Engineering of stable *p*-type contacts towards efficient fully vacuum deposited perovskite solar cells

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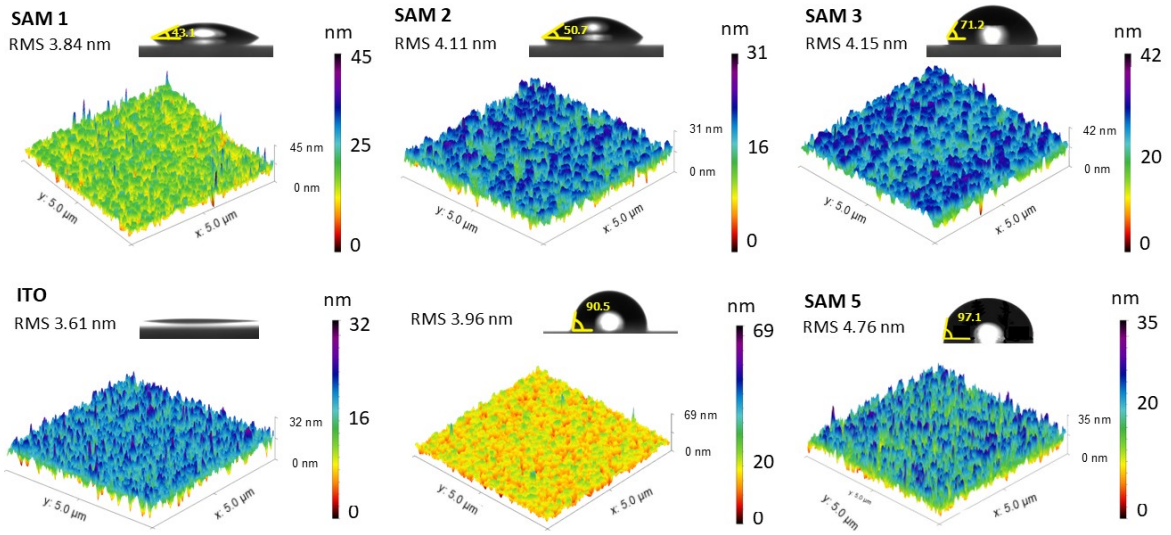

Figure S1. AFM 3D images (5x5 µm) and the corresponding RMS roughness of the ITO-SAM interlayers studied in this work. The bare ITO is also included for reference. The inset shows the contact angle measured for each interlayer.

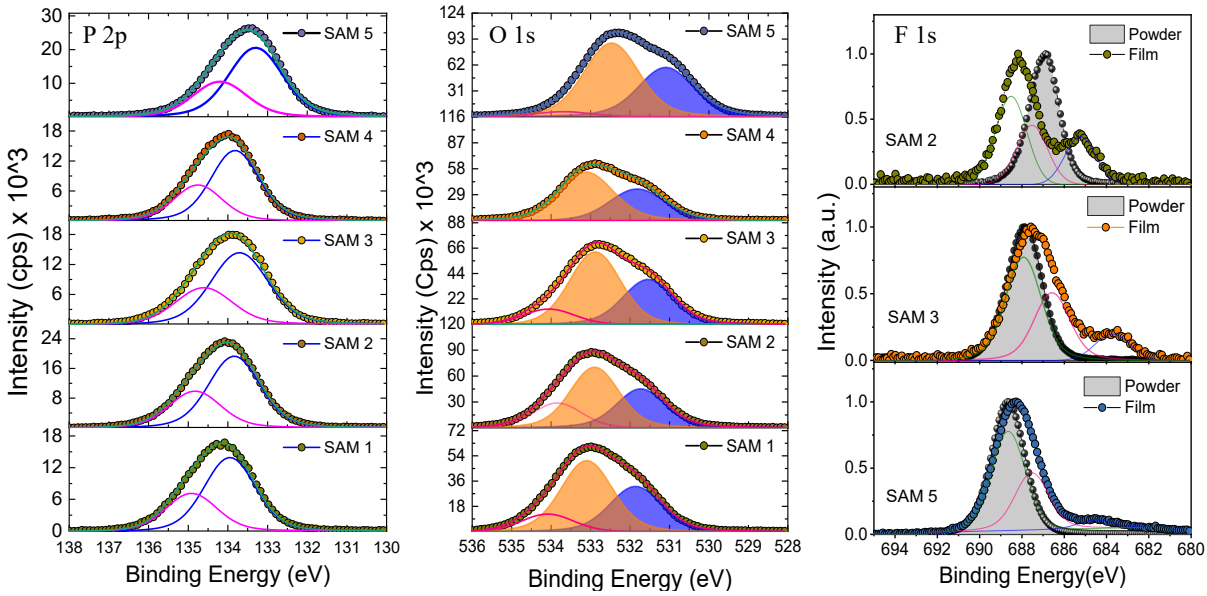

Figure S2. XPS spectra of P 2p, O 1s and F 1s obtained for SAMs 1-5 in powder state. The F 1s also includes the spectra for the thin films for comparison.

Table S1. Photovoltaic parameters obtained for *J-V* curves shown in Figure 3c.

