [120], thiophenes derivatives [121], triazine derivatives [122] and porphyrins derivatives [123].

4.1.3.1. Pyrene derivatives.

Pyrene core derivatives owing to its

efficient charge transport capability are good candidate as HTM. Nam et al. [120] reported three HTMs based on pyrene core named as, 1 (N,N di p methoxyphenylamine)pyrene (Py A), 1,3,6 tris (N,N di p methoxyphenylamine)pyrene (Py B), and 1,3,6,8 tetrakis (N,N di p methoxyphenylamine)pyrene (Py C), The HOMO levels of these HTMs were 5.41, 5.25, and 5.11 eV, respectively, close to that of spiroOMeTAD (5.22 eV). Py B, and Py C delivered efficiencies of ~12.3 and ~12.4%, respectively, comparable to that of spiroOMeTAD (12.7%).

4.1.3.2. Thiophene derivatives. Typically, low glass transition temperature (T_g) and a small molecule size for HTM is preferred in PSCs as it facilitates easy processing of HTM (often at T < 100 °C) and improved infiltration and pore filling. Hairong et al. [121] reported thiophene based HTM on 2,5 bis(4,4' bis(methoxyphenyl)aminophen 4'' yl) 3,4 ethylenedioxythiophene (H101) for PSCs, which has T_g ~73 °C which is lower than that of Spiro OMeTAD (T_g ~125 °C). H101 also provides added features of low cost and easy processability than Spiro OMeTAD. A PCE~13.8% was reported for H101, which is slightly higher than Spiro OMeTAD based device (~13.7%). In another report, the same research group [124] developed two HTMs based on thiophene core, (2,3,4,5 tetra[4,4' bis(methoxyphenyl)aminophen 4'' yl] thiophene (H111) and 4,4',5,5' tetra[4,4' bis(methoxyphenyl)aminophen 4'' yl] 2,2' bithiophene (H112). These HTMs showed superior air stability and higher solubility in common solvents compared to H101, and also deeper HOMO levels (H111 and H112 are 5.31 and 5.29 eV, respectively) than H101 (5.16 eV). This resulted improved PV performance, from ~13.8% for H101 to ~14.7% and 14.9% for H112 and H111, respectively.

4.1.3.3. Triptycene derivatives. Triptycene core has similar twisted and bulky structure like Spiro OMeTAD which provides high thermal stability and a high solubility in common organic solvents [125]. Anurag et al. [126] reported HTMs employing triptycene derivatives such as 2,6,14 Tri(N,N bis(4 methoxyphenyl)amino) triptycene (T101), 2,6,14 Tri(N,N bis(4 methoxyphenyl)amino phen 4 yl) triptycene (T102) and 2,6,14 Tri(5' (N,N bis(4 methoxyphenyl)

Table 4

Photovoltaic performance of various alternative small molecules to expensive Spiro-OMeTAD as a hole transporting material in PSCs. The energy HOMO level (−5.22 eV) of Spiro-OMeTAD is not listed in the Table.

HTMs	HOMO (ev)	Configuration	Perovskite deposition methods	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	PCE (%)	Reference PSC (Spiro-OMeTAD)			Ref.	
								V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF		PCE (%)
Dopant- free small molecules												
TPBS	-5.30	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /TPBS/Au	SD	0.93	15.75	0.70	10.29	0.92	20.03	0.72	13.28	[134]
Triazine-Ph-OMeTPA	-5.11	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /Triazine-Th OMeTPA/Au	SD	0.93	19.14	0.61	10.91	0.94	21.37	0.67	13.45	[122]
TTF-1	-5.05	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /TTF-1/Ag	SD	0.86	19.9	0.64	11.03	0.91	19.8	0.63	11.40	[133]
2TPA-4-DP	-4.9	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /2TPA-4-DP/Au	SD	0.92	17.30	0.69	11.18	0.98	20.08	0.67	13.22	[34]
2TPA-3-DP	-4.92	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /2TPA-3-DP/Au	SD	0.95	18.67	0.68	12.22	0.98	20.08	0.67	13.22	[34]
2TPA-1-DP	-5.00	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /2TPA-1-DP/Au	SD	0.97	19.16	0.66	12.34	0.98	20.08	0.67	13.22	[34]
Triazine-Th OMeTPA	-5.04	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /Triazine-Th OMeTPA/Au	SD	0.92	20.74	0.66	12.51	0.94	21.37	0.67	13.45	[122]
Fused-F	-5.23	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /Fused-F/Au	SD	1.03	17.9	0.68	12.8	1.02	17.2	0.66	11.70	[131]
2TPA-2-DP	-4.96	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /2TPA-2-DP/Au	SD	0.97	18.82	0.70	12.96	0.98	20.08	0.67	13.22	[34]
TPBC	-5.33	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /TPBC/Au	SD	0.94	19.32	0.72	13.10	0.92	20.03	0.72	13.28	[134]
DOR3T-TBDT	-5.1	CL/CH ₃ NH ₃ PbI _{3-x} Cl _x /DOR3T-TBDT/MoO ₃ /Ag	OSSD	0.97	20.7	0.74	14.9	1.04	19.5	0.69	14.00	[142]
Small molecules with dopants												
T101 ^b	-5.29	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /T101/Au	SD	1.00	13.5	0.63	8.4	0.97	20.80	0.63	12.87	[126]
TPA-MeOPh ^a	-5.29	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /TPA-MeOPh/Au	SD	0.99	17.33	0.62	10.79	0.89	19.87	0.72	12.75	[132]
FA-MeOPh ^a	-5.15	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /FA-MeOPh/Au	SD	0.92	18.39	0.69	11.86	0.89	19.87	0.72	12.75	[132]
T102 ^b	-5.35	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /T102/Au	SD	1.03	17.2	0.69	12.2	0.97	20.80	0.63	12.87	[126]
OMeTPA-TPA ^c	-5.13	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /OMeTPA-FA/Au	SD	0.95	20.9	0.62	12.31	0.99	21.57	0.68	14.68	[143]
T103 ^b	-5.33	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /T103/Au	SD	0.99	20.3	0.62	12.4	0.97	20.80	0.63	12.87	[126]
SGT-404 ^c		CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /SGT-404/Au	SD	0.96	19.76	0.69	13.28	1.03	20.31	0.72	15.23	[135]
OMeTPA-FA ^c	-5.14	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /OMeTPA-FA/Au	SD	0.97	21.0	0.76	13.63	0.99	21.57	0.68	14.68	[143]
H101 ^b		CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /H101/Au	SD	1.04	20.5	0.65	13.8	1.05	18.9	0.69	13.70	[121]
SGT-407 ^c		CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /SGT-407/Au	SD	0.99	20.35	0.68	13.86	1.03	20.31	0.72	15.23	[135]
SGT-405 ^c		CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /SGT-405/Au	SD	1.02	20.28	0.71	14.79	1.03	20.31	0.72	15.23	[135]
H112 ^b	-5.29	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /H112/Au	SD	1.07	20	0.71	15.2	1.05	19.9	0.69	14.4	[124]
H111 ^b	-5.31	CL/m-TiO ₂ /CH ₃ NH ₃ PbI ₃ /H111/Au	SD	1.08	19.8	0.72	15.4	1.05	19.9	0.69	14.4	[124]

^a doped with (TBP) and (Li-TFSI).

^b doped with (TBP), (Li-TFSI) and Co-dopant FK102.

^c doped with TBP, Li-TFSI, and FK209.

aminophen 4 yl)thiophene 2 yl) triptycene (T103) and demonstrated a superior FF~0.69 and V_{OC} ~1.03 V than a Spiro OMeTAD based device (FF~0.63, V_{OC} ~0.97 V). The absorption peak of **T102** and **T103** showed a red shift compared to **T101** due to greater π conjugation of the formers. The deeper HOMO level of these HTMs (5.35, 5.33 and 5.29 eV, respectively) explains the origin of the V_{OC} enhancement (Table 4).

4.1.3.4. Triazine derivatives. HTMs based on star shaped triarylamine derivatives have been used in organic solar cells [127]. Recently, Kwangseok et al. [122] synthesized two star shaped 2,4,6 tris[*N,N* bis (4 methoxyphenyl)amino *N* phenylthiophen 2 yl] 1,3,5 triazine (**Triazine-Th-OMeTPA**) and 2,4,6 tris[*N,N* bis(4 methoxyphenyl) amino *N* diphenyl] 1,3,5 triazine (**Triazine-Ph-OMeTPA**) and employed them as HTMs in PSCs. **Triazine-Th-OMeTPA**, owing to its higher hole mobility ($1.74 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) than the latter ($1.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) resulted in a superior PV performance (PCE~12.51% and FF~0.66) compared to **Triazine-Ph-OMeTPA** (PCE 10.90% and FF 0.61). The performance of both these HTMs was, however, lower than a reference **Spiro-OMeTAD** PSC (PCE~13.45% and FF~0.67).

4.1.3.5. Porphyrin derivatives. Zinc porphyrin dyes have demonstrated remarkable PV performance in dye sensitized solar cells [128,129], and recently, as a potential alternative HTM to well known **Spiro-OMeTAD** in PSCs. Hsien Hsin et al. [123] designed zinc porphyrin HTMs, namely, **Y₂** (Full name not available) and **Y₂A₂** (Full name not available). A high PCE~16.6% is achieved by **Y₂** HTM which is comparable to that of **Spiro-OMeTAD** of ~18.03%. The PV performance of **Y₂A₂** based PSCs was relatively poorer (PCE~10.55%) due to large pinholes in its resultant film when deposited on perovskite and its an order of magnitude lower hole mobility ($1.53 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) than **Y₂** ($2.04 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Similarly, **zinc(II) 5,10,15,20-tetrakis[5-(*p*-acetylthiopentyl)oxy]phenyl]porphyrin** [130] was employed as a buffer layer between **PEDOT: PSS** and perovskite films in inverted planar PSCs to modify the interfacial properties. A PCE~14.05% is reported for PSCs employing PEDOT: PSS/porphyrin compared to ~11.35% for pristine PEDOT: PSS. The improvement in PV performance in former is attributed to a reduction in interfacial charge recombination and a better hole extraction owing to higher HOMO level of porphyrin.

4.1.3.6. Triphenylamines derivatives. Tris[[4 [3,3' dihexylsilylene 2,2' bithiophene] 7 [5' n hexyl (2,2';5',2' terthiophene) 5 yl] benzo [c] [1,2,5]thiadiazole] 2,6,10 yl] 4,4,8,8,12,12 hexamethyl 4H,8H,12 Hbenzo [1,9] quinolizino[3,4,5,6,7, defg]acridine; (**Fused-F**)' is another dopant free small molecule with ability to adsorb in the UV region which significantly enhanced the absorption of Fused F/ perovskite film in the visible region [131]. Peng et al. employed mesoscopic PSCs (CL/TiO₂/CH₃NH₃PbI₃/Fused F/Au) with PCE~12.8% and V_{OC} ~1.03 V, slightly higher than the rival doped Spiro OMeTAD (PCE~11.7% and V_{OC} ~1.02 V) [131]. Similarly, planar amine of star shaped triphenylamine small molecules, e.g., tris{bis(4 methoxyphenylethenyl) *N* phenyl}amine (**TPA-MeOPh**) and tris{bis(4 methoxyphenylethenyl) *N* phenyl}amine quinolizinoacridine (**FA-MeOPh**) demonstrated PCE and V_{OC} of ~11.86%, and ~0.92 V and ~10.79%, and ~0.94 V, respectively [132], which is comparable to that of a Spiro OMeTAD based reference device (PCE 12.75%, V_{OC} ~0.89 V).

4.1.3.7. Tetrathiafulvalene derivatives. Liu et al. [133] reported a dopant free tetrathiafulvalene derivative (**TTF-1**) as HTM in architecture CL/mpTiO₂/CH₃NH₃PbI₃/TTF 1/Ag yielding PCE of ~11.03%, and V_{OC} ~0.86 V comparable to Spiro OMeTAD based PSCs ~11.4% and V_{OC} ~0.91 V, thereby evidencing that small molecules based HTM materials can deliver similar or even better performance than Spiro OMeTAD.

4.1.3.8. *N, N, N', N'* Tetra phenyl benzidine (TPB). Despite the advantages small molecule HTMs offer for efficient PSCs, the performance is primarily limited due to inferior V_{OC} originating from (i) the energy offset between HOMO of HTM and HOMO of perovskite and (ii) the charge recombination owing to poor surface coverage of these HTMs. Towards the former, Yakun et al. [134] reduced the band offset of (**TPB**, 5.52 eV) by adding electron donating moieties which increased the electron density and shifted its HOMO level closer to that of HOMO level of CH₃NH₃PbI₃ (5.15 eV). The new dopant free TPB derivatives *N* phenyl *N'* (4 (2 (3,4 ethylenedioxy)vinyl)phenyl) *N,N'* di p tolyl [1,1' biphenyl] 4,4' diamine (**TPBS**) and *N* (4 (2 (9 ethyl 9H carbazol 3 yl)vinyl)phenyl) *N'* phenyl *N,N'* di p tolyl [1,1' biphenyl] 4,4' diamine (**TPBC**) when employed as HTM in mesoscopic PSCs demonstrated PCE~10.29%, and ~13.1%, and V_{OC} ~0.70 V and ~0.72 V, respectively, comparable to that obtained by a doped Spiro OMeTAD counterpart (PCE~13.3% and V_{OC} ~0.72 V).

