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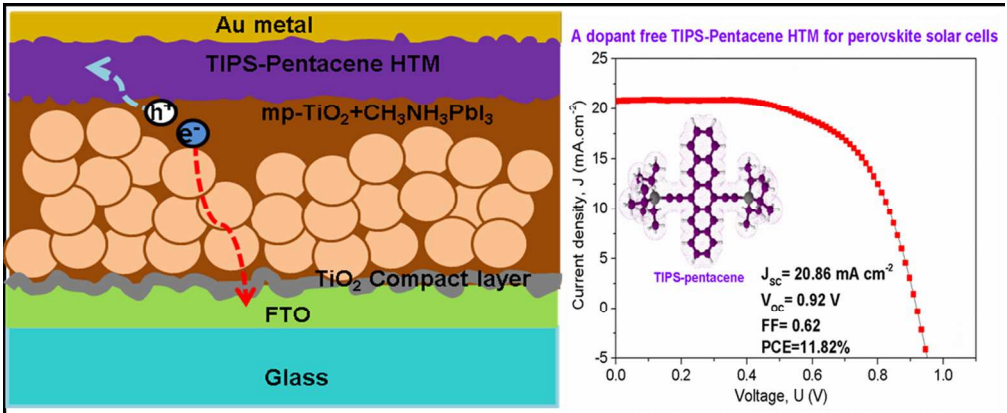


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ARTICLE

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A solution processable, molecular organic semiconductor, 6,13-Bis(triisopropylsilyl)ethynyl pentacene (TIPS-pentacene) was employed as hole transport material (HTM) in mesoscopic methylammonium lead iodide perovskite solar cells. The TIPS-pentacene is potentially cost effective, exhibits relatively higher hole mobility and has favourable HOMO level with respect to the valence band of perovskite. The photovoltaic performance of perovskite solar cell with TIPS-pentacene as HTM in its pristine form and with dopant/additive was investigated and compared with classical Spiro-OMeTAD based devices. Through solvoneering (solvent engineering) and concentration optimization of the TIPS-pentacene in pristine form gave very competitive power conversion efficiency (PCE) of 11.8% under 1 Sun condition. The open circuit voltage 0.92V, and short circuit current density 20.86 mA.cm⁻² for the devices with pristine TIPS-pentacene were higher compared to doped Spiro-OMeTAD based devices under similar conditions. Thus paving the use of TIPS-pentacene as an alternative to an expensive Spiro-OMeTAD for large area integration in perovskite based solar cells.

Introduction

The recent progress in the application of methyl ammonium lead halide perovskite as a light-absorber for thin film solid state solar cells have led to remarkable power conversion efficiency of ~20%, placing them ideally in emerging thin film PV technology.^{1,2} Through solvent-controlled crystal-growth engineering for perovskite infiltration into TiO₂ scaffold and the use of an additional capping layer of perovskite led to attain high power conversion efficiencies (PCE) value and consequently certified PCE value for perovskite solar cells upraised. The potential of perovskites as light absorber was first revealed in 2009 for a liquid electrolyte based dye-sensitized solar cells (DSSCs) with merely 3.8% of PCE³ and currently, over six times higher PCE is being measured in solid state configuration.⁴ This fast unprecedented increase in PCE of perovskites based solar cells motivated many groups to focus on the direction of choice of scaffold, device architecture and optimized crystal formation. In all these architectures Spiro-OMeTAD remains an obvious choice as hole transport material (HTM). Recently, some reports appear on novel molecular organic semiconductor to be used as HTMs, but they suffer from cumbersome synthetic approach and thus limited to a

group of researchers. The classical Spiro-OMeTAD shows the best performance in both perovskites⁵ as well as DSSCs⁶ in its doped state. The first report in solid state solar cells was 0.74% using doped Spiro-OMeTAD,⁷ which after decades of optimization reached to 7.2% using cobalt complex as p-type dopant developed by the Graetzel group.⁶

However, the Spiro-OMeTAD suffer from multiplex synthetic approach and purification, which plagued its commercial viability.⁸ Moreover, it performs efficiently when it is doped with metal complex and/or additives.⁹ The use of dopants/additives in Spiro-OMeTAD induces device instability and also the oxidized form of the Spiro-OMeTAD acts as a filter in the visible region at 520 nm due to absorption.¹⁰ In this direction, different inorganic,¹¹⁻¹³ small organic molecule^{10,14-22} and conjugated polymers^{23,24} were tested as HTM in the fabrication of perovskite solar cells. The best efficiency reported for inorganic CuSCN (12.4%),¹³ carbazole derivatives based small molecule (14.6%)²² and polytriarylamine [PTAA] (16.2%).²⁵ However, CuSCN requires microns thick layer as HTM which was deposited by screen printing method. Low-band gap colored polymers have been used as HTMs similar to their large-band gap counterpart using perovskite as light harvester, and the highest achieved PCE was 9.2%.^{26,27} Among the polymer family,

only PTAA, gave best performance due to its higher hole mobility than others. However, its polymeric nature, will allow defects, low device reproducibility, less affinity towards perovskite as well as instability arising from its exposure to high vacuum conditions during metal cathode evaporation, limits its use in commercial endeavour.

