A Photo-Crosslinkable Bis-Triarylamine Side-Chain Polymer as a Hole-Transport Material for Stable Perovskite Solar Cells

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Introduction

The efficiency of lead-halide perovskite solar cells (PSCs) has improved significantly since their debut in the literature in 2009.\textsuperscript{1-5} A transition to polycrystalline thin films,\textsuperscript{6,7} improvements in film quality,\textsuperscript{8-10} organic and metal contacts,\textsuperscript{11} doping of charge extraction layers,\textsuperscript{13,14} and band-gap tuning\textsuperscript{15,16} have all contributed to the achievement of power conversion efficiency (PCE) values greater than 20%. Nevertheless, the stability of these solar cells must be improved for commercialization of this technology.\textsuperscript{17, 18} and very often the most efficient cells are not the most stable.\textsuperscript{19} Among ways to achieve improved stability, one can use mixed-cation perovskites\textsuperscript{20,21} or a quasi two-dimensional perovskite,\textsuperscript{22-27} and modify the chemical structure of the hole-\textsuperscript{28-31} and electron-transport materials\textsuperscript{32-34} (HTMs and ETMs, respectively) and of the dopants used to enhance their conductivity.

HTMs play a crucial role in PSCs by reducing the charge recombination that occurs at direct perovskite:hole-collecting electrode interfaces. Organic molecules and polymers, as well as various inorganic materials, can be used as HTMs in PSCs.\textsuperscript{35} The development of crosslinkable HTMs and ETMs for multilayer organic electronic devices, such as light-emitting diodes (OLEDs), was motivated by the need to avoid possible dissolution of the first layer during solution deposition of subsequent layers. Once crosslinked (thermally, photochemically, or by acid), the material becomes insoluble, allowing the subsequent layer to be easily processed on top of it and protecting the layer underneath. Crosslinking offers similar advantages for the HTMs of “p-i-n” PSCs, potentially allowing the lead-halide perovskite to be solution-processed without damage to the HTM layer. Easily processed and insolubilized HTMs are also ideal candidates for tandem cells, where many more layers are required to be sequentially processed. A few crosslinkable HTMs and ETMs have been reported to show promise in PSCs applications. Thermal crosslinking has been achieved using HTMs with two or more styrene\textsuperscript{36-38} or other vinyl moieties,\textsuperscript{39} or by reacting thiol-functionalized HTMs with oligo(thiol) derivatives.\textsuperscript{40} While respectable photo and thermal stability, and performance have been achieved with those materials, the high temperature and crosslinking time needed alkene polymerization, and the multiple ways in which the thiols used in the ene/thiol approach can react, are not optimal for multilayer printable electronics.

Lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI), in combination with oxygen exposure, has been the frequently used dopant for HTMs in PSCs, and is typically used in conjunction with 4-tert-butylpyridine (tBP), which helps prevent phase segregation.\textsuperscript{31} Unfortunately, the use of both Li-TFSI and tBP have been shown to degrade performance in long term stability tests, since Li-TFSI is hygroscopic and tBP is volatile.\textsuperscript{18,42} While alternative dopants have not been as heavily investigated, F\textsubscript{2}-TCNQ is commonly utilized in so-called...
positive-intrinsic-negative (p-i-n) PSCs, but has been found to migrate into adjacent layers in device stacks due to its relatively high diffusivity, and is also highly volatile. A dopant-free HTM or one in which dopant diffusion is minimized is clearly desirable for long-term stability. Crosslinking could potentially also help in this regard.

Here we report the use of a photo-crosslinkable HTM, P1-2 (Fig. 1A), in PSCs. We investigate the impact of a crosslinked copolymer of acrylate monomers with bis(triarylamine) and cinnamate side groups on the stability of PSCs. By careful optimization of p-i-n PSCs, we achieve a stable, dopant-free HTM with comparable performance to state-of-the-art p-i-n cells employing F4-TCNQ-doped poly(4-butyl-triphenylamine-4',4''-diyl) (PolyTPD, Fig. 1B) as the HTM.

Results and Discussion

Synthesis and characterization of the HTM

HTMs for PSCs often contain the bis(diarylamino)biphenyl moiety. For example, the widely used spiro-OMeTAD consists of two such moieties linked by a bridging carbon atom. More recently, polymeric materials containing the same moiety, such as PolyTPD and PTAA (poly(2,4,6-trimethyltriphenylamine-4',4''-diyl)), have shown great potential as HTMs in so-called “inverted” (i.e., p-i-n) PSCs, where the HTM is the first layer deposited. Cells using PolyTPD have achieved a record of 19.1% PCE.14 The same bis(diarylamino)biphenyl motif has also been widely used in OLEDs and some of us have previously reported a series of papers in which random copolymers of monomers with bis(diarylamino)biphenyl functionalization and monomers with cinnamate side chains have been used as solution-processible materials that can subsequently be insolubilized through brief UV irradiation to induce a 2+2 cycloaddition of the cinnamate groups. This approach is modular in that the properties of the polymer can be adjusted through varying the HTM:crosslinker ratio, the ionization energy (IE) of the polymer can be varied through the substitution pattern of the HTM monomer, and other polymer properties can be varied through the choice of the polymer backbone. We chose one of these previously reported polymers – P1-2, the copolymer of a bis(diarylamino)biphenyl-acrylate monomer (1) and a cinnamate-acrylate monomer (2)45 (Fig. 1A) – as a candidate HTM for investigation in PSCs.

