Supplementary Information

A Dopant free Linear Acene derivative as a Hole Transport Material for Perovskite pigmented Solar Cells

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UV-Vis absorption spectra of TIPS pentacene film spin coated on quartz substrate:

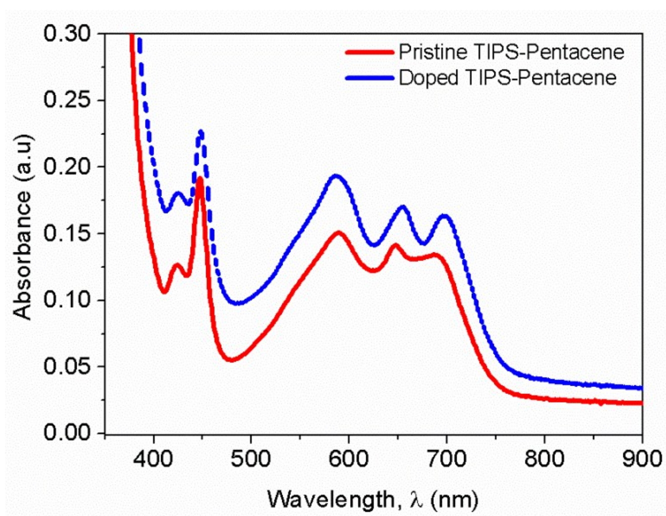

Figure S1: UV-Vis absorbance spectra of TIPS-pentacene film on quartz substrate.

Thermal properties of TIPS-pentacene:

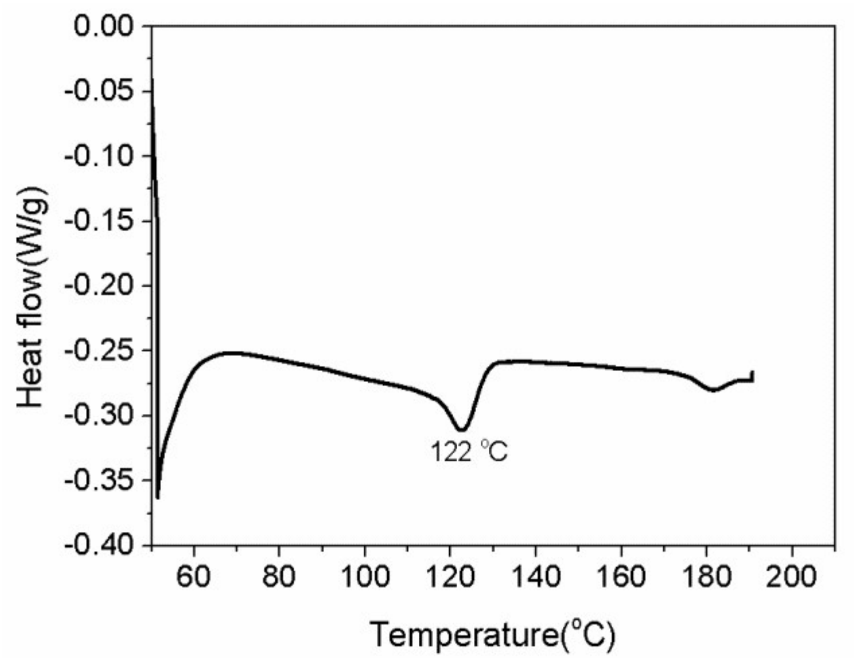

Figure S2 **:** Differential Scanning Calorimetry (DSC) measurement for TIPS-pentacene at a scan rate 5°K/min in nitrogen atmosphere.