4.1.3.9. Carbazoles derivatives. One of the highest performance in PSCs employing small molecules based PSC (other than Spiro OMeTAD) was shown by employing Carbazole structures, **SGT-405** (full name not available) and **SGT-407**(full name not available) belonging to the three arm type structure and SGT 404 for two type structure [135]. Among them, **SGT-405** showed the ability to form a crystalline structure when coated as a film and exhibited the highest conductivity ($\sim 4.2 \times 10^{-8} \text{ S cm}^{-1}$) eventually leading to a remarkable PCE~14.79% and V_{OC} ~1.02 V comparable to ~15.23% and ~1.03 V for a Spiro OMeTAD based device.

4.1.3.10. Phthalocyanine derivatives. Copper phthalocyanine (**CuPc**) is another alternative HTM due to its low cost, high hole mobility ($\sim 10^{-3}$ to $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), stability and long exciton diffusion length ($\sim 68 \text{ nm}$) [136,137]. Kumar et al. [138] employed CuPc as HTM in a mesoporous PSCs that showed J_{SC} ~16.3 mA cm⁻² and V_{OC} ~0.75 V; however, low FF~0.4 due to low shunt resistance which restricted the PCE to ~5%. To overcome this, Soek et al. [139] employed high LUMO (lowest unoccupied molecular orbital) level **po-spiroOMeTAD** doped CuPc to improve its electron blocking characteristics (Fig. 7a). The combination enhanced the PCE from 16.7% (pristine po spiroOMeTAD) to ~19.4% (average value) for the CuPc doped po spiroOMeTAD (Fig. 7b). In another report, Sun et al. [140] fabricated a low cost mesoscopic PSCs by incorporating CuPc nanorods as HTM together with the printable low temperature processed carbon as cathode material. A PCE~16.1% higher than a reference Spiro OMeTAD device (PCE~15%) was demonstrated. Similarly, PCE~15.42% is shown by Yan et al. [141] in a fully vacuum processed device at room temperature using a CuPc.

4.2. Polymer hole transport materials

In pursuit of cost effective and stable HTMs, polymer materials

Fig. 7. (a) Energy level alignment of mesoscopic device (CL/mp $TiO_2/(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}/CuPC$ -po-Spiro-OMeTAD/Au) showing the working mechanism of CuPC, and (b) J-V curve of the best performing device with a CuPC (4.8 wt%)-doped po-spiro HTM at reverse (black) and forward (red) scans. The inset shows the average values of the photovoltaic parameters obtained from J-V curves under both scans. Figure are reproduced with permission from reference [139]. John Wiley and Sons.

with higher hole mobility than dopant free small molecules are also sought in s DSSC as well as in PSCs. Few common examples are **P3HT**, **PTAA** and **PEDOT: PSS** which achieved maximum PCE in PSCs, ~15.3%, ~20.2% and ~18.1%, respectively.

4.2.1. P3HT

P3HT, owing to its relatively cheaper synthesis cost, is a widely employed conducting polymer in organic photovoltaic devices [144] as well as in PSCs [145]. In addition, contrary to Spiro OMeTAD, P3HT is a dopant free HTM and it does not require time consuming oxygen doping (which is required for Spiro OMeTAD based PSCs) for high efficiency thereby making it a material of choice. At an early stage, lower PCE values (<7%) were reported in P3HT based PSCs [43,146,147], due to the fact that the flat molecular structure of P3HT induced substantial charge recombination compared to a Spiro OMeTAD based devices [146]. However, recently comparable PCE to a Spiro OMeTAD device (~13.7% [148,149], ~14.6% [145], ~15.3% [53]) has been reported in planar, mesoscopic and meso superstructured PSCs, respectively.

Zhang et al. reported a PCE of ~6.1% in an architecture CL/mp $TiO_2/CH_3NH_3PbI_{3-x}Cl_x/P3HT/Au$ compared with a HTM free device (PCE~3.5%) and affirmed the role of P3HT as efficient hole extraction layer [43]. In another report, P3HT was shown to outperform Spiro OMeTAD in mesoscopic PSCs employing $CH_3NH_3PbI_2Br$ [147], yielding PCE~6.6% compared to ~5.7% for a rival Spiro OMeTAD device. This could be understood from the fact that, owing to the relatively

inferior infiltration of P3HT, it might not reach conducting substrate which is the case for Spiro OMeTAD. One would expect higher recombination at FTO interface for Spiro OMeTAD if devices employ a poor hole blocking layer. A report by Di Giacomo et al. [150] demonstrated that doped P3HT excels Spiro OMeTAD in performance in a device architecture of FTO/m $TiO_2/CH_3NH_3PbI_{3-x}Cl_x/P3HT/Au$. They achieved a PCE of ~9.3% in P3HT devices compared to ~8.6% in Spiro OMeTAD analogues. Despite the similar J_{sc} and FF, the enhancement in the PCE in PSCs employing P3HT was attributed to rise in the V_{oc} (from ~0.84 to ~0.93 V) due to the difference in the ionization potential of the two HTMs. A remarkable performance (PCE~13.7% and V_{oc} ~0.96 V) using P3HT was reported by Abbas et al. [148] for planar PSCs by optimizing the HTM thickness and using sequential vacuum deposition method for perovskite deposition which resulted in highly crystalline and continuous film as shown in Fig. 8. This hints that an optimization of HTM thickness and a pin hole free morphology is crucial to obtaining high PCEs. Zhang et al. [151] developed a smooth $CH_3NH_3PbI_{2.4}Br_{0.6}$ film using compressed air blow drying method. A high air flow speed resulted in better smoothness and high surface coverage compared to a corresponding one step spin coated perovskite film. The PSCs fabricated using air blow drying method yielding a PCE of ~10.2% with high V_{oc} up to ~1 V using pristine P3HT as HTM.

The PV performance of P3HT based PSCs is generally lower than doped Spiro OMeTAD based PSCs due to the low hole mobility of the former ($3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [43,147]. Efforts have been dedicated to

Fig. 8. (a) SEM image of highly crystalline and continuous $CH_3NH_3PbI_3$ thin film with grain size of 500 nm deposited by sequential vacuum deposition method, and (b) I-V curve of the best device with PCE~13.7%. Figure are reproduced with permission from Ref. [148]. Copy right of AIP Publishing.

Fig. 9. (a) Normalized life time for P3HT and P3HT/GD HTL based PSCs, (b) J-V characteristic curve of the same. Figure are reproduced with permission from Ref. [145]. Copy right of Wiley (c) Cross-section of the complete device showing P3HT/SWNTs nanohybrid mesh in-filled with PMMA and (d) its current – voltage curve of the complete device with (red curve) and without PMMA (grey curve). Figure are reproduced with permission from Ref. [53]. Copy right of American Chemical Society.

enhance hole mobility via carbon nano materials [152,153] and Li salts [154,155] as additives. Heo et al. [155] examined the effect of Li TFSI and TBP additives on the device performance. Li-TFSI and TBP increased the conductivity of P3HT and resulted in PCE~13.7%, V_{OC} ~0.92 V, FF~0.74 for doped P3HT, significantly higher than a pristine counterpart (PCE~5.7%, V_{OC} ~0.55 V, FF~0.67). Chen et al. [153] used multi walled carbon nanotubes (MWNTs) with P3HT which significantly enhanced the conductivity of P3HT an order of magnitude higher than their pristine counterparts and also demonstrated PCE~6.45% compared to a P3HT based device (4.12%). Similarly, Cai et al. [152] employed P3HT/bamboo structure carbon nanotubes (BCN) composite as HTL in mesoscopic PSCs. An optimized concentration (1 wt% of BCN in P3HT solution) increased the conductivity of the composite ~50 times and improved the charge transfer at the

CH₃NH₃PbI₃ HTM interface two folds. The PCE drastically increased to 8.3% from an initial 3.6% for pristine P3HT, primarily due to increase in V_{OC} ~0.86 V and FF~0.52. In another report, Xiao et al. [145] introduced graphdiyne (GD) as an additive to P3HT in mesoscopic PSCs which resulted in a remarkable PCE~14.6% and V_{OC} ~0.94 V. The high PCE is attributed to improved light absorption in PSCs and a shorter life time for P3HT/GD based device (49.1 ns) compared to a pristine P3HT (75.2 ns) as shown in Fig. 9a, which shows accelerated hole extraction at the CH₃NH₃PbI₃/P3HT/GD interface. Similarly, a P3HT/SWNTs (single walled carbon nanotubes) composite embedded in insulating polymer (PMMA) resulted in a remarkable PCE of ~15.3% (V_{OC} ~1.02 V and FF~0.66) [53]. The PMMA was employed to prevent a direct contact between the perovskite absorber and metal back contact (Ag) which could otherwise

Fig. 10. (a) Double-twisted fibrous PSCs structure (PMMA layer not shown), (b) J-V curve of Double-twisted PSCs with best PCE~3.03% and (c) The photograph of the double-twisted fibrous PSCs warped onto a capillary tube with curvature radius of 0.3 mm. Figure are reproduced with permission from Ref. [156]. Copyright of John Wiley and Sons.

Fig. 11. (a) SEM image of $\text{CH}_3\text{NH}_3\text{PbI}_3$ -coated mp- TiO_2 film (top view), (b) a cross-sectional image of mp- $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PTAA}/\text{Au}$ device, and (c) $J-V$ curve for the best performing cells fabricated using PTAA and spiroOMeTAD as HTMs. Figure are reproduced with permission from Ref. [2]. Copy right of nature publishing group.

lead to corrosion of Ag.

P3HT is also used as HTM in fiber shaped PSCs, which is an interesting application area of PSCs as wearable electronics and textiles. Li et al. [156] reported highly twisted flexible CNT fiber used as anode in an architecture CL/mp $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x/(\text{P3HT}/\text{SWNTs})/\text{Ag}$ nanowire, as shown in Fig. 10. PMAA was used as protecting layer to provide a mechanical support and also to prevent moisture ingress [53]. Although a PCE~3%, $V_{\text{OC}} \sim 0.61$ V was achieved, which is not on par with state of the art PSCs, the result is interesting enough to pave way for future self powering e textiles.

4.2.2. PTAA

PTAA is another successful polymer HTM employed in PSCs owing to its higher hole mobility (1×10^{-2} – 1×10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) compared to other polymers (P3HT~ 3×10^{-4} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) [157]. Heo et al. first reported a PCE~12%, $V_{\text{OC}} \sim 0.99$ V, FF~0.72 [2]. They introduced a capping layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$ overlaying the 3D composites of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ as shown in Fig. 11. Moreover, owing to its high molecular weight, PTAA could only partially be infiltrated into the $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ composite unlike the spiroOMeTAD which can be easily infiltrated into composites of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$. This could explain the higher R_s and a low FF~0.58 for spiroOMeTAD based PSCs. The same group subsequently used a mesoscopic architecture (CL/mp $\text{TiO}_2/\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}/\text{PTAA}/\text{Au}$ and showed a certified PCE~17.9%, $V_{\text{OC}} \sim 1.11$ V [158]. As FAPbI_3 exhibits an irregular morphology with bumpy roughness, incorporating MAPbBr_3 into FAPbI_3 (with $x=0.15$) led to uniform and crystalline phase which is reflected by their high performance. Bi et al. [159] grew $\text{CH}_3\text{NH}_3\text{PbI}_3$ film with large crystalline grains on a non wetting PTAA hole transport material which dramatically reduced charge trap density and boosts the PCE to ~18.1% for planar PSCs. In fact, one of the highest reported PCE (~20.2%) also used PTAA and large grain size FAPbI_3 micro structures as HTM [54].

4.2.3. PEDOT:PSS

PEDOT: PSS is one of the most successful HTMs owing to its good film forming properties, its transparency and its high work function (~5.2 eV) [160] which appropriately lies close to the ionization potential of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (see Fig. 3). It is mainly used in inverted planar PSCs (Table 5), an architecture that typically employ organic compact charge extraction layers on the substrates to collect holes whereas the electrons are collected from the metal back contact. PEDOT: PSS is particularly suitable for flexible or low temperature PSCs as it can be processed at low temperature < 100 °C making it compatible with flexible substrates. In inverted planar PSCs, a perovskite layer is sandwiched between thin compact HTM on FTO and ETL on the metal contact, typically PEDOT: PSS and PCBM, respectively [161]. This architecture might employ additional electron and

hole buffer layers to improve interfacial charge transfer.

Docampo et al. compared PEDOT: PSS to NiO and V_2O_5 in device architecture FTO/HTM/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x/\text{PCBM}/\text{TiO}_x/\text{Al}$ resulting high surface coverage ~95% of $\text{CH}_3\text{NH}_3\text{PbI}_3$ above PEDOT: PSS [162]. A PCE~9.8% ($V_{\text{OC}} \sim 0.9$ V, $J_{\text{SC}} \sim 15.8$ mA cm^{-2} and FF~0.66) is reported on FTO. Similarly, Malinkiewicz et al. [163] employed an evaporated $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer between PEDOT: PSS and PCBM and reported PCE~12%. The performance of these inverted PSCs is mostly influenced by the perovskite coverage and its absorption which depends, to some extent, on the morphology of HTM over which perovskite is to be deposited. Jeng et al. [164] reported inverted planar PSCs in architecture (ITO/PEDOT: PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}/\text{BCP}/\text{Al}$) that resulted in a low $V_{\text{OC}} \sim 0.6$ V with maximum PCE~3.9%. The very low PCE in these device was due to un optimized absorber layer thickness (< 50 nm) and poor surface interaction between $\text{CH}_3\text{NH}_3\text{PbI}_3$ film and PEDOT: PSS layer. Similarly, Sun et al. [165] reported a PCE of ~5.2% (FF~0.7 and $V_{\text{OC}} \sim 0.82$ V) in a ITO/PEDOT: PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}/\text{Al}$ architecture where $\text{CH}_3\text{NH}_3\text{PbI}_3$ was deposited using single step solution processing. The PCE and V_{OC} were further increased to ~7.4% and ~0.94 V, respectively using a thicker $\text{CH}_3\text{NH}_3\text{PbI}_3$ film developed via sequential deposition method thereby evidencing that optimization of perovskite layer thickness is crucial to obtain high performance.