The main limitation in perovskite solar cell performance might be the discrepancy between the series and shunt resistance. Usually, a thick layer of HTM is required to avoid short circuit which also leads to high series resistance. Therefore, it is paramount to find a cost effective HTM having desirable conductivity and charge mobility to reduce series resistance and simultaneously create pinholes free thin layer. In our quest of HTMs with having thermal stability, high hole mobility, high conductivity and suitable highest occupied molecular orbital (HOMO) level with respect to the perovskite valence band, the functionalized soluble derivative of pentacene i.e. TIPS-pentacene was exploited. It has matching energetic level to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite valence band, can be a material of choice as HTM. Pentacene has been studied extensively over the decades as p-type semiconductor layer in organic thin film transistor (OTFT)^{28,29} and organic solar cells.³⁰ However pentacene can't be solution processed, thus has a limited deposition scope, while its analogous 6,13-Bis(triisopropylsilyl)ethynyl pentacene (TIPS-pentacene) can be deposited by numerous process.

Here we report on the use of solution processable, p-type organic molecule TIPS-pentacene as HTM for perovskite solar cells. In the past TIPS-pentacene was investigated extensively for OTFT^{28,29} and also exploited as active layer in organic solar cells.³⁰ The two TIPS side groups at the C-6/C-13 position of pentacene stabilize the HOMO level facilitating stability, solubility in various organic solvents and 2-dimensional lamellar structure with brick walls style in the solid state.^{31,32} The cofacial π - π stacking of TIPS-pentacene allows improved charge transport properties over unsubstituted pentacene.³³ TIPS-pentacene is potentially cost effective, easy to synthesize and exhibits relatively higher hole mobility ($>1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^{28,34}, and complementary glass transition temperature. Its HOMO level is energetically favourable with regards to the valence band (VB) of $\text{CH}_3\text{NH}_3\text{PbI}_3$. The PV performance of TIPS-pentacene as HTM in its pristine form as well as with dopant and additive in perovskite solar cells was probed. For comparison purposes, devices were also made with state of the art Spiro-OMeTAD. With solvent and concentration engineering it was found that TIPS-pentacene in pristine form yielded very competitive PCE of 11.8% at 100 mW/cm^2 under AM 1.5G simulated irradiation.

Results and discussion

TIPS-pentacene (Fig.1a) has minimum synthetic steps compared to Spiro-OMeTAD. The substitution of solubilising (triisopropylsilyl)ethynyl (TIPS) group at the carbon-6 and 13 position of pentacene facilitate fine-tuning of electronic properties, and adjustable HOMO–LUMO level making it suitable to use as HTM with perovskite. Furthermore these

TIPS group provide photo-oxidative stability due to stabilized HOMO levels compared to the unsubstituted pentacene.

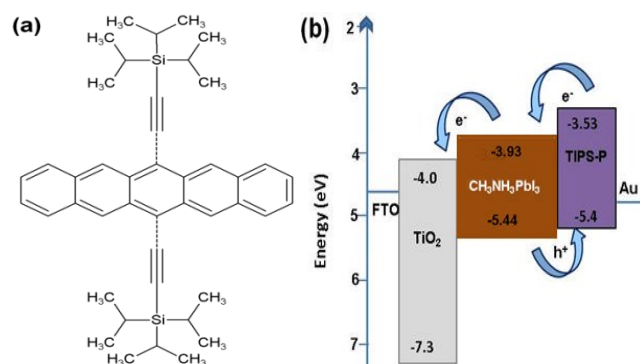


Figure 1. Chemical structure of TIPS pentacene and (b) anatomy of the device showing different layers, Corresponding energy level diagram

Optical and thermal properties:

Contrary to Spiro-OMeTAD, the TIPS-pentacene shows broad absorption in the visible region. Fig. 2 shows the UV-Vis absorption spectra for TIPS-pentacene in solution, while in the film configuration deposited by spin-coating in pristine as well as in doped state is shown in SI (Fig.S1). The UV-Vis absorption spectrum in solution is characterized by three long-wavelength bands at 549, 592, 643 nm, which corresponds to the first singlet exciton excitation and mainly involves one-electron transition from HOMO to LUMO and its accompanied vibrational structure.³⁵ The onset of absorption starts at 663 nm corresponding to optical band gap of 1.87 eV and reaches to λ_{max} at 643 nm. In the film, large red-shift of all three peaks occurs due to π - π^* intermolecular interaction.³⁶ The presence of LiTFSI and t-BP as dopant and additive, does not alter the peak position or show arrival of additional peak at longer wavelength region. It was also observed that the pristine TIPS-pentacene shows lower absorption than its doped state.

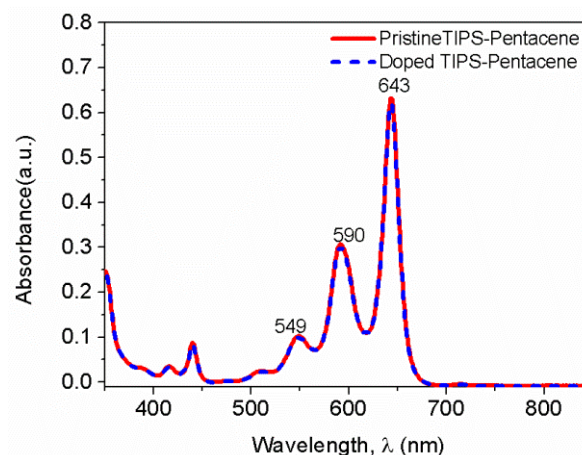


Figure 2. UV-Vis absorption spectra of TIPS-pentacene solution prepared in toluene solvent.