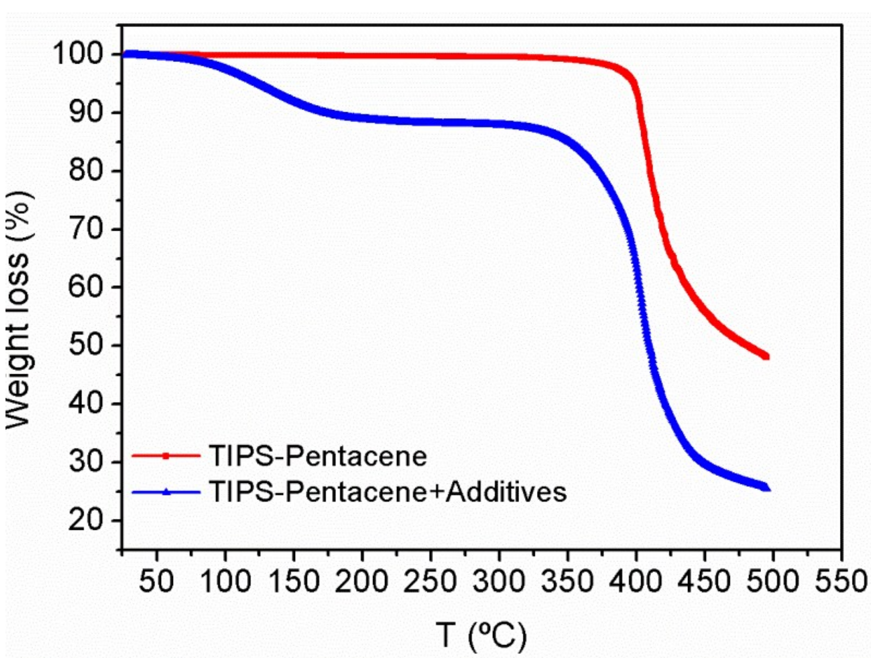

Figure S3 : Thermogravimetric analysis (TGA) of pristine TIPS-pentacene and with LiTFSI and t-BP as additive with scan rate of 10°K·min^{-1}. Pristine TIPS-pentacene is more stable up to temperatures of around 380°C, while the one with additive shows stability up to 330°C.

Impact of dopants and choice of choice

The impact of dopants and choice of solvent was also investigated. Devices were fabricated using 30 mg/ml, TIPS-pentacene and were spun coated atop of perovskites. Unexpectedly, the presence of dopant/additive did not improve the device performance. In solvent such as toluene without doping/additive, in pristine form, the TIPS-pentacene based devices resulted in higher short circuit current (20.86 mA/cm^2), higher Fill Factor (FF= 0.62) and overall higher PCE (11.82%). All other parameters were kept similar.

Table S1: Influence of solvent and dopant on device PV properties

Doping Type	Solvent	J_{SC} (mA/cm^2)	V_{OC} (mV)	FF	PCE (%)
Doped	Chlorobenzene	18.01	928.8	0.54	9.49
Doped	Toluene	17.54	925.6	0.65	10.77
None	Toluene	20.86	0.918	0.62	11.82

Scanning electron microscope images (SEM):

Cross- sectional SEM images for doped TIPS-pentacene

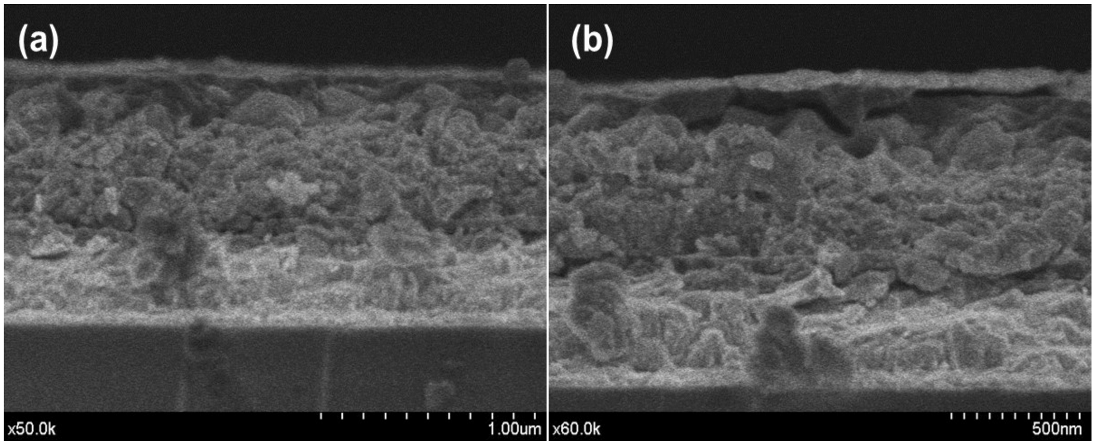

Figure S4 : Cross-sectional SEM image of the $CH_3NH_3PbI_3$ perovskite based devices with doped TIPS-pentacene HTM, (a) at 1-μm scale with low magnification and (b) at 500 nm scale with high magnification. Not so well defined or sharp interface between TIPS-pentacene and perovskite layer can be observed.