Owing to the crucial role of the crystallinity, morphology and surface coverage of the perovskite layer on the photovoltaic performance in PSCs, various research groups introduced additives in the perovskite absorber in inverted PSCs resulting in a high PCE of ~8–11.8% listed in Table 5 [166–168]. Another way to further increase the performance of PSCs is to engineer ITO/HTM interface to overcome the energy mismatch. Towards this end, Lim et al. [169] modified the work function of PEDOT: PSS from 4.86 (pristine) to 5.4 eV (PEDOT: PSS and PFI, (SOHEL) via surface treatment using a perfluorinated ionomer (PFI). They built ITO/SOHEL/ $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}/\text{Al}$ structure with PCE as high as ~11.7% and $V_{\text{OC}} \sim 1$ V (PCE~8.1% and $V_{\text{OC}} \sim 0.8$ V for pristine PEDOT: PSS). Higher PCE in inverted planar PSCs are achieved via optimization of ETL or HTM interface and also by controlling the characteristics of perovskite layer. For example, Chen et al. [170] employed a Sequential Vacuum Deposition method for perovskite deposition in an architecture ITO/PEDOT: PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{C}_{60}/\text{phen}(\text{Bathophenanthroline})/\text{Ca}/\text{Ag}$ and demonstrated a PCE of ~15.4% ($V_{\text{OC}} \sim 1$ V, FF~0.7). Similarly, an optimized PEDOT: PSS morphology yielded a PCE of ~16.3% with $V_{\text{OC}} \sim 1.0$ V, FF~0.7 in conjunction with PC_{71}BM and $\text{CH}_3\text{NH}_3\text{PbI}_3$ as ETL and perovskite, respectively [171].

High efficiency > 17% in p i n PSCs was achieved by controlling the morphology of perovskite and HTM and also by overcoming the energy offset at the three interfaces (ETL/perovskite, HTM/perovskite, and HTM/ITO), which would result in higher V_{OC} and higher PCE thereby

Table 5

Perovskite solar cells employing the three common polymer hole transporting materials (P3HT, PTAA and PEDOT: PSS) along with their device architecture, and details perovskite deposition method.

Device structure	Perovskite deposition methods	Photovoltaic parameters				Ref.
		V _{OC} (V)	J _{sc} (mA cm ⁻²)	FF	PCE (%)	
P3HT						
CL/oriented rod TiO ₂ /CH ₃ NH ₃ PbI _{3-x} Cl _x /P3HT/Au	OSSD	0.74	14.65	0.55	6.06	[43]
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₂ Br/P3HT/Au	OSSD	0.82	12.93	0.62	6.64	[147]
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₃ /P3HT- 1 wt% BCN/Au	SD	0.86	18.75	0.52	8.30	[152]
CL/mp TiO ₂ /CH ₃ NH ₃ PbI _{3-x} Cl _x /P3HT/Au	OSD	0.93	12.00	0.6	9.3	[150]
CL/mp TiO ₂ /CH ₃ NH ₃ PbI _{2.4} Br _{0.6} /P3HT/Au	Air blow-drying	0.952	15.45	0.69	10.2	[151]
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₃ /P3HT-MWNTs/Au	OSSD	0.76	14.8	0.57	6.45	[153]
CL/CH ₃ NH ₃ PbI _{3-x} Cl _x /P3HT/Ag	OSSD	0.98	19.1	0.66	12.4	[154]
CL/CH ₃ NH ₃ PbI ₃ /P3HT/Au	SVD	0.96	21.76	0.65	13.7	[148]
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₃ /P3HT/Au	OSSD	0.92	20.1	0.74	13.7	[155]
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₃ /P3HT-GD/Au	SD	0.94	21.7	0.71	14.58	[145]
CL/Al ₂ O ₃ /CH ₃ NH ₃ PbI ₃ /P3HT/SWNTs/PMAA/Ag	OSSD	1.02	22.71	0.66	15.3	[53]
PTAA						
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₃ /PTAA/Au	OSSD	0.99	16.5	0.72	12.00	[2]
CL/mp TiO ₂ /FAPbI ₃ _{0.85} (MAPbBr ₃) _{0.15} /PTAA/Au	SET	1.11	22.5	0.70	17.9	[158]
PTAA/CH ₃ NH ₃ PbI ₃ /PCBM/C ₆₀ /BCP/Al	TSSD	1.07	22.0	0.76	18.1	[159]
CL/mp TiO ₂ /(FAPbI ₃) _{1-x} (MAPbBr ₃) _x /PTAA/Au	TSSD	1.06	24.7	0.77	20.2	[54]
PEDOT: PSS						
ITO/PEDOT: PSS/CH ₃ NH ₃ PbI ₃ /PCBM/BCP/AL	OSSD	0.6	10.32	0.63	3.9	[164]
PET/ITO/PEDOT: PSS/CH ₃ NH ₃ PbI ₃ /PCBM/BCP/Al	OSSD	0.92	7.93	0.62	4.54	[183]
ITO/PEDOT: PSS/CH ₃ NH ₃ PbI ₃ /PCBM/AL	OSSD	0.90	10.82	0.75	7.41	[165]
ITO/PEDOT: PSS/Cs _{0.1} MA _{0.9} PbI ₃ /C ₆₀ /AL	OSSD	1.05	10.10	0.73	7.68	[184]
ITO/PEDOT: PSS/polyTPD/CH ₃ NH ₃ PbI ₃ /C ₆₀ /Au/LiF	DSVD	1.05	15.88	0.46	7.73	[185]
ITO/PEDOT: PSS/CH ₃ NH ₃ PbI ₃ -BmPyPhB/PCBM/Al	OSSD	0.88	14.7	0.63	8.14	[166]
FTO/PEDOT: PSS/CH ₃ NH ₃ PbI _{3-x} Cl _x /C ₆₀ /TiO _x /Al)	OSSD	0.94	15.8	0.66	9.8	[162]
ITO/PEDOT: PSS/CH ₃ NH ₃ PbI ₃ -NH ₄ Cl/PCBM/Al	OSSD	0.88	14.08	0.80	9.93	[168]
ITO/PEDOT: PSS/CH ₃ NH ₃ PbI _{3-x} Cl _x /PCBM/Al	OSSD	0.87	18.5	0.72	11.5	[186]
ITO/SOHEL/CH ₃ NH ₃ PbI ₃ /C ₆₀ /AL	OSSD	0.99	16.7	0.70	11.7	[169]
FTO/PEDOT: PSS/CH ₃ NH ₃ PbI _{3-x} Cl _x 1% DIO/PCBM/Bis-C ₆₀ /Ag	OSSD	0.92	17.5	0.73	11.8	[167]
ITO/PEDOT: PSS/PolyTPD/CH ₃ NH ₃ PbI ₃ /PCBM/Au	DSVD	1.05	16.12	0.67	12.04	[163]
ITO/1%wtMoO ₃ /PEDOT: PSS/CH ₃ NH ₃ PbI ₃ /C ₆₀ /Bphen/Ag	TSSD	0.96	20.06	0.67	12.78	[187]
ITO/PEDOT: PSS/CH ₃ NH ₃ PbI ₃ /PCBM/PN ₄ N/Al	OSSD	1.00	20.61	0.72	15	[188]
ITO/PEDOT: PSS/CH ₃ NH ₃ PbI ₃ /C ₆₀ /phen/Ca/Ag	SVD	1.02	20.9	0.72	15.4	[170]
ITO/PEDOT: PSS/CH ₃ NH ₃ PbI ₃ /PCBM/C ₆₀ /BCP/AL	TSSD	0.99	19.6	0.79	15.4	[189]
ITO/PEDOT: PSS/CH ₃ NH ₃ PbI ₃ /PC ₇₁ BM/Ca/Al	TSSD	1.05	19.98	0.78	16.31	[171]
ITO/PEDOT: PSS/CH ₃ NH ₃ PbI _{3-x} Cl _x /PCBM/PFN/Al	OSSD	1.05	20.3	0.80	17.1	[173]
FTO/PEDOT: PSS/CH ₃ NH ₃ PbI ₃ /PCBM/Al	Hot-casting technique	0.92	22.4	0.82	18	[172]
ITO/PEDOT: PSS/CH ₃ NH ₃ PbI ₃ /PCBM/Au	OSSD	1.1	20.9	0.79	18.1	[56]

SOHEL=perfluorinated ionomer (PFI)/PEDOT: PSS, BCP =2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline.

DIO=1,8-diiodooctane, BmPyPhB =1,3-Bis[3,5-di(pyridin-3-yl)phenyl]benzen.

[56,172,173]. This also eliminated hysteresis, i.e., drop in power output under an electric bias or light. For example, a high performance PCE~17.1% (V_{OC}~1.05 V, FF~0.80) was reported by You et al. [173] in a device consisting of ITO/PEDOT: PSS/CH₃NH₃PbI₃-xCl_x/PCBM/PFN/Al where polyelectrolyte poly[(9,9 bis(30 (N,N dimethylamino) propyl) 2,7 fluorene) *alt* 2,7 (9,9 dioctylfluorene)] (**PFN**) was used to form an ohmic contact to help electron extraction from the PCBM to Al. Recently, Heo et al. [56] got high quality perovskite using **HI** as an additive resulting in a PCE~18.1% without significant *J* *V* hysteresis. *J* *V* hysteresis free is due to the fact that the thermally annealed PCBM layer on MAPbI₃ could reduce the surface traps significantly. Also important to note that the work function of PEDOT: PSS (4.9–5.2 eV depending on the ratio of PEDOT to PSS) is lower than the valance band edge of perovskite (e.g., 5.4 eV for CH₃NH₃PbI₃), so the potential energy loss at the PEDOT: PSS/perovskite interface decreases the built-in potential in PSCs and eventually their photovoltaic performance increases. Nevertheless, PEDOT: PSS based devices suffer from poor chemical stability due to its hygroscopic nature as well as inefficient electron blocking behaviour which require additional layer for efficient performance [174,175]. It is also noteworthy that PEDOT: PSS is acidic and it may leads to corrosion at substrates, especially in the case of flexible devices, where conducting polymer based plastic substrates are employed [176].

4.3. Other polymer, organic and carbon based HTMs

As the HTM contributes towards the V_{OC} in PSCs (Section 3.2 of this article), i.e. the difference of quasi Fermi energy levels of electron and hole species at the two opposing contacts, screening HTMs with energy levels to favor high V_{OC} is crucial. A mismatch in energy bands between HTM and perovskite will not only effect the V_{OC} but also will reduce the charge transfer at the interface [177]. For example, Cai et al. [83] reported **PCBTDP** as HTM with CH₃NH₃PbBr₃ in mesoscopic PSCs. They obtained a V_{OC}~1.15 V with PCE~3.04% which is significantly higher than a P3HT device (V_{OC}~0.5 V, and PCE~0.76%, respectively). Herein, the lower J_{SC} is due to large bandgap (~2.4 eV) of the perovskite (CH₃NH₃PbBr₃) which limits the maximum obtainable J_{SC} to be ~9 mA cm⁻² only [42,86]. Selecting perovskite absorbers with lower bandgap could help obtaining higher PV parameters. The larger difference in the V_{OC} (~0.66 V) of the two device is due to weaker light filtering effect of the PCBTDP polymer than P3HT, and also due to the fact that the carbazole groups in PCBTDP have favorable effect on device performance owing to a higher hole mobility and deeper HOMO level of the former. Similarly, Nagarjuna et al. [178] employed D A conjugated copolymer (abbreviated as P) as HTM in mesoscopic PSCs (CL/meso TiO₂/CH₃NH₃PbI₃/P/Au) which achieved PCE of ~6.64% and a V_{OC}~0.84 V, notably higher than a P3HT counterpart

(PCE~4.24%, and V_{OC} ~0.64 V). An impressive V_{OC} ~1.3 V was obtained via **PDI** as HTM in meso superstructured PSCs ($Cl/Al_2O_3/CH_3NH_3PbBr_3/PDI/Au$) due to a deeper HOMO level and wide energy gap of $CH_3NH_3PbBr_3$ [86]. Later, the same group used larger band gap absorber (2.3 eV) $CH_3NH_3PbBr_{3-x}Cl_x$ and deeper HOMO level HTM, 4,4' bis(N carbazoyl) 1,1' biphenyl (**CBP**) leading to high V_{OC} (~1.5 V) and J_{SC} ~4 mA cm⁻² compared to V_{OC} ~1.38 V, and J_{SC} ~0.7 mA cm⁻² for $CH_3NH_3PbBr_3$ based mesoscopic PSCs. The higher current in the former is because the use of Cl increased the surface coverage of perovskite layer and consequently resulted in a superior light absorption [41]. The highest V_{OC} ~1.61 V to date in PSCs was obtained using 1',1'',4',4'' tetrahydro di [1,4]methanonaphthalene no[1,2:2',3',5,6,6':2'',3''] [5,6] fullerene C_{60} as an ETL, $CH_3NH_3PbBr_3$ as an absorber and PEDOT: PSS as HTM [42]. The devices showed a PCE 7.5% with a high FF~0.77 and a J_{SC} ~6.04 mA cm⁻². Although the J_{SC} was close to its maximum theoretical limit for the material combination employed (~9 mA cm⁻²), the loss in potential, i.e., $E_G - qV_{OC}$ (~0.7 eV) is still higher and further improvements are possible. Such PSCs are highly suitable as a top cell in tandem device configuration as they have already resulted in V_{OC} as high as ~2.25 V (PCE~10.4%) [179].