To identify the thermal properties of the TIPS-pentacene we undertook, differential scanning calorimetry (DSC) studies (Fig. S2).

The glass transition temperature for pristine TIPS-pentacene was found to be at 122 °C, which is very close to T_g of Spiro-OMeTAD (124 °C). Further to determine the thermal stability range thermogravimetric analysis (TGA) was employed (Fig.S3). Pristine TIPS-pentacene was found to be stable up to 380 °C. It is noted that the addition of LiTFSI and t-BP as additives brings down the thermal stability (to 350 °C) and significant weight loss was observed between 75-175 °C. The addition of additives also changes the surface morphology significantly (Fig.S5). The change of microstructure from small granular to large crystalline spherulites in all like hood points towards its hydrophilic nature after the addition of additives. Thermal studies reveal that TIPS-pentacene in its pristine form is more suitable for practical application.

Electrochemical and electrical measurements:

Cyclic voltammetry

Cyclic voltammograms (CV) of pristine TIPS-pentacene and with LiTFSI and t-BP as additive in dichloromethane are shown in Fig. 3. Similar to the doped Spiro-OMeTAD, the pristine TIPS-pentacene shows a reversible redox couple. In the, pristine TIPS-pentacene the cathodic and anodic peak ratio is close to unity pointing towards the electrochemical reversibility in the system. Doping of TIPS-pentacene with LiTFSI and t-BP as additive, display significant cathodic shift and more importantly, it loses its reversibility. The shift in onset of oxidation potential was found in between the pristine TIPS-Pentacene and doped Spiro-OMeTAD. Further, HOMO energy level is calculated from the oxidation onset potential with Fc/Fc^+ as internal standard (Table 1). The HOMO and LUMO levels of TIPS-pentacene calculated from CV measurements were found to be -5.4 eV and -3.53 eV respectively and the reported value for valence and conduction band of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is -5.44 eV and -3.93 eV,³⁷ well positioned energy level with perovskite for hole transport (Figure 1b). It is well known that in DSSC, the difference between the quasi Fermi level of the TiO_2 and HOMO of the HTM determines the open circuit voltage (V_{oc}). It is worth noting here that the HOMO of TIPS-Pentacene is 300 mV lower than that of Spiro-OMeTAD, which will assist in gaining higher open circuit potential of the devices. Chemical doping is a strategy usually employed to increase the conductivity, and subsequently the device performance.³⁸ It is well reported that Li salt work as ionic dopant for organic semiconductors and increased in conductivity was due to increase mobile charge carriers filling deep trap sites and improve mobilities.³⁸ However, dopant can also act as trapping center³⁹ for holes generated by HTM and hole transfer might takes place from HOMO of TIPS-pentacene to the immobile dopant counter anion acceptor acting as trapping site, so it reduces hole mobility. We have measured the in-plane conductivity of pristine TIPS-pentacene and after the addition of LiTFSI and t-BP additives. As expected, we found increase of two orders of magnitude for TIPS-pentacene, with the addition of LiTFSI and t-BP. The conductivity of pristine TIPS-pentacene was 3.5×10^{-7} S/cm and after addition of the additives 1.0×10^{-5} S/cm. However, in spite of showing high conductivity and high absorbance (in film formation) with dopant/additive, no

significant changes were observed in V_{oc} , moreover the J_{sc} and fill factor decreases. We speculate that the presence of additives in TIPS-pentacene induces some trap site or disorder in chain packing, which was also supported by irreversible CV peaks.

Table 1: Electrochemical and optical parameters of TIPS-pentacene and Spiro-OMeTAD

HTM	$E_{1/2 \text{ ox}}$ (V)	E_{HOMO} (eV)	E_{LUMO}^a (eV)	$E_{g \text{ opt}}^b$ (eV)
Pristine TIPS-P	0.488	-5.4	-3.53	1.87
Spiro-OMeTAD	0.156	-5.07	-2.09	2.98

^a $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g(\text{opt})$. ^bOptical band gap was calculated by onset of absorption.

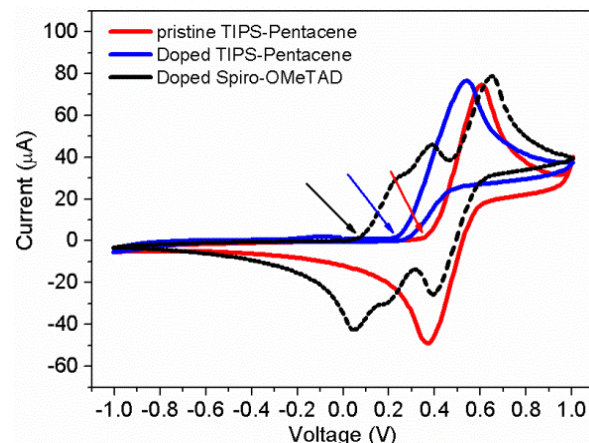


Figure 3 Cyclic voltammogram of Spiro-OMeTAD, TIPS-pentacene in pristine form and with LiTFSI dopant, t-BP additive in dichloromethane solvent.

