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A dopant-free hole-transporting material for efficient and stable perovskite solar cells†

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An efficient pristine hole-transporting material (HTM), tetrathiafulvalene derivative (TTF-1), was introduced into perovskite solar cells, without the use of p-type dopants. As compared to cells based on well-known p-type doping with spiro-OMeTAD, perovskite solar cells based on dopant-free TTF-1 performed with a comparable efficiency of 11.03%; moreover, the stability of the dopant-free TTF-1 based cell was greatly improved two fold in air at a relative humidity of ~40%. To the best of our knowledge, this is the first case of perovskite solar cells employing a dopant-free HTM based on a tetrathiafulvalene derivative yielding an efficiency over 11%. The present finding paves the way for the development of efficient dopant-free HTMs for perovskite solar cells, which promotes the advancement of cost-effective and practical perovskite solar cells.

Organometal halide perovskites have been receiving increasing attention beginning with their incorporation as sensitizers in dye-sensitized solar cells by Miyasaka *et al.* in 2009.¹ Very recently, significant progress has been realized in solid-state inorganic-organic hybrid perovskite solar cells,^{2,3} with high efficiencies over 15%^{4–6} attracting tremendous attention in the field of photovoltaics.^{7–11} ABX₃ light harvesters (A = CH₃NH₃ or NH₄CH₃, B = Pb, and X = Br, Cl, or I) have been shown to possess several appealing features, including intense light absorption, excellent ambipolar charge mobility, and small exciton binding energy,^{12–14} which explain their efficient performance in various cell structures.^{3–6,15–17}

The most efficient perovskite solar cells have usually employed organic hole-transporting materials (HTMs), which play a key role

Broader context

Hole-transporting materials (HTMs) have been shown to be important for high-efficiency perovskite solar cells. So far, HTMs reported for perovskite solar cells have not usually performed efficiently in their pristine form, and p-type dopants (such as lithium salts) have been frequently adopted to improve the cell performance. However, such dopants have aggravated cell performance degradation owing to their deliquescent behavior. Moreover, the p-type doping strategy requires strict optimization of the doping conditions (*e.g.*, the solvent, dopants and doping concentrations). In this study, we have introduced an efficient pristine HTM, tetrathiafulvalene derivative (TTF-1), into perovskite solar cells, without the use of p-type dopants. As compared to cells based on well-known p-type doped spiro-OMeTAD, perovskite solar cells based on dopant-free TTF-1 performed with a comparable efficiency of 11.03%; more importantly, the stability of the dopant-free TTF-1 based cell was greatly improved two fold in air at a relative humidity of ~40%. To the best of our knowledge, this is the first case of perovskite solar cells employing a dopant-free HTM based on a tetrathiafulvalene derivative yielding an efficiency over 11%. The present finding paves the way for the development of efficient dopant-free HTMs for perovskite solar cells, which promotes the advancement of cost-effective and practical perovskite solar cells.

in hole transportation and the retardation of charge recombination.^{18–20} So far, HTMs in perovskite solar cells mainly involve nitrogen-containing donors^{18–25} such as 2,2',7,7'-tetrakis-(*N,N*-dimethoxyphenylamine)-9,9'-spiro-bifluorene (spiro-OMeTAD), poly-(triarylamine) (PTAA),²⁶ and so on. Due to the sp³ hybridization of the nitrogen atom, the inherent triangular pyramid configuration leads to large intermolecular distances, thus they suffer from low hole mobility, low conductivity, or both, in their pristine form.^{27,28} Therefore, "redox active" p-type dopants, such as Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI), have been commonly adopted to increase the conductivity and thereby improve cell performance.^{29–31} However, such dopants have aggravated cell performance degradation due to their deliquescent behaviour (Fig. S1†), and the additional doping materials and doping process increase costs. Moreover, the p-type doping strategy requires strict optimization of the doping conditions (*e.g.*, the solvent, dopants and doping concentrations). In this regard,