A high open circuit voltage ~1.4 V was also achieved when carbon nanotubes (CNTs) were used as a hole conductor in $MAPbBr_3$ PSCs [180] and was due to efficient charge extraction and low recombination of the **CNT** hole conductor. Tandem solar cells with all perovskite absorbers were demonstrated with a $MAPbBr_3/CNT$ top cell and a $MAPbI_3$ bottom cell, achieving a V_{OC} of ~2.24 V in series connection. Habisreutinger et al. [53] replaced the organic hole transport material with polymer functionalized (**SWNTs**) embedded in an insulating polymer matrix, i.e. PMMA. With this composite structure, PCEs of up to ~15.3% were achieved, as well as reduced thermal degradation and improved resistance to water ingress as compared to cells employing state of the art organic hole transporting materials.

Biologically derived materials have also been employed as transport layers in solar cells. Whereas in OPV, deoxyribose nucleic acid (DNA) in its "natural" Na salt form was successfully integrated as an ETL between ITO and the bulk heterojunction polymer active layer [181], in perovskite solar cells a DNA hexadecyl trimethyl ammonium chloride (**CTMA**) complex was used as HTM in an inverted p i n device configuration with PCBM as electron acceptor layer. The cells exhibited a PCE of ~15.9% maintaining more than 85% of its initial value after 50 days in air [182].

4.4. Oligomer HTMs

Oligomer is a molecule of intermediate relative molecular mass which consist of a small plurality of units different than small molecules. Unlike Spiro OMeTAD and PTAA, Oligomer has strong absorption in the visible and near IR region, which contributes to the light harvesting in PSCs. Peng et al. [190] reported oligomer **S197**, a HTM with an order of magnitude higher hole mobility of $\sim 5.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ than Spiro OMeTAD ($\sim 4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) but lower than PTAA ($\sim 3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The lower molecular weight of **S197** facilitates its infiltration into perovskite nanocrystals and capping layer is formed above perovskite which effectively block the electron reaching anode. The devices employing **S197** demonstrated a champion PCE~12% and V_{OC} ~0.96 V.

4.5. Inorganic HTMs

Amongst the various HTM materials employed so far, Spiro OMeTAD and P3HT have shown the best performance typically resulting PCE~15%. Despite the efficient performance, these materials are (i) often characterized by inferior hole mobility in their pristine form, (ii) becomes sensitive to humidity upon addition of dopants (typically hygroscopic Li salts) and (iii) are expensive (1 g of Spiro

OMeTAD cost ~500 \$, see Table 1). The humidity sensitiveness often hinders stable performance of PSCs, as will be elaborated in the stability section of this article. This put stringent conditions on the choice of materials to be used as HTM, particularly when the commercial deployment of devices is considered which requires several years of device operation. This brings into play inorganic p type materials that have already shown promising results in the DSSCs and quantum dot solar cells due to wider band gap and high conductivity [191–193]. Furthermore, numerous reports have demonstrated that these inorganic hole conductors outperformed spiroOMeTAD based counterparts in solid state dye sensitized solar cells [194,195]. Employing such inorganic materials in PSCs will not only lead to high PCEs but also, more importantly, will result in long term operation and cost effective PSCs. Amongst such materials, CuI, CuSCN, NiO, Cu₂O, GO (graphene oxide), MoO₃ and lead sulfide quantum dots (PbS QDs) and offer promising possibilities to be employed as HTM in PSCs as listed in Table 6.

4.5.1. Copper iodide (CuI)

The first inorganic hole transport material which has been used in PSCs is CuI that resulted in a moderate PCE~6% [196] with PV parameters (J_{SC} ~17.8 mA cm⁻², V_{OC} ~0.55 V, FF~0.62) comparable to a spiroOMeTAD based PSC (J_{SC} ~16.1 mA cm⁻², V_{OC} ~0.79 V, FF~0.61% yielding a PCE~7.9%). However, a lowering of ~300 mV in V_{OC} in CuI based PSCs was attributed to the high recombination rate in CuI due to free iodine that could act as valence band trap and work as a recombination channel, as reported for s DSSC [197]. High hole mobility of CuI ($\sim 9.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) which is five orders of magnitude greater than that of Spiro OMeTAD ($\sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) still encourages its use in mesoscopic PSCs (Fig. 12b) [198]. A key obstacle was to deposit CuI from solution as solvents used to dissolve it can dissolve the perovskite layer also. Towards this end, an inexpensive gas solid reaction method was introduced to deposit a CuI thin film on $CH_3NH_3PbI_3$ which yielding an exceptionally high J_{SC} ~32 mA cm⁻². The remarkable J_{SC} was due to interfacial species formed between the $CH_3NH_3PbI_3$ and the CuI (Fig. 12a) resulting in photocurrent collection in NIR region (~1200 nm, Fig. 12c). The devices showed a PCE~7.4% with negligible hysteresis (Fig. 12d) compared to ~9.3% for the spiroOMeTAD counterpart. Chen et al. [58] demonstrated that CuI as HTM in inverted planar PSCs showed PCE~13.6%, V_{OC} 1.04 V owing to its high transmittance and deep valence band (~5.1 eV), and J_{SC} 21.06 mA cm⁻².

4.5.2. Copper thiocyanate (CuSCN)

Marked by good transparency in the visible and infrared regions, high mobility of $\sim 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, higher than Spiro OMeTAD ($4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and high chemical stability [199–201], CuSCN remains another compelling HTM of choice in PSCs. Chavhan et al. achieved PCE~6.4% using CuSCN in planar architecture (FTO/TiO₂/CH₃NH₃PbI_{3-x}Cl_x/CuSCN/Au) with V_{OC} ~0.72 V and FF~0.62. They argued that the lower V_{OC} in CuSCN PSCs compared to Spiro OMeTAD analogues is due to the lower diffusion length of CuSCN than its actual film thickness [202]. Ito et al. [203] confirmed the role of CuSCN as hole extraction layers in PSCs by comparing the device with and without CuSCN. They obtained a PCE of ~1.82% (HTM free, PCE~1.35%) using the following architecture (FTO/TiO₂/thin CH₃NH₃PbI₃/CuSCN/Au) which was further enhanced to ~4.85% by improving the penetration of CH₃NH₃PbI₃ into TiO₂ pores using hot air during spin coating. In another report [204], the same group introduced a Sb₂S₃ layer between TiO₂ and CH₃NH₃PbI₃ and noticed that the Sb₂S₃ layer not only enhanced PCE to ~5.24%, but also increased the device stability under light exposure without encapsulation. However, the enhanced stability is attributed to a less reactive surface of Sb₂S₃ as compared to TiO₂, which is believed to react with perovskite eventually leading to its crystal decomposition [205,206]. Qin et al. [207] achieved a PCE~12.4% using CH₃NH₃PbI₃ based

Table 6
Device architecture and photovoltaic parameters of inorganic hole transport materials based PSCs.

Device Configuration	Perovskite Deposition method	Photovoltaic parameters				Ref.
		Voc (V)	Jsc (mA cm ⁻²)	FF	PCE (%)	
CuI						
CL/mpTiO ₂ /CH ₃ NH ₃ PbI ₃ /CuI/Au	OSSD	0.55	17.8	0.62	6.0	[196]
CuI/CH ₃ NH ₃ PbI ₃ /PCBM/Al	GSC	1.04	21.06	0.62	13.58	[58]
CuSCN						
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₃ /CuSCN/Au	OSSD	0.63	14.5	0.53	4.85	[203]
CL/mpTiO ₂ /Sb ₂ S ₃ /CH ₃ NH ₃ PbI ₃ /CuSCN/Au	OSSD	0.57	17.23	0.52	5.12	[204]
CL/CH ₃ NH ₃ PbI _{3-x} Cl _x /CuSCN/Au	OSSD	0.72	14.4	0.61	6.4	[202]
CL/mes-TiO ₂ /CH ₃ NH ₃ PbI ₃ /CuSCN/Au	SD	1.01	19.7	0.62	12.4	[207]
CuSCN/CH ₃ NH ₃ PbI ₃ /C60/BCP/Ag	SD	0.92	21.4	0.68	13.4	[60]
CuSCN/CH ₃ NH ₃ PbI ₃ /C60/BCP/Ag	OSSD	1.00	21.9	0.75	16.6	[60]
NiO						
CL-NiO/NP- NiO/CH ₃ NH ₃ PbI ₃ /PCBM/Al	OSSD	0.83	4.9	0.35	1.5	[215]
CL-NiO/CH ₃ NH ₃ PbI ₃ /C60/BCP/Al	OSSD	0.74	12.95	0.60	5.7	[219]
NP-NiO/CH ₃ NH ₃ PbI _{3-x} Cl _x /PCBM/Ag	DSVD	0.78	14.2	0.65	7.26	[208]
CL-NiO/CH ₃ NH ₃ PbI ₃ /PCBM/BCP/Al	SD	0.92	11.77	0.68	7.40	[31]
CL-NiO/CH ₃ NH ₃ PbI ₃ /PCBM/BCP/Al	OSSD	0.92	12.43	0.68	7.8	[219]
nc-NiO/CH ₃ NH ₃ PbI ₃ /PCBM/Au	SD	0.88	16.27	0.63	9.11	[216]
CL-NiO/nc- NiO/CH ₃ NH ₃ PbI ₃ /PC ₇₁ BM/BCP/Al	SD	1.00	14.65	0.64	9.44	[31]
CL-NiO/nc- NiO/CH ₃ NH ₃ PbI ₃ /PCBM/BCP/Al	SD	1.04	13.24	0.69	9.51	[31]
CL-NiO/CH ₃ NH ₃ PbI ₃ /PCBM/BCP/Au	SED	1.10	15.17	0.59	9.84	[218]
CL/mp TiO ₂ /NiO/CH ₃ NH ₃ PbI ₃ /carbon	SD	0.89	18.2	0.71	11.4	[73]
CL-NiO/nc- NiO/CH ₃ NH ₃ PbI ₃ /PCBM/BCP/Al	SD	0.96	19.8	0.61	11.6	[220]
CL- NiO/mp Al ₂ O ₃ /CH ₃ NH ₃ PbI ₃ /PCBM/BCP/Ag	OSSD	1.04	17.9	0.73	13.5	[221]
CL/mp TiO ₂ /ZrO ₂ /NiO/carbon-CH ₃ NH ₃ PbI ₃	SD	0.91	21.63	0.76	14.9	[224]
CL-Cu: NiO/CH ₃ NH ₃ PbI ₃ /PCBM/C ₆₀ /Ag	OSSD	1.11	19.01	0.73	15.4	[30]
CL-NiO/CH ₃ NH ₃ PbI ₃ /ZnO/Al	TSSD	1.01	21.00	0.76	16.1	[44]
mp-NiO/CH ₃ NH ₃ PbI ₃ /PCBM/LiF/Al	SET	1.06	20.2	0.81	17.3	[62]
Cu₂O						
Cu ₂ O/CH ₃ NH ₃ PbI ₃ /PCBM/Al	OSSD	0.89	16.52	0.56	8.23	[229]
CL/CH ₃ NH ₃ PbI _{3-x} Cl _x /Cu ₂ O/Au	VASP	0.96	15.8	0.59	8.91	[230]
Cu ₂ O/CH ₃ NH ₃ PbI ₃ /PCBM/Ag	SD	0.95	17.5	0.66	11.03	[231]
Cu ₂ O/CH ₃ NH ₃ PbI ₃ /PCBM/Al/Ca	OSSD	1.07	16.52	0.75	13.35	[64]
CuO _x /CH ₃ NH ₃ PbI ₃ /C ₆₀ /BCP/Ag	FDC	0.99	23.2	0.74	17.1	[232]
GO						
GO/CH ₃ NH ₃ PbI _{3-x} Cl _x /PCBM/ZnO/Al	OSSD	1.00	17.46	0.71	12.40	[242]
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₃ /GO/Spiro OMTAD/Au	SD	1.04	20.2	0.73	15.1	[65]
WO₃						
WO ₃ /CH ₃ NH ₃ PbI ₃ /PCBM/Al	SD	0.92	18.1	0.64	7.68	[253]
WO ₃ /CH ₃ NH ₃ PbI ₃ /PCBM/Ag	TSSD	0.93	16.6	0.64	9.8	[254]
VO_x						
VO _x /CH ₃ NH ₃ PbI ₃ /PCBM/Al	OSSD	0.9	22.29	0.7	14.23	[252]
PEDOT: PSS- V ₂ O ₅ /CH ₃ NH ₃ PbI ₃ /C ₆₀ /BCP/Ag	OSSD	1.05	21.2	0.78	17.5	[251]
Quantum dots						
PbS/CH ₃ NH ₃ PbI ₃ //PCBM/Al	SD	0.86	12.1	0.72	7.5	[265]
CL/mp TiO ₂ /CH ₃ NH ₃ PbI ₃ /CuInS ₂ -ZnS/Au	TSSD	0.92	18.6	0.48	8.38	[266]

FDC: fast crystallization-deposition.

mesoscopic PSCs (FTO/TiO₂/CH₃NH₃PbI₃/CuSCN/Au) with V_{OC}~1.02 V. They used two step deposition technique to control the thickness of perovskite and also to attain an over layer of ~200 nm to prevent direct contact between TiO₂ and CuSCN. The CuSCN layer was deposited using doctor blading technique at 65 °C, a method that is compatible with mass production of PSCs. Devices using CuSCN resulted in 65% and 9% higher J_{SC} and V_{OC} compared to HTM free architecture. Inspired from the progress in mesoscopic PSCs, researchers also employed CuSCN in inverted planar PSCs in following architecture (FTO/CuSCN/CH₃NH₃PbI_{3-x}Cl_x/PCBM/Ag) [208]. Despite the fact that FTO/CuSCN interface demonstrated > 90% PL quenching efficiency (Fig. 13), the PCE was limited to 3.8% due to low shunt resistance for thinner CuSCN layers and higher series resistance for the thicker layers. Further research is required to tune its

performance in planar heterojunction devices.