Surface morphology of TIPS-Pentacene with and without additive and Spiro-OMeTAD with additives based devices:

SEM images were recorded to unravel the top view of devices using different hole transport materials. Pristine TIPS-pentacene, doped TIPS-Pentacene (with LiTFSI and t-BP additives) and it was compared with doped spiro-OMeTAD. A top surface view of the pristine TIPS-pentacene HTM based devices show that TIPS-pentacene fully covers the perovskite without changing the surface morphology in the same way as spiro-OMeTAD does (Figure S5), while in the case of doped TIPS-pentacene abrupt changes was observed. Probably, the presence of t-BP and/or LiTFSI promotes some unwanted chemistry resulting in highly crystalline microstructures. This was also supported by the cross sectional SEM image of the same devices (Fig. S4) and the irreversibility in CV curve (Fig.3) of doped TIPS-Pentacene.

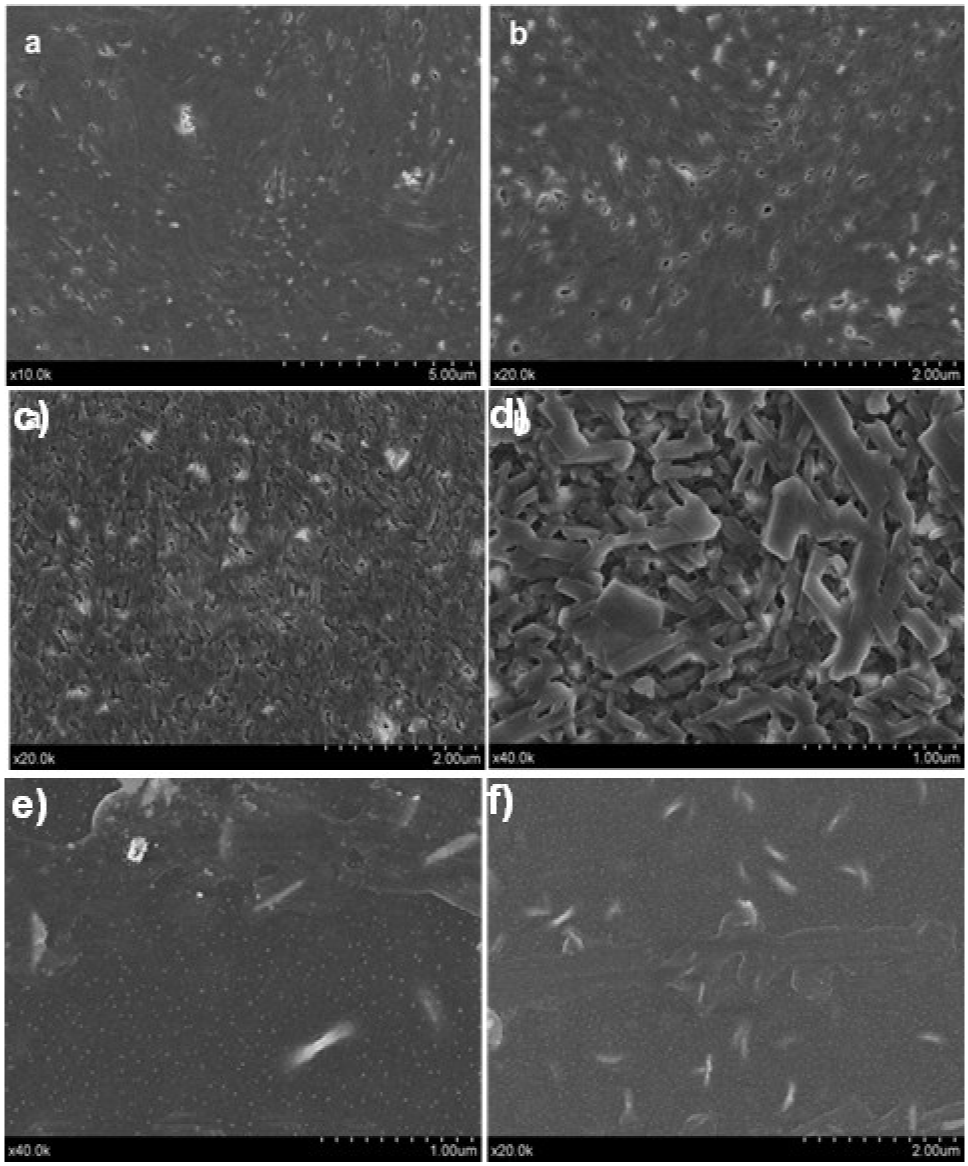

Figure S5: a-b) Surface morphology (top view) of pristine TIPS-pentacene based devices, c-d) morphology of doped TIPS-pentacene and e-f) surface morphology (top view) of doped spiro-OMeTAD based devices at low and high magnification.