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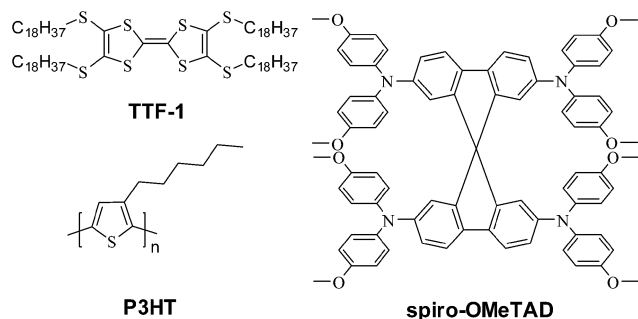
developing dopant-free HTMs is important for efficient and durable inorganic–organic hybrid perovskite solar cells. To this end, one of the potential candidates is sulfur-containing conducting polymers, due to their longer π -conjugations.^{32,33} Those HTMs reported thus far display inferior performance in their pristine form for as-yet-unknown reasons, and in addition, the difficulty in controlling their regularity and their high cost are adverse to practical application. Another promising strategy to be reasonably considered is employing small molecule HTMs with planar configurations, which are conducive to strong intermolecular π - π stacking, as appropriate candidates. To the best of our knowledge, however, the application of such dopant-free HTMs in perovskite solar cells has rarely been reported to enable high performance.

In this study, we have introduced an efficient dopant-free HTM for perovskite solar cells based on a small organic molecule, tetrathiafulvalene derivative TTF-1 (Scheme 1). The device achieved a power conversion efficiency of 11.03%, comparable to that of a p-type doped spiro-OMeTAD based device. More importantly, the former device was two times more stable than the latter in air at a relative humidity of 40%. The improved performance may be due to the following merits of tetrathiafulvalene (TTF). TTF has remarkable redox properties, with the first oxidation potential of 0.34 eV vs. Ag/AgCl corresponding to a highest occupied molecular orbital (HOMO) level of approximately -5.0 eV vs. vacuum level.³⁴ This matches well with the valence-band level of the organo-metal halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ (approximately -5.4 eV vs. vacuum level), ensuring sufficient driving force for hole transport from the perovskite into the active layers. Owing to the strong electron donating ability of the TTF moiety and the feasibility of substitution at its 2,3,6 and 7 positions, it is easy to construct p-type semiconductors with efficient carrier mobility and to tune their molecular energy levels.^{35–37} The inherent π - π stacking and strong S–S interactions between adjacent and highly rigid conjugated units cause the hole conductivity of TTF derivatives to be efficient, but result in them being less soluble or insoluble in most common solvents. Thus, the use of expensive and time-consuming vacuum sublimation is required to fabricate their thin films. The long alkyl chains in TTF-1 not only improve its solubility for solution processes, but also keep a certain amount of intermolecular stacking because of the fastener-effect of the

long alkyl chains. The highest hole mobility of a TTF-1 thin film of close to $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been reported.³⁸ For comparative analysis, two model HTMs, poly(3-hexylthiophene) (P3HT) and spiro-OMeTAD, were also studied (Scheme 1).

UV-vis absorption spectra of TTF-1, P3HT and spiro-OMeTAD in dichloromethane (DCM), and their thin films, are shown in Fig. 1. In the DCM solutions, TTF-1 and spiro-OMeTAD show absorption bands in the UV region. In contrast, P3HT shows an absorption band in the visible region due to its longer π -conjugated backbone. In the thin film states, both TTF-1 and P3HT exhibit approximately 100 nm red shifts compared to their absorption bands in solution. These results imply that there is a certain amount of intermolecular π - π stacking in their thin film states, probably due to the strong S–S interaction, the fastener-effect of the long alkyl chains, or both. However, similar absorption properties of spiro-OMeTAD were observed both in solution and in the thin film state, indicating poor π - π intermolecular interactions in its thin film state.

To investigate the potential application of TTF-1 as an HTM in hybrid perovskite solar cells, its electrochemical properties were studied by cyclic voltammetry in anhydrous DCM containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte, in a three-electrode system (Fig. S3†). A sulfur-containing analogue, P3HT, was also studied for comparative analysis. Both HTMs exhibit well-defined reversible oxidative waves. The highest occupied molecular orbital (HOMO) level of TTF-1 (-5.05 eV vs. vacuum), estimated from its ground state oxidation potential in cyclic voltammograms, was slightly higher than that of P3HT (-5.20 eV vs. vacuum). This result is in accord with the stronger electron-donating ability of the TTF core compared to the thiophene moiety. Unfortunately, the slightly higher HOMO level of TTF-1 may result in a lower photovoltage in the device, which will be discussed later. The optical band-gap energies (E_g) were estimated from the intersection between the normalized absorption and emission spectra in DCM (Fig. S2†). The lowest unoccupied molecular orbital (LUMO) energies were calculated by adding



Scheme 1 Molecular structures of TTF-1, P3HT and spiro-OMeTAD.