The highest PCE (~16.6%) in PSCs using CuSCN is reported by Ye et al. in the inverted planar PSCs [60] of ITO/CuSCN/CH₃NH₃PbI₃/C60/BCP/Ag architecture. The CuSCN layer was electrodeposited leading to a lower surface roughness and smaller contact resistance between the CH₃NH₃PbI₃ layer and CuSCN thereby. The perovskite film was deposited via drop casting assisted one step spin coating leading to high perovskite coverage. The device showed a high V_{OC}~1 V and FF~0.75, higher compared to ~0.9 V and ~0.68 for corresponding devices made via a typical sequential deposition method of perovskite. It is clear that deposition method of the HTM, as well as that of the perovskite absorber, play an important role in the performance of the PSCs. A dense and thin HTM layer (~100 nm) lead to excellent transparency in the visible light spectrum range and also an efficient

hole transfer at the HTM/perovskite interface. Moreover, the perovskite surface roughness and surface relaxation affects the performance of PSCs. Smoother perovskite film may reduce cost of PSCs as thinner HTM coverage is needed compared to rough films.

4.5.3. Nickel oxide (NiO)

Since the work of Irwin et al. reporting enhancement in performance of polymer bulk heterojunction solar cells (BHJ) by replacing the PEDOT: PSS layer by a thin p type semiconducting NiO layer [209], it became one of the HTM of choice in OPV and DSSCs [210–214]. Owing to large energy gap, good conductivity of holes and deep VB edge level (5.2–5.4 eV), which match well with the VB of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite (5.4 eV), NiO is marked as a promising material for p type or inverted PSCs. Docampo et al. [162] first reported a thin NiO layer as HTM using $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ PSCs and noticed that a low coverage of perovskite surface lead to direct contact between the HTM (NiO) and the ETL (PCBM) resulting in low device performance $\text{PCE} \sim 0.1\%$. Subsequently, Tian et al. reported mesoporous NiO as HTM in mesoscopic architecture (CL NiO/NP NiO/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Al) [215] with notable rise in PCE ($\sim 1.5\%$) by controlling the thickness of the BL NiO and NP NiO to be 80 and 120 nm, respectively.

The PCE for the NiO based inverted mesoscopic PSCs has been further improved by Zhu et al. using NiO nanocrystal (NC) [216]. Sol gel and two step deposition methods have been used to control the thickness of NiO layer and perovskite, respectively. An optimized

thickness of NiO NC and perovskite (~ 40 nm and ~ 250 nm thickness, respectively) yielded $\text{PCE} \sim 9.1\%$ and $V_{\text{OC}} \sim 0.88$ V in inverted PSCs (NiO NC/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Al). Similarly, post treatment of NiO layer by O_2 plasma showed a $\text{PCE} \sim 7.3\%$ with $V_{\text{OC}} \sim 0.78$ V [208]. The NiO was electrodeposited whereas the perovskite layer was synthesized via vacuum evaporated technique in a device architecture FTO/NiO/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ /PCBM/Ag. In a similar work, Hu et al. [217] carried out UVO treatment for NiO layers in a planar inverted PSC (ITO/NiO (solution)/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM/Al) while also controlling the pin hole free structure of perovskite layer using sequential deposition method. An optimized thickness of NiO and a 10 min UVO treatment yielded a $\text{PCE} \sim 7.6\%$ and impressive $V_{\text{OC}} \sim 1.05$ V. These studies showed that the quality of NiO film and its surface treatment to remove defect states and impurities is crucial to obtaining high PCE in PSCs. Nevertheless, various reports employed NiO as HTM in the inverted planar structure and the reported PCE is in the range of ~ 6 – 10% [216,218,219]. The higher $\text{PCE} \sim 15.4\%$ ($J_{\text{SC}} \sim 19$ mA cm^{-2} , $\text{FF} \sim 0.73$ and $V_{\text{OC}} \sim 1.1$ V) for the NiO based inverted planar PSCs is reported by Kim et al. [30] using solution processed Cu doped NiO_x which is remarkably higher than a pristine NiO based device ($\text{PCE} \sim 8.9\%$, $J_{\text{SC}} \sim 4.1$ mA cm^{-2} , $\text{FF} \sim 0.6$ and $V_{\text{OC}} \sim 1.1$ V). The enhancement of J_{SC} and FF is due to the improved electrical conductivity of 5 at% Cu: NiO_x which enabled more efficient charge extraction from the $\text{CH}_3\text{NH}_3\text{PbI}_3$ absorber. Moreover, the general applicability of Cu: NiO_x in perovskite of larger E_g [$\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$] solar cells has been demonstrated which exhibit

Fig. 12. (a) X-ray spectroscopy image confirm diffusion of Cu atoms into the perovskite layer at the interface of perovskite/CuI (rectangular box), (b) Cross sectional FE-SEM images of the TiO_2 /perovskite/CuI layer, (c) Photon-to-electron conversion efficiency of PSCs with CuI (red curve) and Spiro-OMTAD (blue curve) as HTM, and (d) J-V curves of devices prepared with CuI as the HTM in the scan direction of forward bias to short circuit (FB-SC) and short circuit to forward bias (SC-FB). Figure are reproduced with permission from Ref. [198]. John Wiley and Sons.

Fig. 13. (Left) Photoluminescence (PL) intensity of CH₃NH₃PbI_{3-x}Cl_x on (i) glass, (ii) FTO, (iii) FTO/NiO, and (iv) FTO/CuSCN. Maximum charge quenching is showed for perovskite on FTO/CuSCN, and, dark I-V curves of NiO and CuSCN based PSCs (right). Figures are reproduced with permission from [208]. Copyright of American Chemical Society.

high V_{OC} ~1.1–1.2 V [30].

Chen and Guo groups reported a systematic study on the effect of HTM and perovskite morphologies and a correlation between band alignment and the PV parameters in NiO based inverted PSCs [31,219,220]. In the inverted planar PSCs (CL NiO/CH₃NH₃PbI₃/PCBM/bathocuproine BCP/Al), they reported PCE~7.8% and V_{OC} ~0.92 V for a ~60 nm thick perovskite layer which is nearly double than that of PSCs employing PEDOT: PSS (PCE~3.9% and V_{OC} ~0.62 V). The higher PV parameters in the former are due to good alignment of the VB of NiO with VB of perovskite. Another reason for the high V_{OC} in NiO PSCs is their better perovskite surface coverage, 93% for ITO/NiO compared with 85% for ITO/PEDOT: PSS, which prevents contact of the HTM with the ETL and thereby avoids charge recombination. In another report, the same group enhanced the PCE to ~9.51% using mesoscopic inverted structure composed of (ITO/NiO (solution)/NiO_{nc} CH₃NH₃PbI₃/PCBM/(BCP)/Al) structure [31]. The high PCE was attributed to the mesoporous layers (NiO_{nc}) which accommodated thicker perovskite layers and prevented the risk of morphological defects, that could otherwise determine a decay of photovoltaic performance in the planar structure (PCE 7.8%). To fill the nano pores of the NiO_{nc} with high surface coverage, sequential deposition method was used that led to ~250 nm thick mesoscopic junction, which is large enough to absorb 90% of the incident light. An increased light harvesting efficiency (LHE) was observed in the mesoscopic device compared to a planar one. While the IPCE for planar device was still higher in the short wavelength range (400–500 nm), the mesoscopic devices possessed enhanced IPCE at longer wavelengths.

The PCE was further enhanced to ~10.7% by the same group when the NiO was deposited using sputtering to get a homogenous and uniform HTM layer [220]. Such a layer not only improved its contact with the substrate but also allowed them to obtain a uniform morphology of perovskite layer over it. The PCE was further increased to ~11.6% at optimized oxygen doping in argon atmosphere.

In order to minimize the losses during light harvesting and charge transfer at the interfaces, Chen et al. [221] reported a hybrid interfacial layer of “compact NiO/mp Al₂O₃” in inverted PSCs device of CL NiO/Al₂O₃/CH₃NH₃PbI₃/PCBM/BCP/Ag with high PCE~13.5% with impressive V_{OC} ~1.04 V. This interfacial layer exerted an important “dual blocking effect” as shown in Fig. 14. It acts as a barrier between the FTO and CH₃NH₃PbI₃ and also helps to block the shunt paths between NiO/PCBM via the mp Al₂O₃ layer filled with perovskite crystals.

Another interesting device design for PSCs is metal back contact free, inspired from monolithic DSSCs [222,223]. Typically, carbon black/graphite are stacked on top of perovskite layer. Mei et al. used 5 ammoniumvaleric acid iodide modified perovskite ((5 AVA)_x(MA)_{1-x}PbI₃) as an absorber in HTM free PSCs that resulted in PCE~12.8%

[29]. These results demonstrate the potential of earth abundant carbon materials for cost effective PSCs. Zonghao Liu et al. [73] replaced mesoporous ZrO₂ by NiO in the state of the art monolithic PSCs which resulted in an impressive PCE~11.4% (V_{OC} ~0.89 V and FF~0.71). In the PSCs with architecture CL/mpTiO₂/NiO/C (CH₃NH₃PbI₃), CH₃NH₃PbI₃ was deposited via a two step deposition method while the mesoporous NiO and TiO₂ layers are fabricated by screen printing technique. Subsequently, Xu et al. [224] reported a structure of TiO₂/ZrO₂/NiO/carbon CH₃NH₃PbI₃ with PCE~14.9% and V_{OC} ~0.91 V which was higher compared to a TiO₂ only based counterpart (PCE~10.4% and V_{OC} ~0.86 V). Cao et al. [225] added a 800 nm mesoporous NiO layer screen printed just underneath of the 10 μ m carbon black/graphite top contact to improve charge collection and reduce charge recombination leading to a PCE~15%. The highest PCE~17.3%, V_{OC} ~1.06 V achieved by Seok et al. [62] using inverted planar PSCs, in which a well ordered nanostructured NiO film was prepared through a pulsed laser deposition (PLD) method. This efficiency is the highest so far for PSCs using inorganic HTMs.

In summary, the p type semiconductor NiO has been demonstrated to be an efficient HTM in PSCs with impressive photovoltaic performance with V_{OC} ~1.11 V, closer to that achieved in a state of the art mesoporous PSCs configuration using spiroOMeTAD. The robust and abundant NiO material promises a cost effective and potentially stable commercially deployable perovskite solar cells.

4.5.4. Cuprous oxide (Cu₂O)

High hole mobility 100 cm² V⁻¹ s⁻¹ [63], long carrier diffusion length and direct band gap (~2.17 eV) [226] are the main reasons for using Cu₂O as HTM in heterojunction solar cells [227]. Moreover, simulation results showing that a PCE > 13% could be achieved with an optimized Cu₂O as HTM in PSCs [228]. Therefore, owing to natural abundance of Cu₂O becomes a promising alternative HTM in PSCs resulting in high PCE~8–17% [64,229–231] as listed in Table 6. Nejand et al. [230] deposited Cu₂O layer on pinhole free CH₃NH₃PbI_{3-x}Cl_x using magnetron sputtering in planar structure, yielding a PCE~8.93% with V_{OC} ~0.96 V compared to ~11.5% and ~0.99 V pin hole free Spiro OMTAD device shown in Fig. 15. Similarly, Yu et al. [231] sputter Cu with a thermal oxidation control to get ultrathin Cu₂O layer (5 nm) as HTM in inverted planar PSCs. A PCE~11.03% with V_{OC} ~0.95 V was demonstrated. To simplify the film process of HTM and improve the PCE of PSCs Zuo et al. [64] presented a facile low temperature method to prepare Cu₂O and use it as HTM in the inverted structure ITO/HTM/CH₃NH₃PbI₃/PCBM/Al/Ca which showing a significantly enhanced V_{OC} ~1.07 V, J_{SC} ~16.52 mA cm⁻², FF~0.75 and high PCE~13.35% compared with V_{OC} ~0.95 V, J_{SC} ~14.82 mA cm⁻², FF~0.78 and PCE~11.04% for PEDOT: PSS based device. However, the highest PCE~17.1% and V_{OC} ~0.99 V reported by

Fig. 14. The energy levels (versus vacuum) of various material components employed in the device showing the dual blocking effect of the hybrid “compact NiO/mp-Al₂O₃” interfacial layer and J-V curves of the compared solar cells measured at 1 sun (and also their dark J-V curves). The devices were scanned from J_{SC} to V_{OC} . Figure is reproduced with permission from reference [221]. Copyright of Royal society of chemistry.