Champion device fabricated with pristine TIPS-pentacene:

J-V curve was measured in both reverse and forward direction with scan rate 0.1 V/s. The V_{oc} and fill factor was decreased in case of forward bias.

Pristine TIPS-Pentacene	J_{SC} (mA.cm^{-2})	V_{OC} (mV)	FF	PCE (%)
Reverse bias (From V_{oc} to J_{sc})	20.86	918.32	0.62	11.82
Forward bias (from J_{sc} to V_{oc})	21.22	902.09	0.57	10.90

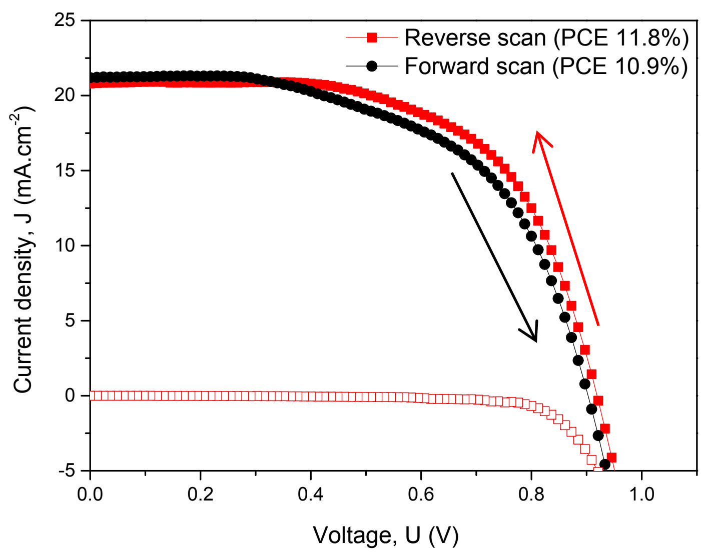

Figure S6: Current-voltage characteristics of champion device prepared with pristine TIPS-pentacene as HTM measured in forward (from short circuit current to open circuit voltage) and reverse (from open circuit voltage to short circuit current) bias scan.

We have measured the hysteresis on fresh samples of pristine TIPS-pentacene, doped TIPS-Pentacene, doped spiro-OMeTAD at 0.05 V/s rate with 10 mV voltage steps. The scan was started at 1V to 0 V and then back to 1 V. The hysteresis index was calculated using equation given in the recent article on hysteresis by N.G Park et al., (J. Phys. Chem. Lett. 2014, 5, 2927−2934.). It was found that the degree of hysteresis was least in case of pristine TIPS-pentacene and highest for doped TIPS pentacene. If the value of hysteresis index is 0 then it predicts no hysteresis and if the value is 1 then hysteresis is as high as photocurrent. The degree of hysteresis was least in 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 obtained by Park et. al for the same HTM based devices. (N.-G. Park et al, J. Phys. Chem. Lett. 2014, 5, 2927−2934.), while, hysteresis index value for TIPS-pentacene (0.041) was found to be lower than spiro-OMeTAD based devices.

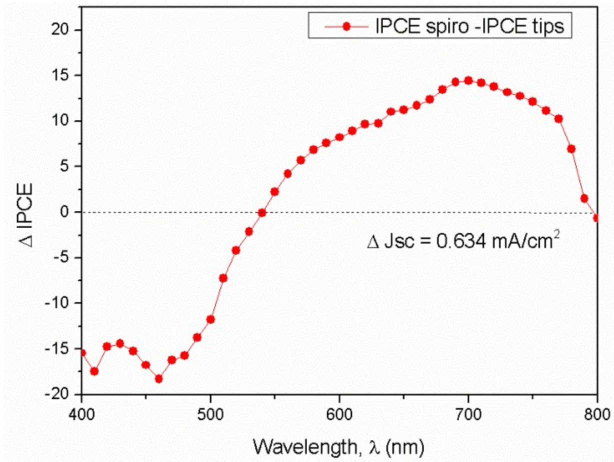

Figure S7. Difference of IPCE spectra (ΔIPCE = IPCE $_{spiro}$ - IPCE $_{(pristine\ TIPS\text{-}pentacene)}$. The difference in IPCE results in a difference of J_{sc} of about 0.63 mA/cm^2.