Figure 1b shows the corresponding energy level diagram for $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite based solar cells employing TIPS-pentacene as HTM. Under illumination, the perovskite as well as TIPS-pentacene captures the incident visible light and photo-generation of charge carriers occurs in both, where electrons are transferred through the mp- TiO_2 layer into the TiO_2 conduction band of compact layer, and collected through FTO anode, while the corresponding holes are transported from perovskite to the Au (cathode) through the TIPS-pentacene hole-transporting layer. However, the contribution to generate photocurrent from TIPS-pentacene towards electron is insignificant in comparison to perovskite. In order to confirm the contribution of TIPS-pentacene for light harvesting in visible region, devices were also prepared without gold (cathode). Absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ were measured in the presence of TIPS-pentacene in its pristine form and with LiTFSI and t-BP additive. Fig.4 illustrates that the TIPS-pentacene add value to the absorption of perovskite film with respect to Spiro-OMeTAD in higher wavelength-region (500-750 nm). This additional light absorption from TIPS-pentacene might be result of filtering of unabsorbed photons from perovskite layer to TIPS-pentacene, which finally contribute to the overall photocurrent generated by the cell.

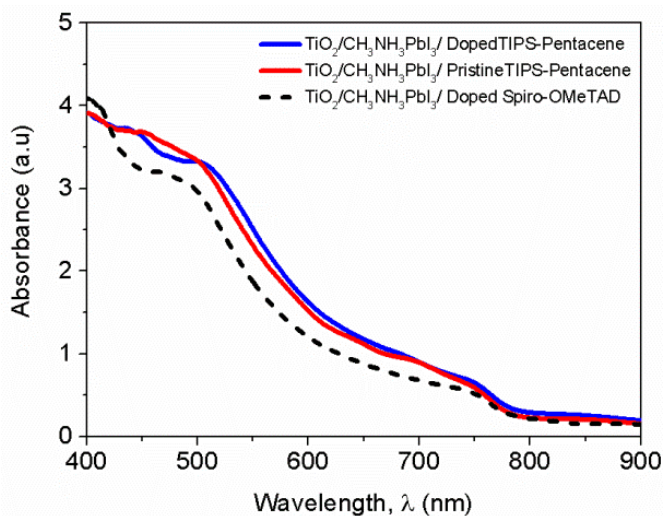


Figure 4. UV-Vis absorption spectra of devices prepared without Au metal contact under the same conditions as full device.

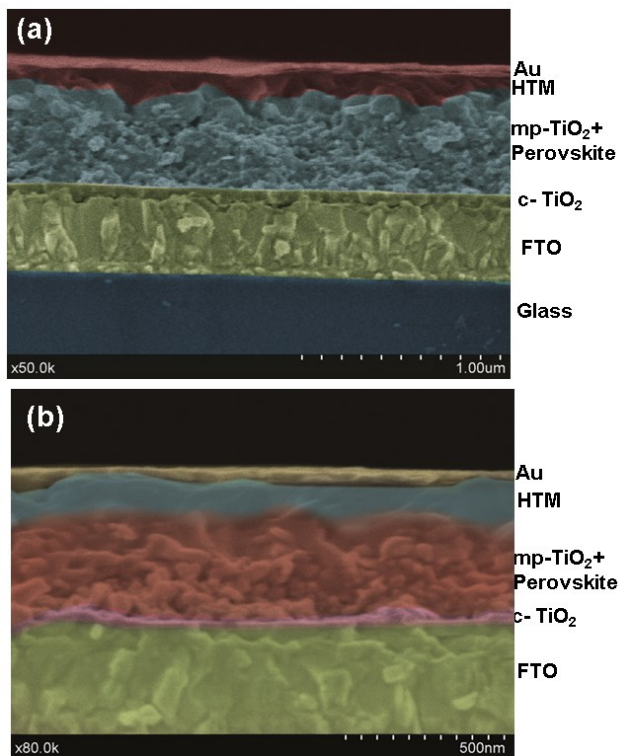


Figure 5. Cross-sectional SEM of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite based device with pristine TIPS-pentacene HTM, (a) with low magnification and (b) with high magnification. Both images shows a clear interface between TIPS-Pentacene and perovskite layer.

A cross-sectional scanning electron microscopy (SEM) image of the solar cell fabricated using pristine TIPS-pentacene as HTM shows the typical anatomy of the solid state mesoscopic perovskite solar cells (Fig. 5). The complete infiltration of $\text{CH}_3\text{NH}_3\text{PbI}_3$ into the 250 nm thick mesoporous TiO_2 layer, placed over a ~ 80 nm thick TiO_2 compact layer can be clearly observed and a ~ 150 nm TIPS-pentacene, HTM layer is formed over the perovskite capping layer. Fig.5b shows the magnified

version of the image and very intimate and defined contact between the perovskite and TIPS-pentacene can be witnessed. A Cross-sectional SEM image of the solar cell fabricated using doped TIPS-pentacene with additive is shown in SI (Figure S4). Several processing parameters such as TIPS-pentacene concentration, solvents, spinning speeds and additive