Sun et al. [232] using CuO_x from facile solution processed in inverted planar PSCs. Therefore, low cost, facile synthesis, and high device performance, recommended Cu₂O as HTM for facilitating the development of industrial scale perovskite solar cell technology.

4.5.5. Graphene oxide (GO)

GO has also been used as an HTM in polymer solar cells owing to its suitable VB (5.2 eV) [233], high charge mobility (3000–27,000) cm² V⁻¹ s⁻¹ and electronic conductivity [234–236]. It is also equipped with unique properties ranging from superior thermal conductivity ~600 W m⁻¹ K⁻¹ [237,238], and high optical transmittance [239]. Owing to their unique characteristics, nanocomposites of GO/TiO₂ are used as ETL in PSCs which not only assisted to decrease the deposition temperature from 500 to 150 °C but also enhanced the photovoltaic performance from PCE~10%, V_{OC} ~1 V in pristine TiO₂ PSCs to PCE~15.60%, V_{OC} 1.05 V [240]. Moreover, an ultrathin graphene quantum dot layer between TiO₂ and perovskite layer enhanced the PCE from ~8.81 to ~10.15% [241]. These results encouraged Wu et al. [242] to investigate suitability of GO as a HTM using the inverted planar architecture ITO/GO/CH₃NH₃PbI_{3-x}Cl_x/PCBM/ZnO/Al. A ~2 nm thick layer of GO improved CH₃NH₃PbI_{3-x}Cl_x crystal domain and the surface coverage which led to high PCE~12.4% with high V_{OC} ~1.0 V and J_{SC} ~17.46 mA cm⁻². Li et al. [65] improved the interface between perovskite and HTM (Spiro

OMeTAD) using GO as a buffer layer which decreased the contact angle between perovskite and HTM from ~13.4 to zero degree (as shown in Fig. 16) resulting in an enhancement of the J_{SC} from ~18.5 to ~20.2 mA cm⁻². Moreover, this buffer layer retarded the charge recombination leading to significant enhancement in V_{OC} and FF from ~0.93 V and ~0.64 to ~1.04 V and 0.73, respectively. Consequently, the PCE increased by ~45%, i.e., from ~10 to ~15.1% using GO as dual function buffer layer in mesoscopic PSCs. The best performance ~18.2% in GO based PSCs is reported when it is inserted as a buffer layer between Spiro OMeTAD and perovskite to improve hole extraction [89]. Notably the device also showed a stable performance for 16 h under continuous light soaking.

4.5.6. Molybdenum oxide (MoO₃)

MoO₃ has been used to improve hole injection and extraction in organic photovoltaics (OPVs) [243,244] and organic light emitting diodes (OLEDs) [245], respectively. Therefore, several attempts have been done for using it in PSCs as HTM due to its non toxicity and ambient conditions stability. Kim et al. [246] used MoO₃ as an interfacial layer combine with N,N'-Di(1 naphthyl) N,N'-diphenyl (1,10 biphenyl) 4,40 diamine (NPB) as HTM in the fully vacuum processed inverted planar PSCs. MoO₃ developed an ohmic contact between ITO and perovskite layer resulting in a high built in field and showed V_{OC} ~1.12 V and PCE~13.7% in the above device. Similarly,

Fig. 15. Cross sectional (a) FE-SEM and (b) EDS map of pinhole-free FTO/TiO₂/CH₃NH₃PbI_{3-x}Cl_x/Cu₂O indicating the presence of Cu (red) and Pb (light blue) atoms and (c) J-V curves of prepared device using pinhole-free perovskite layers with a scanning direction of forward bias to short circuit (FB-SC) or short circuit to forward bias (SC-FB). Figure are reproduced with permission from Ref. [230]. Copyright of Wiley.

Fig. 16. Comparison of the contact angle between HTM (Spiro-OMeTAD) and perovskite layer without (a) and (b) with GO, and (c) J-V curve for the champion device with GO layer. Figures are reproduced with permission from Ref. [65]. Copy right of Royal Society of Chemistry.

Hou et al. [187] incorporated a MoO_3 with PEDOT: PSS as HTM in inverted planar PSCs. MoO_3 dramatically increased the PCE to 14.78%, which is $\sim 30\%$ higher compared to pristine PEDOT: PSS based device. Moreover, a thin MoO_3 layer has been used in the conventional structure PSCs (n i p architecture) between the HTM and metal contact to reduce contact resistance at the interfaces, which not only increase the PCE but also increase the stability of the device [247–250].

4.5.7. Vanadium oxide (VO_x)

The fact that inorganic HTMs typically require high temperature deposition hampers the choice of substrates and inhabits the large scale production. A remedy is low temperature solution processable VO_x which also shows high transmittance; and therefore, allow maximum sunlight to reach the perovskite absorber layer [251,252]. Haocheng et al. [252] reported PCE $\sim 14.14\%$ in inverted PSCs based on VO_x . A notable $V_{oc}\sim 0.9\text{ V}$ and negligible hysteresis were reported. Similarly, Haitao et al. [251] used V_2O_x as a buffer layer between perovskite and PEDOT: PSS that enhanced the VB of the latter from ~ 5.1 to $\sim 5.4\text{ eV}$. A remarkable hysteresis free PCE $\sim 17.5\%$ and V_{oc} of 1.05 V were achieved. The performance was significantly higher when compared to pristine PEDOT: PSS (PCE 14.2% and V_{oc} 0.85 V) and pristine V_2O_x (PCE 14.8% , V_{oc} 0.98 V).

4.5.8. Tungsten oxide (WO_x)

WO_x is another low temperature inorganic HTM reported for PSCs. Zhiwei et al. [253] reported a solvothermal method to fabricate WO_3 nanocrystal as HTM in inverted PSCs and showed PCE 7.68% (V_{oc} 0.92 V). Subsequently, Zong Liang et al. [254] treated WO_3 with UV ozone to improve the surface coverage of perovskite layer that resulted in PCE 9.8% .

4.5.9. Nanocrystals

Nanocrystals of CuInS_2 and $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) are known as promising light absorbing materials due to their direct band gap (1.5 eV) [255] and low temperature solution processability [256,257]. The VB level of CuInS_2 (5.6 eV) matches well with that of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (5.6 eV); and therefore, could be a promising HTM. Chong et al. [258] employed CuInS_2 via low temperature processing in a device (ITO/ $\text{CuInS}_2/\text{Al}_2\text{O}_3/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Ag}$) with a Al_2O_3 as scaffold layer and showed an optimized PCE of $\sim 5.3\%$. Later on, Laraib et al. [259] introduced CZTS nanocrystal as HTM synthesized at $T < 100^\circ\text{C}$ in planar PSCs. CZTS showed an excellent HTM characteristics as interface layer which enhanced the charge transfer yielding a PCE of $\sim 15.4\%$ and an exceptionally high FF ~ 0.81 .

4.5.10. Quantum dots

A strategy to improve PV performance of solar cells is broaden the light harvesting to near infrared (NIR) region which has been widely utilized in quantum dots (QDs) sensitized solar cells [260] An example

for this is PbS QDs that are characterized by a large excitonic Bohr radius $\sim 18\text{ nm}$, a low bulk energy band gap of about 0.41 eV [261], which is tunable with size [262]. Recently, PbS QDs are reported as a co sensitizer together with $\text{CH}_3\text{NH}_3\text{PbI}_3$ in a heterojunction solar cell by Etgar et al. [263] also Seok's group [264] however, the PCE was limited $< 4\%$. An improvement in PCE to 7.5% is reported by Long et al. [265] which employed colloidal PbS QDs as HTM for planar PSCs by tuning the VB level close to the $\text{CH}_3\text{NH}_3\text{PbI}_3$. Another QD HTM is CuInS_2 , reported by Mei et al. [266] in mesoporous PSCs. CuInS_2 QDs provides a PCE $\sim 6.57\%$ further improved to $\sim 8.38\%$ by modifying the surface of CuInS_2 QDs by cation exchange to form $\text{CuInS}_2/\text{ZnS}$ core/shell QDs. The modified HTM enhanced charge transport/transfer and the device performance thereby. These QDs could offer a versatile and new pathway for the future development of cost effective inorganic HTMs.

5. Hole transport materials and stability of perovskite solar cells

High efficiency, long term stability, and a low cost are the main factors determining the success of a PV technology [267–270]. Although PSCs can be fabricated via solution processing, a method that can be applied for cost effective mass production, and their PCE has reached a value as high as $\sim 22.1\%$ [21], they are typically unstable when exposed to humidity, high temperatures, and light [271,272]. The factors inducing instability in PSCs can be classified as intrinsic and extrinsic as in Fig. 17 [273]. Whereas intrinsic instability in the devices arises from (i) structural instability, (ii) ionic polarization of perovskite crystals in presence of electric field (hysteresis), and (iii) selective contacts, i.e., ETL and HTM and their interfaces with perovskite, the external instability is caused due to electrical biasing, prolonged light soaking, UV irradiation, humidity, oxygen, and temperature [29] [174,274].

Crystalline phases of the perovskite can change as a result of different temperatures and pressures which consequently affects the stability of the device. The structural stability of common perovskite ABX_3 can be understood from the tolerance factor (t), which is given by the following Eq. (1).

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1)$$

where r_A , r_B and r_X are the ionic radii of the A, B and X ions, respectively. For a perfectly packed cubic perovskite structure $t=1$ [288]. Moreover, temperature has also a significant impact on the structural stability of the perovskite because of the fact that rising temperature transforms the symmetry from tetragonal to cubic [289]. Density functional theory study showed that the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ trans form from $Pm3m$ to $Im3$ just below 1 GPa pressure and amorphization occurs at $\sim 2.8\text{ GPa}$ without the cations undergoing long range orienta

Fig. 17. Factors inducing instability in perovskite solar cells can be classified as external, i.e., temperature [275,276], moisture [277,278], oxygen [279], light (including UV light) [280 282] and electric field [283–287], and internal [206,281].

tion. The major source of volume reduction under compression is from the tilting, and to a lesser extent shrinking, of the PbBr_6 octahedra. The amorphized sample was recrystallized upon release of pressure [290].

During the process of synthesizing, assembling and outdoor testing of PSCs, oxygen and moisture in the atmosphere may attack and enter the device causing degradation [291]. This is due to the fact that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ is very sensitive to water, which hydrolyzes and consequently degrades the perovskite accordingly to Eq. (2) [292].

$\text{CH}_3\text{NH}_3\text{I}$ decomposes into CH_3NH_2 and HI as shown in reaction (2a) where the HI degrades in two ways either in the presence of oxygen (2b) or due to photochemical reaction under UV irradiation (2c).

Fig. 18. (a) Illustration of the possible degradation pathway of the perovskite in the presence of water. A water molecule, a, is required to initiate the decomposition process where both hydrogen iodide (b, soluble in water) and methyl ammonia (c, volatile and dissolve in water). Finally a yellow solid is formed showing presence of PbI_2 , d [293], and (b) schematic of perovskite degradation when exposed to sunlight [204]. Figure reproduced with permission from the reference. Copy right of American Chemical Society.

Fig. 19. Comparison of normalized PV parameters (a–d) of the planar PSCs as a function of irradiation and without irradiation time for 90 min at high humidity (50–60%), (e and f) SEM images of fresh and degraded perovskite layer in dark, (g) normalized PV parameters and their comparison with the renewal of Au electrode, and (h) compared the XRD pattern of exposed device and unexposed one [295]. Figure reproduced with permission from the reference. Copy right of The Royal Society of Chemistry.

The perovskite crystals decompose under exposure of light, ingress of water, humidity, and temperature. One simple plausible mechanism proposed by Jarvist et al. [293] is shown in Fig. 18a. When a perovskite layer is exposed to water, a single water molecule is sufficient to initiate the reaction and degrade the material. It is a well known fact that TiO_2 contains oxygen vacancies, particularly at the surface which are considered to be electron donating sites [280]. The electrons in these sites reside ~ 1 eV below the conduction band interacting with the oxygen molecules present in the atmosphere.

Similarly, instability in PSCs also partly arises in the presence of UV light and also due to a possible reaction between the TiO_2 ETL and perovskite [280]. The degradation occurs at TiO_2 nanoparticle layer and perovskite interface introduces a possibility of ion migration at the ETL perovskite interface thereby leading to decomposition of perovskite crystal, even in absence of humidity [205,294]. Fig. 18b shows the schematic representation of perovskite degradation in the presence of light exposure which decomposes to PbI_2 , CH_3NH_2 and HI (Eq. (3)). Furthermore, it is observed that the perovskite layer degrades upon exposure to constant illumination at the TiO_2 perovskite interface as described in Eq. (3c) [204].