Aging effect on the efficiency and stability:

The devices were prepared and measured and then it was kept in dark and inert atmosphere. In case of pristine TIPS-pentacene, the photovoltaic data are summarized in below Figure (S8). The short circuit current (J_{sc}) was improved in all three cases, while V_{oc} was improved only for pristine and doped TIPS-Pentacene. However, fill factor did not improve significantly in case of TIPS-Pentacene and decreased for spiro-OMeTAD after 6 days.

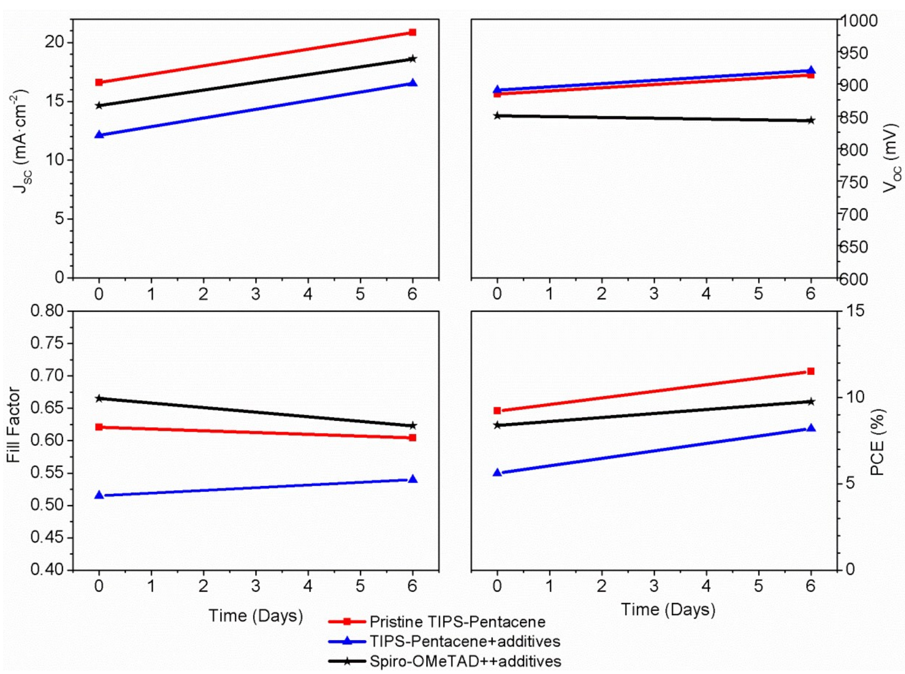

Figure S8 : Aging effect in pristine TIPS-Pentacene, doped TIPS-Pentacene and doped spiro-OMeTAD based devices.

Furthermore, we also tested the TIPS-Pentacene based devices with and without additive. Devices were kept in dry box without encapsulation for 80 and 12 days for pristine TIPS-pentacene and doped TIPS-Pentacene respectively. The photovoltaic parameters are summarized in Figure S9. *J-V* measurements were made at irregular intervals for both devices. The results shows that pristine TIPS-pentacene based devices showed an improvement in PCE even after 7 weeks, followed by this moderate decrease in performance by 4.7 % was observed due to slightly decreased J_{sc}, V_{oc}, FF. For doped TIPS-Pentacene based devices, the PV performance improved until 7 days in terms of J_{sc}, V_{oc} and FF but after this, J_{sc}, FF decreased significantly while V_{oc} moderately decreased. The decrease in J_{sc} and FF were mainly credited to degradation of the $CH_3NH_3PbI_3$ perovskite because gradual changing of dark brown colour into pale yellow colour of PbI_2 was observed over time. The drop in performance for pristine and doped TIPS-Pentacene was 4.7 % till 80 days and 42 % till 12 days respectively.