Monomers 1 and 2 and copolymer P1-2 were synthesized as previously described.45 Films of the polymer were insolubilized using a short illumination time at 356 nm, which does not significantly degrade the HTM unit of the polymer. From the point of view of PSC fabrication, this facile photocrosslinking is potentially advantageous over alternative thermal crosslinker approaches that require high temperatures >150 °C since the process can be done at ambient temperature on plastic substrates. Moreover, for n-i-p structures, the low power UV-lamp used would not degrade the underlying perovskite layer, whereas the temperatures required for many thermal crosslinking reactions would.

P1-2 has a slightly higher energy onset of optical absorption than PolyTPD (Fig. 1C, Table 1), which is potentially advantageous in allowing more of the solar spectrum to reach the active layer, potentially reducing parasitic absorption and
maximizing current density. Electrochemical measurements on the monomer 1 in CH2Cl2/0.1 M Bu4NPF6, showed a reversible oxidation at +0.26 V vs Fe(Cp)2, from which an IE of 5.1 eV is estimated, similar to that of PolyTPD (Table 1). Addition of F4-TCNQ to solutions of either PolyTPD or P1-2 leads to only moderate changes in the optical spectra, suggesting inefficient doping with this oxidant. This is further illustrated by Fig. 1D, where the effects of successive dopant addition are shown for the case of P1-2. The low yield of oxidized HTM in each case is expected given the redox potential of F4-TCNQ (+0.15 V in the CH2Cl2/0.1 M Bu4NPF6).53,54

<table>
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<tr>
<td>λmax, abs nm</td>
<td>377 (338)</td>
</tr>
<tr>
<td>λmax, vib nm</td>
<td>417 (441)</td>
</tr>
<tr>
<td>IE± / eV</td>
<td>5.2±</td>
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<tr>
<td>EA± / eV</td>
<td>2.1</td>
</tr>
<tr>
<td>Eopt, gap / eV</td>
<td>3.06</td>
</tr>
<tr>
<td>σ± / S m-1</td>
<td>0.010 ± 0.001</td>
</tr>
<tr>
<td>Tc / °C</td>
<td>230</td>
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* The spectra were measured in toluene. * Measured at 0.1 absorbance. * Estimated according to IE (eV) = 4.8 + Eout (V), where the Eout is relative to Fe(Cp)2. * Electron affinity estimated from EA = IE - Eopt, gap. * Optical gap calculated using the crossing of normalized absorbance and fluorescence spectra. * Measured by 4-point probe of the undoped films. * According to literature: PolyTPD,55 P1-2 (prior to crosslinking). * From ref. 55. * Estimated from EUL of monomer 1. * Measured on the crosslinked film CL1-2.

Characterization of HTM films and perovskite growth

Atomic force microscopy of thin films of CL1-2 and PolyTPD on glass substrates showed similar homogeneity and smoothness (see Fig. S2†). Perovskite films crystallized on top of the two HTM layers on FTO substrates also appeared similar by scanning electron microscopy (SEM), although we observed a larger distribution of bright color grains on the HTM films on top of the two different HTMs, suggesting inefficient doping with bathocuproine. The two HTM layers had approximately the same thickness (~6-8 nm as determined by profilometry). Both pristine and doped CL1-2 showed similar PL quantum yield quenching compared to that of PolyTPD, indicating comparable hole-extraction capability of both HTMs at the perovskite/HTM interface, but different PL lifetimes (see below).

Finally, to investigate the charge transfer at the perovskite and the HTM interface, we performed steady-state photoluminescence (PL) measurements (Fig. S5†). The doped CL1-2 showed similar PL quantum yield quenching compared to that of PolyTPD, indicating comparable hole-extraction capability of both HTMs at the perovskite/HTM interface, but different PL lifetimes (see below).