It is believed that the photo induced degradation occurs mainly at the HTM/metal (Au) interface [295]. Due to the solar irradiation, the PSCs performance deteriorated and the PCE plummeted to 2.46% from 18% in just 180 min as shown in Fig. 19d [295]. As can be seen (Fig. 19a–c), a significant decline in J_{sc} and FF can be observed while the degradation of V_{oc} is slow. Meanwhile, the morphological comparison of the perovskite films with and without UV irradiation shows minor change with irradiation, as illustrated in Fig. 19(e and f). Interestingly the degradation recovered partially when the illuminated device was kept in the dark for about 90 min as can be seen from Fig. 19g. However, the fact that most of the photoinduced degradation was irreversible led to an assumption that the degradation might be due to moisture because the devices were tested at the ambient condition. In order to know the cause of degradation, same fresh devices were kept in the dark where they showed relatively lower degradation as compared to those under light irradiation (Fig. 19a–d). This demonstrated that degradation is not significant in the presence of humidity alone and it is triggered when humidity is coupled with photon dose, as also recently indicated by Manshor et al. [281]. Wei et al. [295] compared the photoinduced degradation effect in both

mesoporous and planar PSCs where they showed relatively higher degradation in the latter. The mesoporous device maintains 60% of its initial PCE value while the planar rivals showed merely 20% performance at similar experimental conditions. The XRD pattern of the both fresh and degraded devices were measured where all the peaks can still be indexed to the perovskite (Fig. 19h). It shows that the photoinduced degradation is different than the moisture induced one as the latter showed PbI₂ peaks after decomposition whereas the former did not. Initially the cause of this degradation was understood to be UV light that creates electron hole pairs in the mesoporous TiO₂ structure [280]. Subsequently Wei et al. [295] reported higher degradation in planar counterparts where thinner TiO₂ ETLs should be less effected by UV light. This demonstrated that besides the TiO₂/perovskite interface, degradation also takes place at the HTM/perovskite or HTM/Au interfaces, respectively. The performance of their degraded cells recovered when the back contact (Au) of the degraded device was replaced with the fresh one (Fig. 19g). Similarly, the TiO₂ perovskite interface is also known to cause degradation in PSCs owing to the reactivity of mesoporous TiO₂ or planar layer [206] which is overcome by introducing thermodynamically stable TiO₂ nanorods [205,296,297].

The HTM is considered to be one of the dominant factors inducing instability in these devices. The most successful employed HTMs are organic HTM layer (~300 nm), typically small molecules (spiroOMeTAD), conducting polymers (P3HT, PTAA and PEDOT: PSS etc.), and inorganic HTMs (CuPc, NiO, CuO etc.), as a hole selective contact [48]. The organic HTMs among these are sensitive to moisture and oxygen; and therefore, cause degradation in PSCs [29,83,110,292,298–305]. A common example is the widely employed Li salt (Li TFSI) doped spiroOMeTAD react with humidity and degrades in a few seconds owing to its hygroscopic nature [133,142,306–310]. Towards stable PSCs, research on HTM perspective can be classified as: (i) dopant free HTMs [142,307,309,310], (ii) inorganic [224,311–313] or organic alternatives [302,303,314] to the typically employed hygroscopic Spiro OMeTAD, (iii) post modification of HTM or encapsulation to protect the device from humidity [298,300,305,315–317], and (iv) alternative additives to Li salt [110,318–320]. We divide our discussion in two sub section: (i) n i p device (mesoporous or planar), employing an n type layer over the TCO in conjunction with perovskite and a thin layer of HTM (typically spiroOMeTAD), and (ii) p i n devices, also called inverted planar PSCs, employing a p type layer, typically PEDOT: PSS on FTO followed by a perovskite and ETL layers on it. Following the scope of this paper, our discussions are limited to the role of HTM layer in these architectures to achieve stability.

5.1. Degradation induced by spiroOMeTAD and P3HT

High efficiency PSCs often employ P3HT and spiroOMeTAD as HTMs [321,322]. The amorphous spiroOMeTAD has a low hole mobility, which could be improved by p dopants such as Li salts. However, the dopant, owing to its hygroscopic nature, acts as a humidity centre. Snaith et al. [53] showed that Li doped spiroOMeTAD degrades significantly faster than that of pristine spiroOMeTAD counterpart.

The HTM forms the outermost layer in a typical PSC architecture and serves as a protective shield to the perovskite layer. Apart from the intrinsic electronic properties of the HTM, three basic features such as hydrophobicity, permeability and density are pre requisite for an efficient stable PSCs. Towards this end, PMMA is employed as HTM in PSCs which is hydrophobic in nature; and therefore, it simultaneously inhibit the ingress of moisture and evaporation of MAPbI₃ as shown in Fig. 20a. However, PMMA owing to insulator behaviour is not capable to transport charges; and therefore, it is composited with a high conducting p type conductors such as SWNTs. The P3HT SWNTs composite is one of the best candidates due to the exceptional charge

transport properties together with its chemical stability. The composite P3HT/SWNTs PMMA as HTM not only acted as a strong protective layer against moisture ingress but also showed outstanding thermal stability compared to other HTMs as shown in Fig. 20b.

The faster degradation of spiroOMeTAD is also evident in another report by Cao et al. [323] PSCs with perthiolated trisulfur annulated hexa *peri* hexabenzocoronene (TSHBC) as HTM retained >85% of their initial PCE (12.8% for pristine and 14% when doped with graphene) after 10 days (devices were stored in air with humidity ~45%). In contrast, PSCs fabricated using spiroOMeTAD retained only 20% of their initial PCE at similar experimental conditions (Fig. 21a). In addition, the contact angle of water on both TSHBC and TSHBC/graphene were 107° while it was 70° only on spiroOMeTAD confirming the hydrophobicity of the former. Another alternative to spiroOMeTAD is PEDOT: PSS, which is also widely employed in high performance inverted BHJ PSCs; however, its hygroscopic and acidic characteristics are unfavourable for stable device operation. The device stability is improved significantly when polymer such as PMMA or polycarbonate (PC) mixed with carbon nanotubes are employed as HTM. The stability is also improved when hydrophobic HTMs replaced the hygroscopic Li salt [324].

Despite the fact the Spiro MeOTAD is one of champions and arguably most employed HTMs, it is recently shown to induce degradation at HTM/perovskite interface due to the chemical reaction between Spiro MeOTAD⁺ and I⁻ [325]. This puts a question mark on whether PSCs employing Spiro MeOTAD could really deliver long term operational stability. A remedy could be to employ buffer layers between perovskite and HTM, as reported by Koushik et al. [90]. An ultrathin Al₂O₃ layer between perovskite and HTM not only demonstrated a remarkable stabilized PCE 18%, but also showed a stable shelf life for 70 days (retaining 60–70% of initial performance). A reference device without the buffer layer only retained 12% of initial PCE. A similar improvement in stability is reported when montmorillonite layer is employed between HTM and perovskite [326].

The Spiro MeOTAD can in fact also induce degradation by reacting with metal back contact (Ag/Au) at alleviated temperature (> 70 °C) due to diffusion of metal ions into the HTM [327]. This is overcome by employing a thin buffer layers such as Cr.

5.2. Alternative HTMs towards stable perovskite solar cells

Alternative THMs (to commonly employed organic and unstable Spiro OMeTAD and PEDOT: PSS) such as hydrophobic CuI showed excellent ambient stability compared to PEDOT: PSS (Fig. 21b) [323]. The CuI based device retained 90% of its initial efficiency after 14 days whereas the PEDOT: PSS rivals showed only 27% of the initial performance. Another stable inorganic HTM is CuPc, a p type semiconductor which is characterized by a lower band gap, and higher hole mobility (10⁻³ to 10⁻² cm² V⁻¹ s⁻¹) compared to spiroOMeTAD (4×10⁻⁴ cm² V⁻¹ s⁻¹) [140]. A remarkable PCE~16.3% was achieved so far using CuPc as HTM and carbon as counter electrode. The CuPc based PSCs showed a more stable performance compared to a doped spiroOMeTAD counterparts when tested for 600 h. Erin et al. [249] investigated a range of metal contact HTM configurations such as Au, Ag, MoO_x/Au, MoO_x/Ag, and MoO_x/Al. The devices based on MoO_x/Al exhibited higher stability than relatively expensive Ag and Au electrodes. In addition, the thickness of the MoO_x interlayer demonstrated a profound impact on the device stability and other PV parameters where the devices exhibited optimal performance with thin MoO_x interlayer.

Recently, an interlayer of graphene oxide (GO) between the perovskite and HTM demonstrated excellent stability and also PV performance (18.2%) [89]. Although the addition of GRMs does not influence the shelf life, it is beneficial for the stability of PSCs under several aging conditions. In particular, mTiO₂+G PSCs retain more than 88% of the initial PCE after 16 h of prolonged 1 sun illumination at the maximum power point. Moreover, when subjected to prolonged

Fig. 20. (a) Effect of protective HTM layers on perovskite films at elevated temperature and humidity. The colour of PSCs changes from almost black to yellow for all organic HTMs except for the films covered with PMMA only or a composite of CNT and PMMA, (b) PCE of PSCs employing range of HTMs as a function of temperature [53]. Figure reproduced with permission from the reference. Copy right of American Chemical Society.

Fig. 21. (a) PV performance of various PSCs as a function of time stored under illumination at AM1.5G and a humidity ~45%. The PSCs compared in (a) employ spiroOMeTAD, TSHBC and TSHBC/graphene [323] as HTM. Figure (b) shows normalized PCE of PEDOT: PSS and CuI based PSCs as a function of storage time in air [58]. Figure reproduced with permission from the references.

heating at 60 °C, the GO based structures show enhanced stability with respect to mTiO₂+G PSCs, as a result of thermally induced modification at the mTiO₂+G/perovskite interface. Similarly, a remarkable stability under 1 sun illumination was also shown by incorporating inorganic selective contacts such as NiMgLiO and TiO_x (in conjunction with PCBM). The devices showed > 90% of initial performance after 1000 h of light soaking. This important report employed large area PSCs of area 1 cm², contrary to typical devices size ~0.1 cm² [328].

5.3. Dopant free hole transport materials for stable PV operation

Chemical doping, often used to improve the electric conductivity of the HTMs, not only induces instability in devices but also increases its cost. Initially it was observed that HTMs in their pristine form yielded inferior performance due to their poor charge mobility; however, recently PSCs with high performance were fabricated even without doping. Xiao et al. employed DR3TBDTT along with polydimethylsiloxane (PDMS) as HTM without additives and showed a more stable performance as compared to Li TFSI and TBP doped spiroOMeTAD [305]. Similarly, Han et al. [133] employed a new p type dopant free HTM called (TTF 1), which yielded a PCE~11.03% and notably higher stability compared with a spiroOMeTAD analogue. In Fig. 22a the performance of TTF 1 as HTM is compared with that of p type spiroOMeTAD. The estimated life time of PSCs based on

TTF 1 was about 360 h while it was only 120 h for spiroOMeTAD based devices. A promising dopant free polymer based HTM (TTF 1) showed a comparable performance to that of spiroOMeTAD doped with Li TFSI and 3 times higher stability to the former credited to its hydrophobic alkyl chain and dopant free nature.

Furthermore, Wang et al. [329] employed dopant free HTM (SAF OMe, to be defined later) with a PCE~12.4% which is comparable to the chemically doped spiroOMeTAD (PCE~14.84%). Fig. 22b compared the stability of PSCs based on N₂,N₂,N₂',N₂',N₇,N₇,N₇',N₇' octa kis(4 methoxyphenyl) 10 phenyl 10H spiro[acridine 9,9' fluorene] 2,2',7,7' tetraamine (SAF OMe) and spiroOMeTAD under ~30% humidity without any encapsulation. The devices were tested for ~240 h and ~39% and ~53% drop in power output was observed for SAF OMe and spiroOMeTAD, respectively. Moreover, the SAF OMe device showed larger contact angle (86.6°) versus the spiroOMeTAD counterpart (76.1°) which confirmed the more hydrophobic nature of the former.

5.4. Non conventional HTMs (including composite HTM)

A stable PSC employing 2TPA n DP (where n=1, 2, 3, 4, full name not given) as HTM with an optimized PCE~12.86% is shown in Fig. 22c. It was revealed that the charge transfer resistance was higher

Fig. 22. Stability test of PSCs based on various HTMs (a) TTF-1 pristine and spiroOMeTAD doped HTM [133], (b) SAF-OMe and spiroOMeTAD [329], (c) efficiencies of PSCs with 2TPA-n-DP (n=1, 2, 3, 4) as a function of storage time [34], (d) PEDOT, GO/PEDOT, and GO [330], (e) normalized PCE of cells using Spiro-OMeTAD (red) and RGO (blue) [331], and (f) long-term stability for the PSCs containing (FA)_{0.25}(MA)_{0.75}PbI₃ [332]. Figures are reproduced with permission from the references.

for the device incorporating an HTM as compared a HTM free rival, showing better electron blocking ability of the 2TPA n DP. Moreover, these devices exhibited stable performance when tested at room temperature for ~900 h [34]. Kim et al. [330] employed composite of GO and PEDOT: PSS as HTM in PSCs and were tested for long term stability (temperature of ~21–24 °C and humidity of ~38–55%) without any encapsulation (Fig. 22d) with the best PCE~9.7%. The PCE of PEDOT: PSS HTM declined sharply; however, the stability improved to some extent by making a composite with GO (PEDOT: PSS/GO). An even better and more stable performance was achieved with GO only as HTM. The composite HTM based device showed stable performance as compared to pristine counterpart. The better performance of composite HTM might be due to fact that GO could prohibit direct contact of ITO with highly acidic PEDOT: PSS.