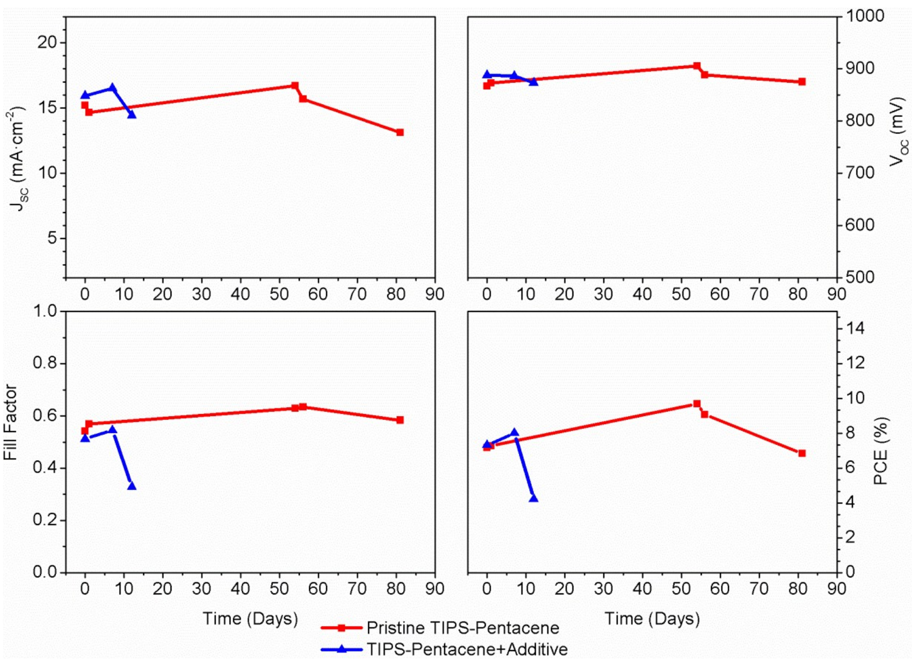

Figure S9 : Evolution of device parameters with time. Devices were kept in drybox and the efficiencies were measured by taking them out on then returned it back in the drybox.

Device statistics*:* Figure S10-S13 represents device statistics data in different solvent. The figure represents the effect of solvent as well as the effect of dopant. In the case of doped TIPS-Pentacene, lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) and 4-tert-butylpyridine (t-BP) were used as dopant/additives.

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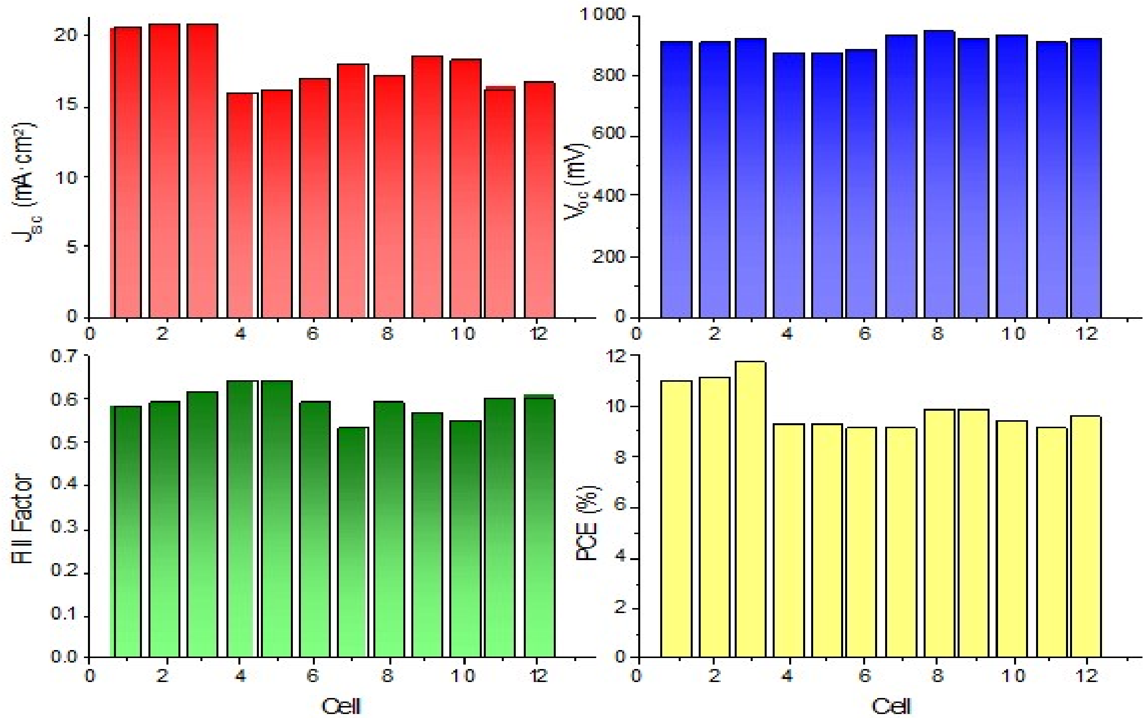