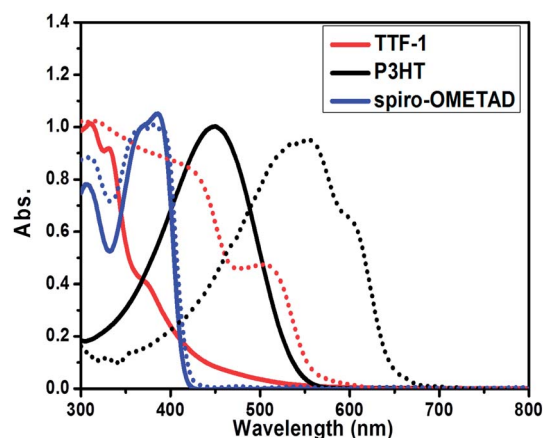


Fig. 1 Normalized absorption spectra of TTF-1, P3HT and spiro-OMeTAD in DCM (solid line), and in the thin film state (dotted line).

the E_g values to the HOMO energies. An energy level diagram of the corresponding materials employed in the perovskite solar cells is shown in Fig. 2.¹⁹

The preparation of the corresponding materials used in the fabrication of the perovskite solar cells is detailed in the ESI.[†] The solar cells were fabricated with a typical structure of FTO/compact TiO_2 /mesoporous TiO_2 /perovskite/HTM/Ag (Fig. 2). The perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ was deposited using a two-step sequential deposition method, which was first developed by Burschka *et al.*⁵ The resulting perovskite films were coated with the HTM *via* a solution process, both in their pristine form and in the presence of Li-TFSI and *tert*-butylpyridine (TBP). Details about the components and concentrations are provided in the ESI.[†] It is noted that the cells employing TTF-1 should be annealed at 65 °C in argon (20 °C below a solid-solid phase transition and 25 °C below the melting point, according to differential scanning calorimetry analysis, Fig. S6[†]) for 24 h to induce self-healing and diminish the density of defects existing at intergrain boundaries, thus enhancing their photovoltaic performance. The cross-sectional structure of a representative device was investigated by scanning electron microscopy (Fig. S4c[†]). All devices employed the same conditions, except for the HTM, and their light harvesting efficiencies were considered to be reasonably similar (Fig. S7[†]).

The photovoltaic characteristics of typical small-area perovskite solar cells (0.09 cm^2) based on three dopant-free HTMs (TTF-1, P3HT, and spiro-OMeTAD) were primarily evaluated under AM 1.5 G irradiation at 100 mW cm^{-2} (Fig. 3). The data are summarized in Table 1. The device based on dopant-free TTF-1 achieved an open-circuit voltage (V_{OC}) of 0.86 V, a short-circuit current (J_{SC}) of 19.9 mA cm^{-2} , a fill factor (FF) of 0.644, and an overall conversion efficiency (η) of 11.03%. As shown in Fig. S8,[†] the incident photon-to-current conversion efficiency spectrum (IPCE) of perovskite solar cells based on dopant-free TTF-1 ranged from the UV region to 800 nm, which was matched well with that of the UV-vis absorption spectrum of the light harvester $\text{CH}_3\text{NH}_3\text{PbI}_3$ (Fig. S7[†]). However, devices based on dopant-free P3HT and dopant-free spiro-OMeTAD showed lower performances, the efficiencies being around 6%, mainly due to their lower J_{SC} and FF values, respectively (Table 1). The low FF (0.465) of perovskite solar cells based on dopant-free spiro-OMeTAD can partly be explained by their high series resistance ($R_s = 158.2 \Omega$) due to the lower conductivity of spiro-OMeTAD in its pristine form. The fact that the photocurrent of

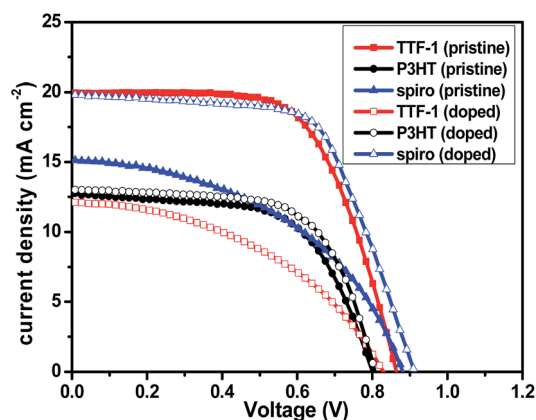


Fig. 3 Current-voltage curves of typical small-area (0.09 cm^2) perovskite solar cells based on TTF-1, P3HT and spiro-OMeTAD in their pristine form or doped with Li-TFSI and TBP.