Table 2 Photovoltaics parameters derived from $J-V$ measurements of mesoporous $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite based devices with TIPS-pentacene and Spiro-OMeTAD as HTM^a

Device	R_s (ohm·cm ²)	R_{sh} (ohm·cm ²)	J_{sc} (mA·cm ⁻²)	V_{oc} (mV)	FF	PCE [%]
Pristine TIPS-Pentacene	23.65	10197.28	20.84±0.01	913±5.2	0.60±0.01	11.51±0.31
TIPS-Pentacene +LiTFSI+ tBP	43.80	1549.54	16.51±0.49	920±3.7	0.54±0.01	8.20±0.23
Spiro-OMeTAD	23.68	2793.19	18.61±0.78	843±4.9	0.62±0.01	9.77±0.35

^a Average data with standard deviation were based in a single batch; FF=fill factor, PCE =power conversion efficiency, R_s =series resistance, R_{sh} =shunt resistance of the cell. The devices were masked with a black aperture to define the active area of 0.283 cm².

concentration were optimized for maximum light harvesting abilities. Devices were fabricated with and without LiTFSI and 4-tert-butylpyridine (t-BP) which were used as dopant/additive. Through solvoneering (solvent-engineering), toluene was found to be an ideal solvent for TIPS-pentacene, and quality films were made using toluene with and without dopant/additive. We have observed that the devices showed best performance after few days of storage. It is known that TIPS-pentacene shows slow crystallization behaviour, in high boiling point solvent (such as toluene) in its fully soluble form and normally produces larger grains.⁴⁰ These grain sizes have profound effect on charge transport in TIPS-pentacene.⁴¹

The current-voltage ($J-V$) characteristics of $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cell with TIPS-pentacene as HTM measured in dark and under illumination is shown in Figure 6a, and the corresponding photovoltaic parameters are summarized in Table 2. For comparison, a reference cell with Spiro-OMeTAD with LiTFSI dopant and t-BP additive as HTM was also fabricated under similar conditions. Pristine TIPS-pentacene based devices gave enhanced PV performance after aging (in dark condition) resulted predominantly in increased J_{sc} and V_{oc} , while the fill factor remains unaltered.

The devices fabricated with TIPS-pentacene in pristine form gave competitive PCE (11.5%) while the one doped with LiTFSI and t-BP as additive attained an average PCE of 8.20%. In the same batch, the fully optimized reference device with Spiro-OMeTAD with LiTFSI dopant and t-BP additive achieved 9.77% efficiency (Table 2). It is clear from the table

that the device with pristine TIPS-pentacene had higher current density (J_{sc}) than doped TIPS-pentacene as well as Spiro-OMeTAD. The open circuit voltage (V_{oc}) of the device with TIPS-pentacene as HTM was higher than that of classical Spiro-OMeTAD confirming the lower Fermi level of TIPS-pentacene than Spiro-OMeTAD. Possibly, the high J_{sc} obtained from the device with pristine TIPS-pentacene might be due to the improved light harvesting and the effective charge separation and collection.

The fill factor (FF) of pristine TIPS-pentacene based devices were similar to that of doped Spiro-OMeTAD confirming low series resistance, possibly due to similar hole mobility of TIPS-pentacene. Table 2 shows that the pristine TIPS-pentacene has almost equal series resistance to the doped Spiro-OMeTAD based devices. Due to low conductivity in pristine form, Spiro-OMeTAD requires LiTFSI dopant and 4-tert butyl pyridine (t-BP) additive to make it more conductive.⁶ In order to further push the PCE, we designed the experiment with lower loading of dopant i.e. 0.011 M LiTFSI and 0.06 M t-BP for TIPS-pentacene. Contrary to this, we found the PCE of such device was even lower than that of pristine TIPS-pentacene based device, which can be attributed to unfavorable packing of structure hindering the mobility of the TIPS-pentacene.

Differences in behaviour of the devices can be analysed by current–voltage characteristics in dark (Fig.6a) and extracted value of the series resistance (R_s) and the shunt resistance (R_{sh}) of each device is presented in Table 2. TIPS-pentacene based devices shows comparatively lower dark current and delayed turn-on of the device in forward direction than that of doped Spiro-OMeTAD and doped TIPS-pentacene. We also found that the V_{oc} is intensely interrelated to the turn-on point of the dark current under forward bias and delayed turn-on of the device will result in to a high V_{oc} . The turn-on of the devices will takes place when injected electrons and holes are recombined under forward bias. The finite value of the R_{sh} indicates the leakage current pathways and/or bimolecular recombination of the charge carriers. However, a larger value of R_{sh} in case of pristine TIPS-pentacene reflects lower leakage current than the doped TIPS-pentacene and Spiro-OMeTAD.

In contrast, a small variation was found in case of R_s , R_s is increased by a factor of two in case of doped TIPS-pentacene, while Spiro-OMeTAD based devices have similar R_s . The lower leakage current and delayed turn on of the forward current in dark suggests that pristine TIPS-pentacene has good electron blocking ability, resulting in reduced rate of charge recombination than Spiro-OMeTAD. Therefore the delayed turn-on point of the dark current in case of pristine TIPS-pentacene and doped TIPS-pentacene signifies reduced rate of charge recombination and attain high V_{oc} . The best champion device with pristine TIPS-pentacene shows a short-circuit current density (J_{sc}) of 20.86 mA/cm², an open-circuit voltage (V_{oc}) of 918 mV and a fill factor (FF) of 0.62, leading to overall PCE of 11.8%. (Fig. 6b). Device statistical data in individual piece of cells is shown in S10-13. Pristine TIPS-pentacene based devices showed almost negligible degree of hysteresis.