Figure S10: Statistical data of the devices, where TIPS-pentacene was solution processed in toluene and used as an HTM layer.

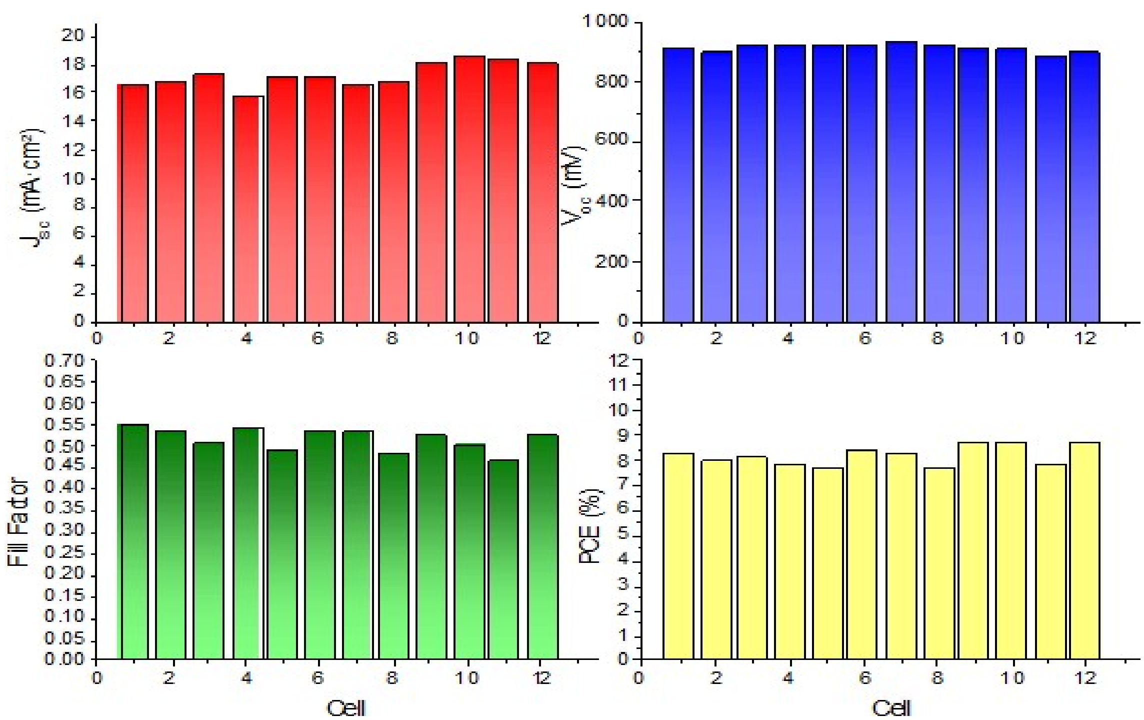

Figure S11: Statistical data of the devices, where doped TIPS-pentacene, was solution processed in toluene and used as an HTM layer.