**Device fabrication and characterization**

The photovoltaic performance of CL1-2 and PolyTPD as HTMs in PSCs was compared using the architecture: FTO/HTM/Cs0.05(FA0.85MA0.15)0.33Pb(I0.83Br0.17)3/PCBM/BCP/Au (or Cr/Au for thermal stability tests), where FTO = fluorine-doped tin oxide, MA = methylammonium, FA = formamidinium, PCBM = phenyl-C61-butyric acid methyl ester, and BCP = bathocuproine. The two HTM layers had approximately the same thickness (~6-8 nm as determined by profilometry). Both pristine and doped CL1-2 showed similar performance to PolyTPD. The current-density-voltage (J–V) characteristics were measured under a simulated AM 1.5G (100 mW cm⁻²) sunlight (see Fig. 3, Fig. S6-7† and Table S1†).
Fig. 3 (A) SEM device cross section with FTO (blue), C11-2, C_{60}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.9}Br_{0.1})_{3} (gray), PCBM and BCP (purple), and Ag electrode (yellow). (B) Schematic representation
Only a slight improvement was noticed when CL1-2 was doped using F₄TCNQ (see Fig. S8† and Table S2†), while a significant improvement was obtained for PolyTPD devices. The devices using undoped CL1-2 in its optimal condition (see ESI† Fig. S9-10 and Table S3-4 for optimization of CL1-2 concentration and annealing temperature), shows a PCE of (16±2)% , which is similar to the control device with doped PolyTPD ((16±2)%; Table S1†). Fig. S11† shows the low hysteresis present in the cells presented here. The SPO provides a more complete view of solar cell performance under operating conditions and avoids the ambiguities associated with JV hysteresis. CL1-2 achieves 18.7% SPO, matching its scanned efficiency, while PolyTPD achieves 17.7% and exhibits a transient decay. Typically, when SPO is lower than scanned efficiency it is related to hysteresis induced by ion migration and unbalanced charge extraction rates at selective contacts.⁶⁰,⁶¹ yet with doped PolyTPD we observe SPO decay without accompanying J-V hysteresis. This behavior may be related to a photo instability, such as the evolution of photo-induced trap states, rather than to mobile ions and unbalanced charge extraction. In such a case, a J-V scan collected over a few seconds may not reflect the longer term SPO. This possibility is consistent with photoluminescence quantum efficiency for half devices (FTO/PolyTPD/perovskite), collected at comparable time scales to the SPO, and the intermediate term UV stability of full devices. Both measurements reflect an illumination- and time-dependent decay similar to that observed in the SPO, as discussed further in the device stability section. The performance of the cells over time is consistent with the trend seen on the J-V curves. Despite the longer wavelength onset of absorption seen for PolyTPD, all devices gave similar external quantum efficiency (EQE) spectra, which is consistent with the similar Jsc measured in the J-V scans. Moreover, PSCs made with F₆0₄AsCs₃0₃PbI₃Br₀·₈₂ had also showed comparable performance with CL1-2 and PolyTPD (see Fig. S12† and Table S5†), showing that this HTM also performs well with this more stable double-cation perovskite.

One way that the solar-cell performance of cells with PolyTPD and CL1-2 HTMs differ is that the latter exhibit somewhat larger Voc values (Fig. 3C). It has previously been shown that Lewis base-containing HTMs or small molecules can passivate the surface traps and electronic disorder at the surface of the perovskite layer;⁶¹,⁶²-⁶⁴ in the present case coordination of the multiple ester moieties presents in CL1-2 to the perovskite surface might act in a similar way, thus reducing recombination and increasing Voc (Fig. 3C). PL lifetime experiments on films of perovskite in contact with undoped CL1-2 or doped PolyTPD (Fig. S5†) are consistent, the former exhibiting longer lifetimes associated with bimolecular recombination. Correlations between PL decay and Voc have been reported in the literature.⁵⁵,⁶⁷ In addition, several previous studies have found esters can play a useful role in perovskite growth and/or passivation: poly(methyl methacrylate) has been codeposited with the active layer of n-i-p cells,⁶⁸ and used an interlayer between perovskite and HTM in both n-i-p⁶⁹ and p-i-n⁷⁰ cells. Perovskite growth using more planar substrates

While no major differences were noticed on the perovskite film on top of FTO/HTMs by SEM and PXRD, a major difference in the perovskite growth is noticeable when glass or tin-doped indium oxide (ITO), both of which are considerably smoother substrates than FTO, are used as the substrate. ITO has achieved slightly higher transmittance in the visible spectrum and can offer somewhat lower resistivity than FTO, making it attractive when maximum current density and fill factor are desired.⁷¹,⁷² The CL1-2 film displays slightly more hydrophilic surface, with a water contact angle, θ, of (82±3)°, than the PolyTPD film (θ = 93±6)°, which could explain why it is easier to spin-coat perovskite on smooth CL1-2 films on glass or ITO, while it is not possible or difficult for PolyTPD films on glass and ITO. Stronger perovskite-HTM interactions could also be the cause for the improved wettability of CL1-2 relative to PolyTPD. Indeed, the esters and ether on CL1-2 could possibly...
hydrogen bond with the cations of the perovskite to facilitate its deposition, or the carbonyl group could form an intermediate adduct with PbI$_2$ and hypotheses such as this will be probed in the future. While PolyTPD can be treated with UV Ozone to improve its wettability, sufficient treatment time to ensure full perovskite film coverage of the substrate substantially degrades photovoltaic device performance. In order to make PSCs on ITO using PolyTPD, we tested a polyelectrolyte that has previously been used to improve the wettability and performance of PTAA in p-i-n PSCs, as shown in Fig. S13-14 and Table S6. We find that (9,9-bis(3-(N,N-dimethylamino)propyl)fluorene-2,7-diyl)-alt-(9,9-dioctylfluoren-2,7-diyl) (PFN) treatment on PolyTPD degrades fill factor and the SPO of the PolyTPD devices.