Recently Palma et al. [331] employed reduced graphene oxide (RGO) as HTM and tested its shelf life stability for ~2000 h and for ~120 h under light soaking (Fig. 22e). The devices were unsealed and kept at ambient temperature in the dark and at a relative humidity ~50%. The control spiroOMeTAD based device showed notable drop in power output: the PCE, FF, V_{OC} , and J_{SC} dropped by 85%, 5%, 6%, and 51%, respectively, whereas the drop in these values were much lower for RGO based PSCs. The deterioration in the device performance was due to Li TFSI which dissociated from the spiroOMeTAD owing to its hydrophilic nature at relative humidity and at ambient temperature.

5.5. Stability of HTM free and monolithic perovskite solar cells

HTMs contribute ~15–20% of the total material cost for unencapsulated PSCs [45]. Therefore, a cheaper HTM or HTM free device with high performance will significantly reduce the cost. Monolithic PSCs (those employing a thick carbon layer as back contact) by Mei et al. [29] which employed TiO₂ and ZrO₂ scaffold infiltrated with perovskite reported a PCE~12.8% and also showed very stable performance for ~1000 h under 1 sun light soaking. In another report on HTM free PSCs [332] which used various ratio of methylammonium to form

minium (MAPbI₃ and MA_{0.75}FA_{0.25} PbI₃), a stable performance was noted for ~750 h (Fig. 22f).

In another report [333] on HTM free device (TiO₂/CH₃NH₃PbI₃/Carbon), long term stability was demonstrated for over 2000 h (Fig. 23a). The devices were stored at room temperature without any encapsulation. The V_{OC} showed a slight decline (from 0.87 to 0.83 V) while FF exhibited relatively stable performance. The PCE decreased mainly due to drop in the J_{SC} . The PCE dropped to ~3.72% from the initial value of ~6.21%. A similar report on HTM free PSCs [334] showed a drop in PCE, FF and J_{SC} (Fig. 23b); however, the V_{OC} showed a slight increase. Long term stability of PEDOT: PSS and CuO_x HTMs are compared in Fig. 23c where the CuO_x maintained 90% of its initial PCE after 200 h while the PEDOT: PSS showed a 50% drop [232].

Finally, as shown in Fig. 23d the PCE of MAPbBr₃ device showed retention even after an air exposure of ~300 h [335]. The FF (~0.67) remained roughly constant while a slight increase in the J_{SC} from ~14.5 mA cm⁻² to ~15.0 mA cm⁻² and V_{OC} from ~1.04 to ~1.05 V was observed. The PCE increased notably, especially during the initial days, and remain constant afterwards. It is clear that HTM free or environmentally friendly HTM alternatives exhibited stable performance along with a comparable V_{OC} to the expensive and toxic counterparts. The stability of various PSCs as a function of different HTMs is listed in Table 7. In general, inorganic HTMs and HTM free PSCs demonstrated superior stability compared to their organic counterparts.

6. Outlook

Perovskite solar cells can be conceptually seen as a multilayer structure with the perovskite layer sandwiched between a hole transport material (HTM) and an electron transport layer and two conductive electrodes. In this article we have reviewed the HTMs developed in perovskite solar cells. Being one of the three main layers constituting the perovskite solar cell, apart from the electrodes, HTMs have a huge bearing on performance, i.e. power conversion efficiency and stability. From reviewing the literature, just noting the sheer breadth and number of the materials and their derivatives

Fig. 23. (a) Long-term stability performance of various HTM-free PSCs stored in air at room temperature without encapsulation [333], (b) photovoltaic parameters as a function of aging time for the device with a 35 nm $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ [334], (c) stability test of unencapsulated PSCs employing PEDOT:PSS and CuO_x as HTM performed in air [232], and (d) stability of the device subjected to light soaking at room temperature without encapsulation [335]. Figures are reproduced with permission from the references.

investigated whilst at the same time observing that the costly Spiro OMETAD continues to be a hugely popular choice in laboratories world wide, it becomes apparent that there is still work to do to confidently develop or identify a handful (or less) of consensus HTMs. These must guarantee high efficiency, high stability, low cost, and good film forming properties over large areas all at the same time.

A good HTM possesses relevant energy levels that ensure facile passage of photogenerated holes from the perovskite layer into the HTM (i.e. matching ionization potentials) whilst also ensuring selectivity, i.e. impeding the recombination of electrons at such a contact (thus low electron affinities are sought). To ensure minimal losses during transport in order to maintain high fill factors, HTMs also require large hole mobilities (and relatively small thicknesses) as well as high transparency to ensure passage of light (either from the bottom TCO electrode or reflected from the top metal electrode). Spiro OMETAD, initially developed for solid state dye sensitized solar cells, has been adopted since the very first investigations as a common HTM with various additives in order to enhance performance. Although PCEs reached with this material are remarkable, considerations on costs and stability have led researchers to develop and incorporate a vast number of alternatives. These range from organic based semiconducting and conducting polymers (e.g. PTAA, PEDOT: PSS, P3HT, CNT composites) as well as inorganic materials such as CuI , CuSCN , NiO , Cu_2O , MoO_3 and GO . Sifting through the literature some general trends start to appear. Firstly, that doped organic transport layers, although typically guaranteeing higher efficiency, tend to be more prone to degradation over time compared to their pristine counterparts. Secondly that some of the inorganic HTMs may result in improved stability, especially if replacing a material like

PEDOT: PSS which is affected by humidity due to its hygroscopic nature. One can draw parallels with the field of organic semiconductor light emitting diodes and solar cells, for example, where these inorganic layers have become more favored in time, mainly as a result of their stronger stability. We envisage a similar trend also for perovskite solar cells as a result of stability being one of the major issues related to this technology. It is also interesting to note that the importance of the properties of the transport layer depends on different illumination and operating conditions. Whereas the role of the electron extracting layers has been highlighted for delivering remarkable performance not only under 1 sun but also under artificial indoor illumination [349,350], the role of HTMs under these light harvesting conditions remains to be investigated. Additionally, as a general remark it, however, remains to be investigated on a larger number of studies how the inorganic HTMs are deposited and perform over the large area module scale rather than just on the small cell level. Furthermore, although at the start it is best to adopt the solution that works best for each layer, for long term massive throughputs it is still not clear, apart from general remarks that can be found in some articles what is the impact of vacuum based vs solution based deposition on costs of the PV technology (which is a crucial parameter for entering the market). Thus we call for more detailed future studies on this aspect.

In fact a good HTM requires good film forming properties ensuring as uniform coverage as possible. In the common n i p architecture, furthermore, the HTMs lie just under the top electrode so it is the first material (barring lateral permeation) to come into contact with humidity and oxygen as well as interfacing with the perovskite. Thus, its resistance to chemical degradation as well as guaranteeing a stable

Table 7
A comparison of stability of various hole transporting materials or HTM free (with and without dopants).

HTM	Device configuration	Dopant	Initial PCE	Percentage reduction in PCE	Rel. H (%)	Test duration	Ref.
DR3TBDTT+PDMS	FTO/CL/MAI ₃ xCl _x /HTM/Au	No	8.3	2%	> 50	3 days	[305]
Spiro-OMeTAD+AgTFSI	FTO/CL/nc-Al ₂ O ₃ /MAPbI ₃ xCl _x /HTM/Ag	Yes	12.0	15%	< 15	120 days	[108]
PMMA	FTO/CL/Al ₂ O ₃ -perovskite/perovskite/HTM/Ag		11.1	~9%		90 h	[53]
2TPA- <i>n</i> -DP	FTO/CL/MAPbI ₃ /HTM/Au		12.96	10%		900 h	[34]
HTM free	FTO/MAPbI ₃ /SBNP+NA	No	13.5	0%		30 days	[336]
HTM free	FTO/TiO ₂ /MAPbI ₃ /Carbon	No	13.53	5%	High%	20 days	[70]
PEDOT: PSS	FTO/HTM/MAX ₃ /PCBM/Al		13.28	80%		350 h	[58]
TTF-1	FTO/CL/mp-TiO ₂ /MAI ₃ /HTM/Ag	No	11.03	20%	40	360 h	[133]
TSHBC	FTO/TiO ₂ /MAI ₃ /HTM/Au		12.8	15%	45	240 h	[323]
CzPAF-SBF	ITO/ZnO/MAPbI ₃ /HTM/Au	No	17.03	29%	28	500 h	[303]
Spiro-OMeTAD	ITO/ZnO/MAPbI ₃ /HTM/Au	Yes	16.45	55%	28	500 h	[303]
CzPAF-SBFN	ITO/ZnO/MAPbI ₃ /HTM/Au	No	15.90		28		[303]
CuPc	FTO/mp-TiO ₂ /MAPbI ₃ +HTM/carbon	No	16.1	< 10%		600 h	[140]
P3HT/SWNTs-PMMA	FTO/CL/Al ₂ O ₃ -perovskite/perovskite/HTM/Ag	No	12.9	~5%		60 s	[53]
PTAA	FTO/TiO ₂ /MAPbI ₃ /HTM/PEDOT: PSS/ITO	No	15.8	< 5%		20 days	[337]
CuI	FTO/HTM/MAX ₃ /PCBM/Al		13.58	90%		14 days	[58]
CuOx	ITO/HTM/MAPbI ₃ /C ₆₀ /BCP/Ag		17.1	10%		200 h	[74]
NiOx	FTO/NiOx/MAPbI ₃ /PCBM/Ag	No	14.42	~20%	45 56%	150 h	[338]
Cu-NiOx	ITO/Cu-NiOx/MAPbI ₃ /PC ₆₁ BM/Au	Yes	15.40	10%		240 h	[30]
Random copolymer	FTO/SnO ₂ /MAPbI ₃ /RCP/Au	No	17.3	0% drop	75%	1400 h	[339]
MeOTPA	FTO/ <i>c</i> -TiO ₂ //TiO ₂ -MAPbI ₃ /HTM/Au	No	16.1	0% drop	30%	1000 h	[340]
Polymeric triarylamine	FTO/mp-TiO ₂ //MAPbI ₃ /HTM (V873)/Au	No	12.3	0% drop		40 h	[341]
TPA	FTO/ <i>c</i> -TiO ₂ //TiO ₂ -MAPbI ₃ /HTM(Z1013)/Au	No	15.4	0% drop	30%	4 weeks	[342]
ODA-FeS ₂ NPs	FTO/mp-TiO ₂ /MAPbI ₃ /HTM/Au	No	12.6	8% drop	50%	1000 h	[343]
pBBTa-BDT2	FTO/ <i>c</i> -TiO ₂ /MAPbI ₃ /HTM/Au	No	12.3	0%	65%	500 h	[344]
DEPT-SC	FTO/ <i>c</i> -TiO ₂ /mp-TiO ₂ /MAPbI ₃ /HTM/Au	Yes	11.52	30%	35%	240 h	[345]
X25	FTO/ <i>c</i> -TiO ₂ /mp-TiO ₂ /MAPbI ₃ /HTM/Au	No	17.4	< 3%	10%	15 days	[346]
Cu-CrOx	FTO/HTM/MAPbI ₃ /PCBM/Ag	Yes	11.48	10%	25%	144 h	[347]
DNA-CTMA	FTO/HTM/MAPbI ₃ /PCBM/Al	No	13.6	12%	40%	50 days	[182]
CSWNT-GO	FTO/TiO ₂ /MAPbI ₃ /HTM/Au	Yes	10.4	~5%	70 80%	10 days	[348]

CzPAF-SBF: 7-(9,9'-spirobifluorene-2-yl)-N-(7-(9,9'-spirobifluorene-2-yl)-9,9-dioctyl-9H-fluorene-2-yl)-N-(4-(9H-carbazol-9-yl)phenyl)-9,9-dioctyl-9H-fluorene-2-amine.
CzPAF-SBFN: 7-(7'-carbonitrile-9,9'-spirobifluorene-2-yl)-N-(7-(7'-carbonitrile-9,9'-spirobifluorene-2-yl)-9,9-dioctyl-9H-fluorene-2-yl)-N-(4-(9H-carbazol-9-yl)phenyl)-9,9-dioctyl-9H-fluorene-2-amine.
ODA-FeS₂ NPs: octadecylamine-capped pyrite nanoparticles.
pBBTa-BDT2: 4,8-dithien-2-yl-benzo[1,2-d;4,5-d']bistriazole-*alt*-benzo[1,2-b;4,5-b']dithiophenes.
DEPT-SC: α, α' -diethoxyethyl-oligothiophenes.
X25: Full name is not available.

electronic interface is mandatory. Examples of solutions developed to ensure stability involve guaranteeing stable electronic properties and stable materials over broad temperature ranges and against the permeation of water vapors. We have detailed examples of HTMs made of composite materials/layers, even deposited from different techniques in the case of bilayers, leading to better performance/stability. Although increasing manufacturing costs, these may be considered effective strategies to decouple the different effect of HTMs (e.g. interfacial and permeation barriers effects vs bulk mobility, blocking and film coverage effects) so further studies along these lines will lead to further understanding on the different properties and effects of HTMs on overall device efficiency and stability.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2017.02.025.

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