the perovskite solar cells based on P3HT was lower than the photocurrents of the cells based on the small molecule HTMs, TTF-1 and spiro-OMeTAD, was probably due to the large molecular size of the P3HT polymer. The inferior pore-filling of P3HT resulted in a smaller interface between the perovskite and HTM, leading to poor hole extraction and aggravated charge recombination.¹⁸ Our results suggest that dopant-free HTMs using TTF-1 operate more efficiently than the well-known spiro-OMeTAD and P3HT HTMs for perovskite solar cells. We anticipate that employing dopant-free HTMs in perovskite solar cells will be synergistically beneficial in terms of cell durability by avoiding the use of deliquescent lithium salt (*vide infra*).

To compare with the common p-type doping strategy, perovskite solar cells based on these three HTMs with model additives (Li-TFSI and TBP) were also investigated. As summarized in Table 1, after p-type doping, the perovskite solar cells based on spiro-OMeTAD achieved higher J_{SC} , V_{OC} , and FF values, thus yielding a higher efficiency of 11.4%. The decrease in R_s from 158.2 to 70.6 Ω after p-type doping supports the increased FF of the cells, thus primarily contributing to the performance improvement. Such an effect of p-type dopants on spiro-OMeTAD for solid-state solar cells has been discussed in depth by Snaith^{29,39} and Seok.³⁰ In contrast, perovskite solar cells based on p-type doped TTF-1 exhibit lower performance,

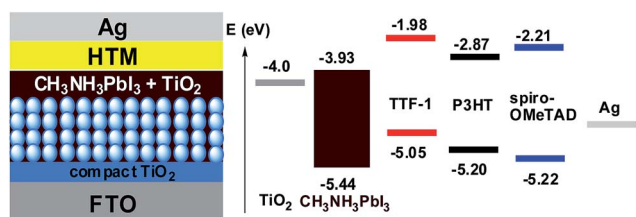


Fig. 2 Diagrammatic representation of the photovoltaic device structure (left); energy level diagram of the materials used in the perovskite solar cells (right).

Table 1 Photovoltaic performance of perovskite solar cells based on HTMs in their pristine form or doped with Li-TFSI and TBP^a

HTM (form)	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)	R_s (Ω)
TTF-1 (pristine)	19.9	0.86	0.644	11.03	64.3
TTF-1 (doped)	12.1	0.83	0.439	4.41	162.4
P3HT (pristine)	12.8	0.80	0.607	6.22	72.1
P3HT (doped)	13.0	0.81	0.638	6.72	67.2
Spiro-OMeTAD (pristine)	15.1	0.88	0.465	6.18	158.2
Spiro-OMeTAD (doped)	19.8	0.91	0.631	11.4	70.6

^a Measurements were performed under the following conditions: AM 1.5 G irradiation; cell area, 0.09 cm^2 determined by metal mask.

especially in terms of FF and J_{SC} ; the exact mechanism responsible for this abnormal phenomenon is unclear. The small distinction of photovoltaic performance in perovskite solar cells based on P3HT with or without p-type doping reveals that the lower performance seems to not originate from hole transport or conduction in the HTMs, but is probably caused by the larger size and inferior interface in turn.

The fact that both IPCE spectra and J_{SC} values obtained from the optimized perovskite solar cells based on dopant-free TTF-1 and p-type doped spiro-OMeTAD were almost the same (Fig. S8†). The results indicate that there is little difference in the charge collection of both. However, the photovoltage values in these two cases were somewhat different. The V_{OC} is related to the difference between the conduction band of TiO_2 and the HOMO level of the hole conductor (theoretical photovoltage), and various interface losses in the photovoltaic system (charge recombination). According to the energy level diagram in Fig. 2, the theoretical photovoltage of perovskite solar cells based on TTF-1 is 170 mV lower than in the case of spiro-OMeTAD. However, a discrepancy of only 50 mV was observed between the V_{OC} values for the two cases. This result implies that TTF-1 may have an electron-blocking ability superior to that of spiro-OMeTAD, and thus may be able to reduce the V_{OC} loss, but no systematic investigation was undertaken in the present communication. Whether the long alkyl chains have an effect on the retardation of the charge recombination, electron blocking, or both, should be further investigated in future research. Similar phenomena have been discussed in depth in dye-sensitized solar cell systems.⁴⁰