The hysteresis index was calculated according to⁴² and it was minimum in the case of pristine TIPS-pentacene (0.041) and highest for doped TIPS-pentacene (0.154). The obtained hysteresis index of spiro-OMeTAD based devices (0.072) was in close vicinity of 0.080 recently reported⁴². Hysteresis index value for TIPS-pentacene was found to be lower than spiro-OMeTAD based devices. The first attempt to deposit TIPS-Pentacene by vacuum evaporation, yielded a promising PCE of c.a. 6%, which we believe can be further optimized.

The incident photon-to electron conversion efficiency (IPCE) spectra were recorded (Fig.7) for the devices measured in figure 6a. Diverse spectral response was observed in the case of TIPS-pentacene based devices compared with respect to the Spiro-OMeTAD one. The pristine TIPS-pentacene and Spiro-OMeTAD based devices showed higher IPCE than that of doped TIPS-pentacene. In the visible part of spectra higher conversion efficiencies close to 75% was recorded in the case of pristine TIPS-pentacene, while its counterpart exhibits lower IPCE indicating that it play a synergistic role of hole transporter adding contribution in photocurrent generation. In order to elucidate it further, whether TIPS-pentacene contributes in photocurrent generation, the spectral difference of the IPCE of a Spiro-OMeTAD and pristine TIPS-pentacene based device is shown in the supporting information (Figure S7). The difference in IPCE lies exactly in the wavelength region < 500 nm region where TIPS-pentacene absorbs. As a result of the IPCE data, a difference of J_{sc} for these two cells of about 0.634 mA/cm² is derived.

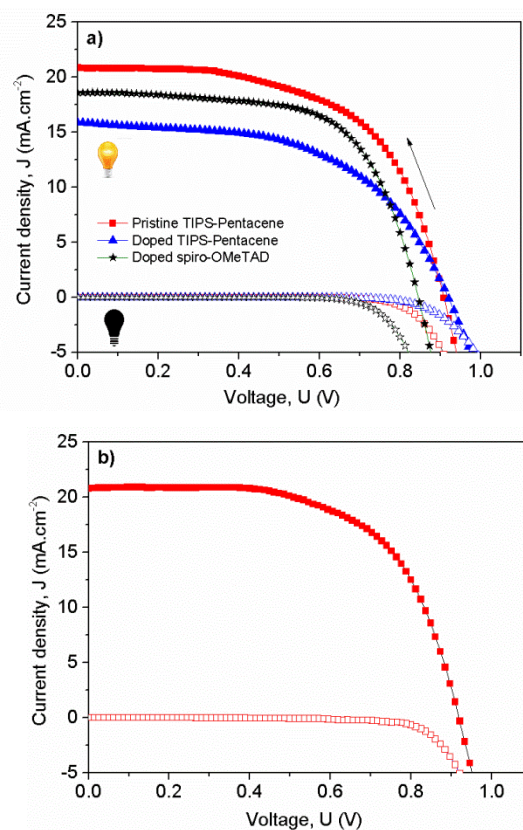


Figure 6 (a) Current-voltage characteristics of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite based devices with pristine TIPS-Pentacene (red), TIPS-Pentacene with additives (blue) and Spiro-OMeTAD (black) as the HTM measured under dark and illumination at AM 1.5G, 100 mW.cm^{-2} in reverse bias scan (b) Current-voltage characteristics of champion device with pristine TIPS-Pentacene as HTM measured in reverse bias scan.

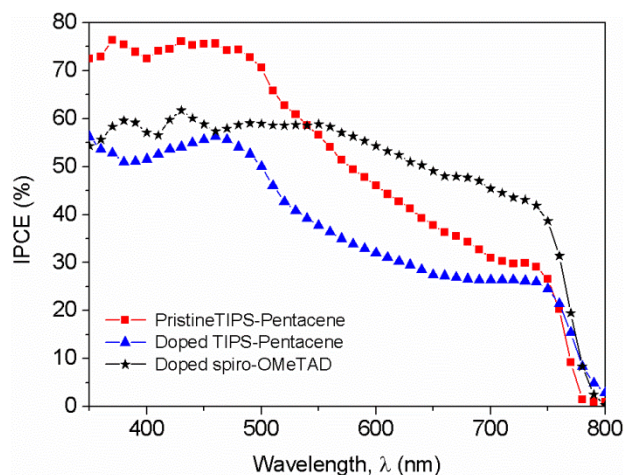


Figure 7. The corresponding incident photon to electron conversion efficiency (IPCE) spectra of devices shown in Fig. 7a.

Experimental Section

Materials

All chemicals were obtained from Sigma Aldrich, Acros or Merck KGaA and were used without any further treatment. $\text{CH}_3\text{NH}_3\text{I}$ was synthesized following the previous literature.⁴ The $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers were prepared by sequential deposition method following the recipe using $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 .

Synthesis and characterization of TIPS pentacene

Pentacene-6,13-quinone.