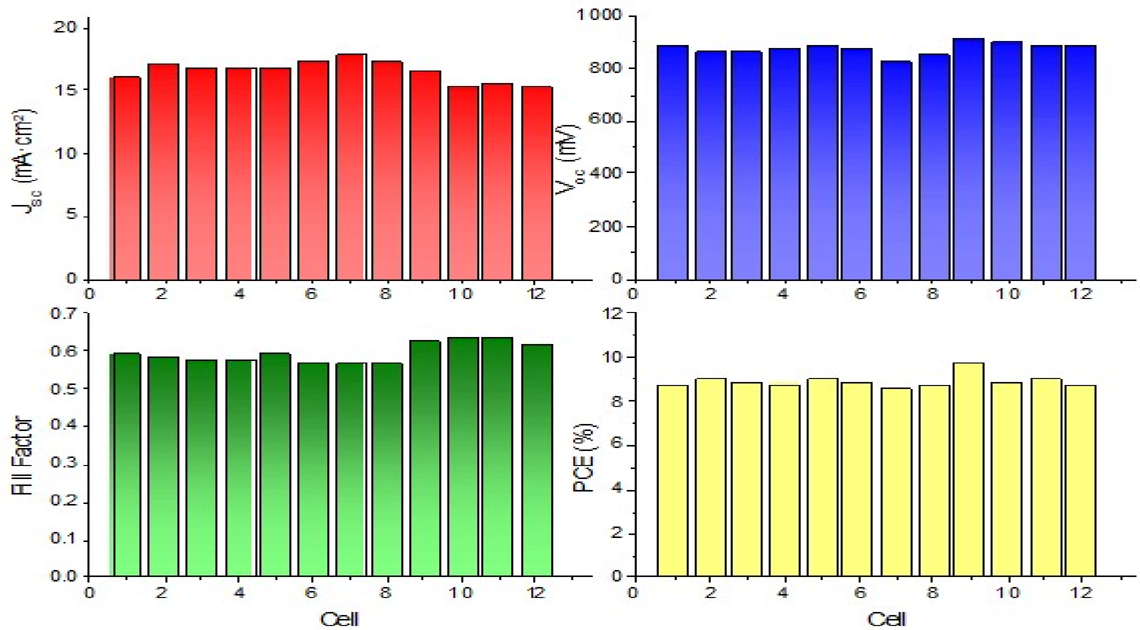

Figure S12: Statistical data of the devices, where TIPS-pentacene was solution processed in chlorobenzene and used as an HTM layer.

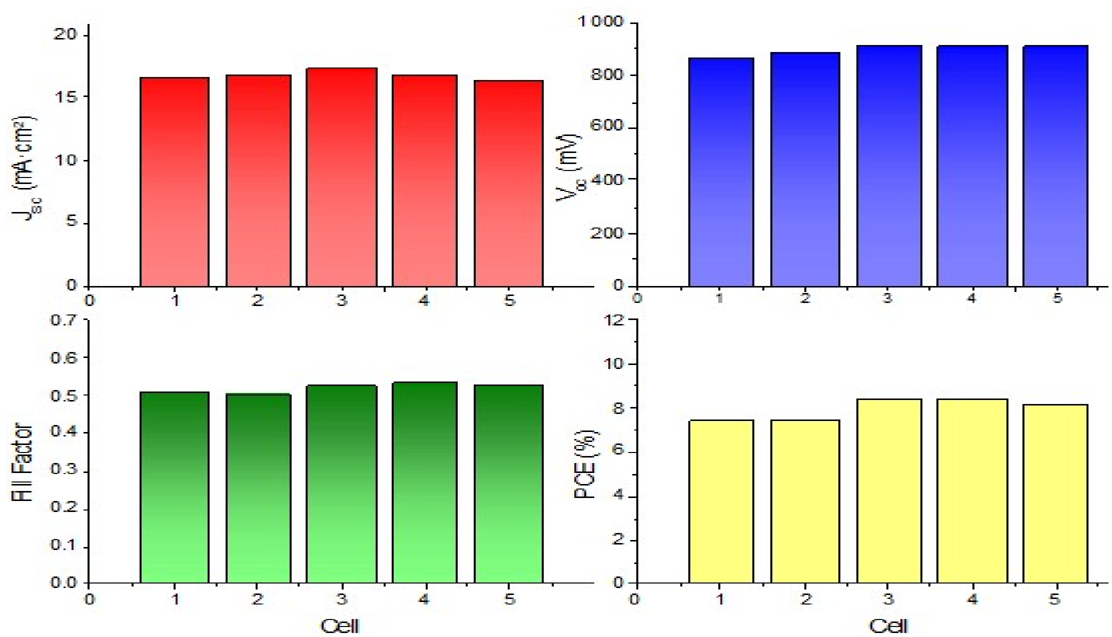

Figure S13 : Statistical data of the devices, where doped TIPS-pentacene, was solution processed in chlorobenzene and used as an HTM layer.

References

1 J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park, N.-G. Park. *Nanoscale* **2011**, 3, 4088

2 J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, M. Grätzel. *Nature,* **2013**, 499, 316.