For the advancement of practical perovskite solar cells, the cell durability is an important issue. Actually, there are many factors that influence the stability of perovskite solar cells, such as temperature, moisture and so on. In this study, we have confirmed the expectation that using dopant-free HTMs is significant for cell durability enhancement. As shown in Fig. 4, the cells based on dopant-free TTF-1 without encapsulation do exhibit slight and slow degradation under ambient conditions

at room temperature with a humidity of about 40%, which is more stable than the cells based on common p-type doped spiro-OMeTAD under the same conditions. On the basis of the degradation time associated with a 20% decrease of efficiency, we estimate the lifetime of the cells based on dopant-free TTF-1 (~360 h) to be three times that of the cells based on p-type doped spiro-OMeTAD (~120 h). The enhanced durability of the perovskite solar cells based on dopant-free TTF-1 compared with the cells based on p-type doped spiro-OMeTAD can be attributed mainly to the avoidance of the use of deliquescent additives. In addition, hydrophobic alkyl chains in the TTF-1 molecules may also contribute to this improvement. Furthermore, a device based on dopant-free TTF-1 with a larger area (1.00 cm^2) was also prepared and evaluated under AM 1.5 G irradiation at 100 mW cm^{-2} (Fig. S9†). The J_{SC} , V_{OC} , and FF values (16.4 mA cm^{-2} , 0.83 V, and 0.594, respectively) were slightly lower than the corresponding values obtained with a small-area cell. An overall power conversion efficiency of 8.08% was obtained with this larger cell. These results highlight the potential application of organolead halide perovskite as a light harvester and TTF-1 as a dopant-free HTM in hybrid solar cells.

In summary, TTF-1, a member of the tetrathiafulvalene family, has been shown, for the first time, to be a promising HTM candidate for perovskite solar cells without using lithium salts and TBP. To the best of our knowledge, this is the first case of perovskite solar cells employing a dopant-free HTM based on a tetrathiafulvalene derivative yielding an efficiency over 11%, which is comparable with that obtained using the well-known p-type doped spiro-OMeTAD; moreover, the stability of the dopant-free TTF-1 based cells was greatly improved two fold in air at a common relative humidity of 40%. The present results show that TTF-1 is superior to spiro-OMeTAD and P3HT as a dopant-free HTM in these hybrid solar cells. The fact that a module ($1\text{ cm} \times 1\text{ cm}$) based on dopant-free TTF-1 yielded an efficiency over 8% highlights its potential application in perovskite solar cells. The feasibility of tailoring the structure and tuning the properties of TTF derivatives guarantees their bright future as dopant-free HTMs in perovskite solar cells. Further enhancement of the efficiency could be realized by developing new tetrathiafulvalene derivatives with excellent electrical properties and proper oxidation potentials with respect to the energy levels of perovskite. Work on these, and systematic investigation of the effect of long alkyl chains on cell performance and stability, is now in progress.

Acknowledgements

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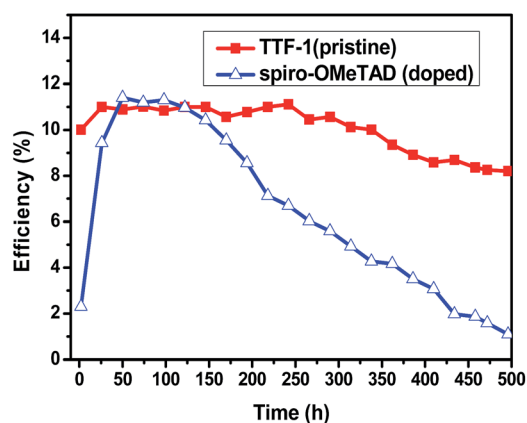


Fig. 4 Efficiency variation of the optimized cells based on dopant-free TTF-1 (pristine) and p-type doped spiro-OMeTAD (doped). Unencapsulated cells were stored in air at room temperature with a humidity of about 40% and were measured under illumination at AM 1.5 G.

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