4.02 g (30.0 mmol) of ortho-phthalicdialdehyde and 1.68 g (15.0 mmol) of cyclohexanedione were dissolved in 450 mL of ethanol. 15 mL of a 15% aqueous KOH solution was added, upon which the solution turned brownish and a yellow/orange precipitate formed. For completion of the reaction the mixture was stirred for an additional 4 h at 60 °C. After cooling the solid was filtered and thoroughly washed with acetone, giving the product as a yellow solid (3.95 g, 12.8 mmol; 85 %). ¹H-NMR: (400.1 MHz, CDCl_3): δ = 7.71 (dd, 4 H), 8.12 (dd, 4 H), 8.94 (s, 4H).

6,13-Bis(triisopropylsilyl)ethynyl)pentacene (TIPS-pentacene).

Under an atmosphere of argon, 16.2 mL of n-butyllithium (40.5 mmol, 2.5 M solution in hexane) was added drop wise to 9.1 mL (40.5 mmol) of triisopropylsilyl acetylene in 50 mL of dry tetrahydrofuran at 0 °C. The mixture was kept at 0 °C for another 40 min before it was transferred to a solution of 6,13-pentacenequinone (5 g, 16.2 mmol) in 50 mL of dry tetrahydrofuran at 0 °C. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched with 15 mL

of 10% HCl and then subjected to a $\text{CHCl}_3/\text{H}_2\text{O}$ workup. The solvent was removed, and the resulting solid was collected by filtration. The crude solid was dissolved in 50 mL of acetone, and then a solution of tin(II) chloride dihydrate (9.2 g, 40.5 mmol) in 50% acetic acid (50 mL) was added dropwise. This mixture was stirred at room temperature for 24 h. The resulting blue solid product was filtered. The solid was then dissolved in hexane, washed with water and saturated sodium bicarbonate solution, and then dried over magnesium sulfate. The hexane solution is then poured onto a silica plug, which is flushed with hexane (200 mL), followed by 9:1 hexane/methylene chloride to elute a deep blue solid (9.5 g, 92%): mp 220-221 °C; ¹H NMR (300 MHz, CDCl_3) δ 9.31 (s, 4H), 7.98 (dd, 4H), 7.42 (dd, 4H), 1.39 (s, 42H).

Physical Characterization of TIPS-Pentacene

Optical measurements were carried out in 1 cm quartz cuvette and films were cast on quartz substrate. UV-Vis spectra were recorded with a Cary 60 UV-Vis spectrometer. Cyclic voltammetry was measured with an Autolab Eco Chemie cyclic voltammeter in dichloromethane solvent. The experimental setup consisted of a glassy carbon working electrode, platinum wire counter electrode and platinum reference electrode. All samples were deaerated by bubbling with pure nitrogen gas for ca. 5 min at room temperature. The system was initially calibrated with ferrocene/ferrocenium (Fc/Fc^+) redox couple. Differential scanning calorimetry (DSC) and Thermo gravimetric analysis (TGA) measurements were carried out in nitrogen atmosphere using Mettler Toledo equipment (Star System). In-plane conductivity of TIPS pentacene with and without additives was measured on OFET substrates purchased from Fraunhofer Institute for Photonic Microsystems (IPMS).

Device fabrication

FTO-coated glass, either TEC7 or TEC15 from Pilkington, were patterned by laser etching. Then, the substrates were cleaned using Hellmanex solution and rinsed with deionized water and ethanol; subsequently they were ultrasonicated in 2-propanol and then rinsed using ethanol and acetone and finally dried with compressed air. Prior to the compact layer deposition, the samples were cleaned with an ultraviolet/ O_3 treatment during 30 minutes.

A TiO_2 compact layer was deposited by spin coating 2M solution of TiCl_4 on etched FTO glass at 5000 rpm and heated at 70°C for 30 minutes. Following this, the samples were washed again with deionized water, annealed at 500 °C for 15 minutes and were left to cool down slowly. After that, on top of it, the mesoporous TiO_2 was spin-coated at 5000 rpm using 18NR-T followed by gradual sintering at 500 °C for 1 h in air. After that, perovskite was prepared by sequential deposition method. More precisely, lead iodide (PbI_2) film was deposited by spin coating using a solution of *N,N*-dimethylformamide (DMF). After the spin coating, the cells were placed onto a hot plate at 100°C for 30 minutes for annealing, and after cooling down the samples, the photoanode were dipped in methyl ammonium iodide (MAI) solution in 2-propanol and rinsed in

pure 2-propanol. Subsequently, the samples were annealed again at 100°C for 20-30 minutes.

For hole transporting layer 6,13-Bis(triisopropylsilyl)ethynyl)pentacene (TIPS-pentacene) was used and spun coated on top of perovskite layer at 2000 rpm for 30s using toluene solvent. Several parameters such as TIPS pentacene concentrations, solvents (chlorobenzene and toluene), spinning speeds and additive concentration were tested and optimized to achieve best PV properties. TIPS-pentacene concentration was varied from 10-70 mg/ml and in our case, we found 30mg/ml gave better PV properties. In the case of dopant, lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) and 4-tert-butylpyridine (t-BP) were used as dopant/additives. It was found that toluene is an ideal solvent and gave better PV results. Devices were prepared without and with 18.8 μL of LiTFSI dopant and 9.4 μL of t-BP additives. For reference cell, Spiro-OMeTAD in chlorobenzene was used as hole transport material; 17.5 μL of lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) and 28.8 μL of 4-tert-butylpyridine (tBP) were added to the Spiro-OMeTAD solution as additives and finally devices were prepared under same fabrication conditions. Finally, 70 nm of gold were thermal evaporated on the top of the cell as cathode under a vacuum level between 1×10^{-6} and 1×10^{-5} torr.