Another consequence of the improved growth of perovskites on CL1-2 on a smooth substrate relative to that on PolyTPD is shown in Fig. 4. Here we show that a layer of MAPbI$_3$ can be successively coated onto CL1-2 deposited onto FA$_{0.83}$Cs$_{0.17}$Pb(I$_{0.90}$Br$_{0.10}$)$_3$ (itself grown on FTO), whereas it does not coat an analogous structure using a PolyTPD interlayer. This result suggests cross-linked organic semiconductors may help facilitate solution processing of tandem solar cells, where the crosslinking approach could potentially be extended to allow for a recombination layer that is itself a multilayer composed of sequentially deposited and crosslinked materials with separate hole- and electron-transport functions and potentially with and without dopants. Although multilayer recombination layers of this kind have been fabricated using organic semiconductors, they generally require vacuum evaporation to avoid the deposition of one layer leading to dissolution of another. An alternative solution-processed approach involves the use of PEDOT:PSS and ITO nanoparticles, but the former may lead to incorporation of traces of water in the device, and both can impair transmission.

Device stability studies

The photo- and thermal-stability of the Cs$_{0.05}$(FA$_{0.85}$MA$_{0.15}$)$_{0.95}$Pb(I$_{0.90}$Br$_{0.10}$)$_3$ PSCs incorporating CL1-2 and PolyTPD were studied without encapsulation in a N$_2$-filled glovebox. The devices were periodically removed to ambient atmosphere for measurements under an AM 1.5G solar simulator, where the stabilized power output was measured after 50 s. Fig. 5A shows the stability in an oven at 85 °C; CL1-2 showed similar stability to PolyTPD devices. Remarkably, the devices show an improvement in performance over the first 1000 hours of aging, and retain greater than their initial efficiency until after 3000 h, which to the best of our knowledge is the longest 85 °C thermal stability timescale reported in the literature (see Fig. S15 for picture of the device after 3000 h of aging).

Photostability was studied under a high intensity LED array (365 nm LED, equivalent to 12 suns UV component of the AM 1.5G spectrum). Initially, a drop in SPO is seen for the PolyTPD devices, while the CL1-2 devices stayed approximately at the same initial SPO (Fig. 5B). The current density decreased at a greater extent for PolyTPD devices (Fig. 5C). In order to study this instability, we measured the photoluminescence quantum efficiency (PLQE) over time of the perovskite film crystallized on top of the HTM layer on FTO. We observe a 70% drop in PolyTPD PLQE after stabilization (2 min), while the CL1-2 doped and pristine PLQE retained 81% and 87% of their initial PLQE respectively (Fig. 5D and Table S7).
Fig. 5 Normalized stabilized power output (SPO) over 50 s after (A) aging the devices at 85 °C in an oven inside a N₂-filled glovebox without encapsulation, (B) aging the devices
Conclusion

In summary, we have described the first use of a photo-crosslinked HTM in PSCs. The crosslinkable acrylate copolymer with bis(triarylamine) and cinnamate side chains presented in the visible region, while PolyTPD is not; and the perovskite is stable and improved PSC UV photo stability. Solar cells using CL1-2 match the state-of-the-art HTM PolyTPD in terms of both performance and stability under 85 °C. We also demonstrated multiple advantages of CL1-2 over PolyTPD: CL1-2 does not need to be doped, while PolyTPD does; we achieved highly reproducible photovoltaic performance across multiple batches of devices; the HTM is transparent in the visible region, while PolyTPD is not; and the perovskite is easier to process on top of the CL1-2 HTM, which together suggest that the crosslinkable polymeric CL1-2 is a promising candidate for single junction and tandem solar cells.

Conflicts of interest

HJS is co-founder and Chief Scientific Officer of Oxford PV Ltd.

Acknowledgements

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Notes and references

The redox potentials of the


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Q. Sun, G. Subramanyam, L. Dai, M. Check, A. Campbell, R.


Crosslinking group

Polymer

HTM

P1-2

206x157mm (200 x 200 DPI)