Device Characterization

The UV-Vis absorption was measured for TIPS-pentacene in toluene solutions as well as in films using Cary 60 spectrophotometer.

Current-voltage (I - V) curves were obtained with a Keithley 2400 source-measurement-unit (SMU) under AM 1.5 G 100 mW cm^2 illumination from a certified CLASS AAA ORIEL® Sol3A™ 2×2, 450W solar simulator (model 94023A). Light output power was calibrated using a NREL certified calibrated mono-crystalline silicon solar cell (model 91150V).

The incident photon conversion efficiency (IPCE) was measured using a 300 W xenon lamp (Oriel) fitted with a motorized monochromator with 2 gratings to cover from 200nm up to 1400nm (Cornerstone 260, Model 74125) as a monochromatic light source.

Both for J - V and IPCE measurements, a black mask with a circular aperture (0.28cm^2), was used though the active area was 0.5cm^2 . For IPCE measurements, a constant white light bias (5% of the received light) was recommendable to measure perovskite cells, this was achieved by an array of white LEDs. In our observation we have found the device PV properties improved with time, and the best results were always obtained in aged devices after 6-7 days. This was possibly due to fine crystal structure formation in TIPS-pentacene which is well known.

The cross section of the devices were imaged by a field-emission scanning electron microscope (FE-SEM) using a Hitachi S5200 field emission microscope operated at 5.0 keV.

Conclusions

We have developed solution processable, cost effective and easily synthesized TIPS-pentacene as a hole transport material for perovskite solar cell. The devices gave very competitive performance 11.8% without the need of additional dopant or additives. Remarkably, TIPS-pentacene as such gave enhanced performance, compared to the classical Spiro-OMeTAD in doped state to rival its usage. These results show the potentiality of TIPS-pentacene as HTM in perovskite solar cells and represent a promising candidate to achieve efficient and cost effective thin film photovoltaic devices. This is pointing towards further exploitation of other family members of pentacene derivatives as an HTM.

Conflict of interest

Some of the authors (from Abengoa Research) may have competing interests as Abengoa is an international company and has significant interest in the renewable energy sector. Patent disclosing the work is pending.

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Notes and references

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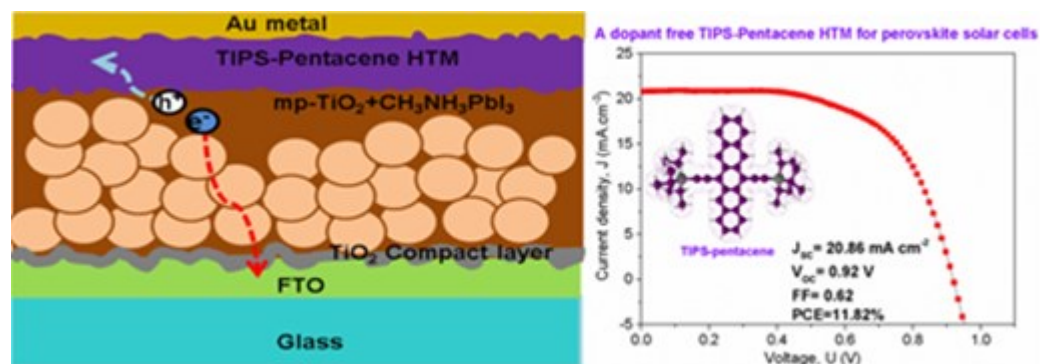
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ARTICLE

Boarder Context

Solar energy is an ideal source of energy to make our environment clean and green. It's conversion to electricity by the means of photovoltaic technology at cost competitive price is a societal concern. Perovskite pigmented solar cells has made a stunning entry in the photovoltaic domain and now emerged as a viable technology in thin film category for fabrication of highly efficient and low-cost photovoltaics. Regardless of the high efficiencies reported (20%), Spiro-OMeTAD remains a material of choice for transporting of holes inside the perovskite solar cells. Spiro-OMeTAD was developed almost two decade ago and after ages of improvement it still suffers from desirable electrical properties and requires doping. With the renaissance of perovskite solar cells recently some new hole transport materials (HTM) are reported but they too need doping. Here we report our findings of the use of linear acene derivatives as an efficient HTM in its pristine form. TIPS-pentacene was introduced as HTM into perovskite solar cells fabrication and competitive power conversion efficiencies were measured, without the use of any dopant or additives. A dopant free perovskite based solar cells yielded close to 12% efficiency. To the best of our knowledge, this is the highest number reported for dopant free HTM for perovskite solar cells, moreover with the use of a very common p-type semiconductor. These finding will be of interest for further advancement perovskite solar cells technology.

Table of Content entry



Linear acene derivatives as hole transporter in perovskite solar cells.