		PCE	Voc	Jsc	FF
TaTm (7nm)	**Forward**	12.16	1.09	20.06	55.69
	Reverse	12.53	1.09	20.12	57.04
F6-TCNNQ/TATM	**Forward**	17.64	1.10	21.01	76.13
	Reverse	17.74	1.10	21.07	76.33
MoO3/TATM	**Forward**	18.73	1.11	20.55	81.86
	Reverse	18.64	1.11	20.6	81.38

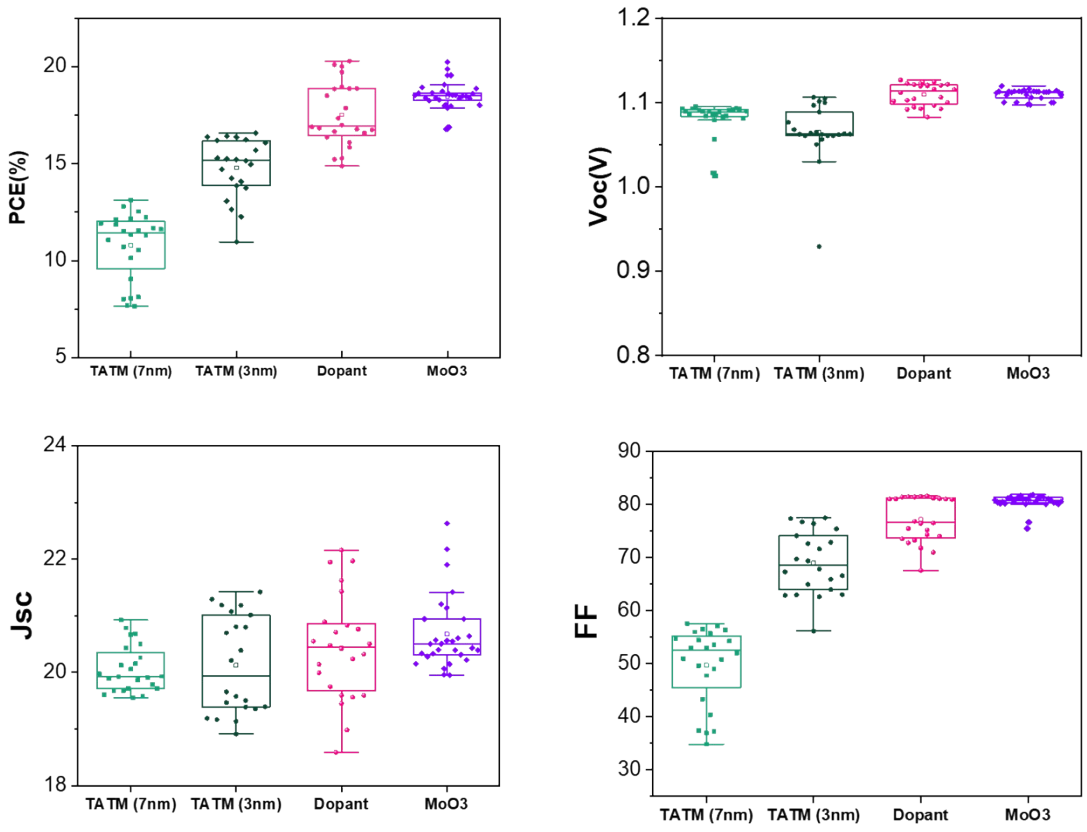

Figure S3. Statistical data for PCE, Voc, Jsc and FF obtained from more than 100 cells (at least 23 cells per condition) prepared with the different interlayers investigated in this study. The top bar shows the maximum value, the bottom bar shows the minimum value, and the rectangle

shows the region containing 25–75% of the data, obtained for each condition. The total device area is 0.0825 cm², with an illuminated area of 0.05 cm².

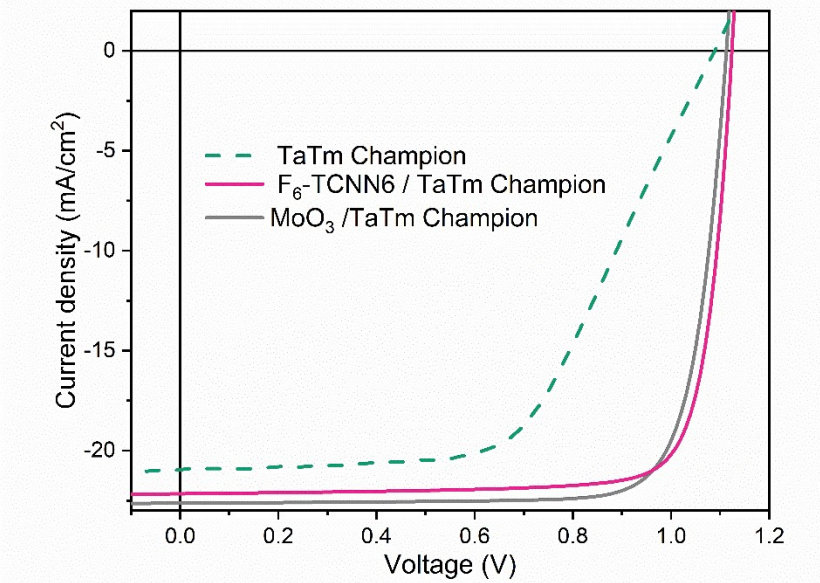

Figure S4. *J–V* scans obtained for the champion cells containing TaTm (7nm), MoO_3/TaTm (7nm) and F6-TCNN6/TaTm (7nm) as interlayers. The total device area is 0.0825 cm², with an illuminated area of 0.05 cm². The cells, measured in air, are encapsulated with 30nm of Al_2O_3.

Table S2. Photovoltaic parameters of the *J–V* scans shown in Figure S4.

	PCE	**Voc**	**Jsc**	**FF**
TaTm (7nm)	13.12	1.08	20.92	57.56
F_6-TCNNQ /TaTm	20.29	1.12	22.15	81.44
MoO_3/ TaTm	20.24	1.11	22.63	80.37

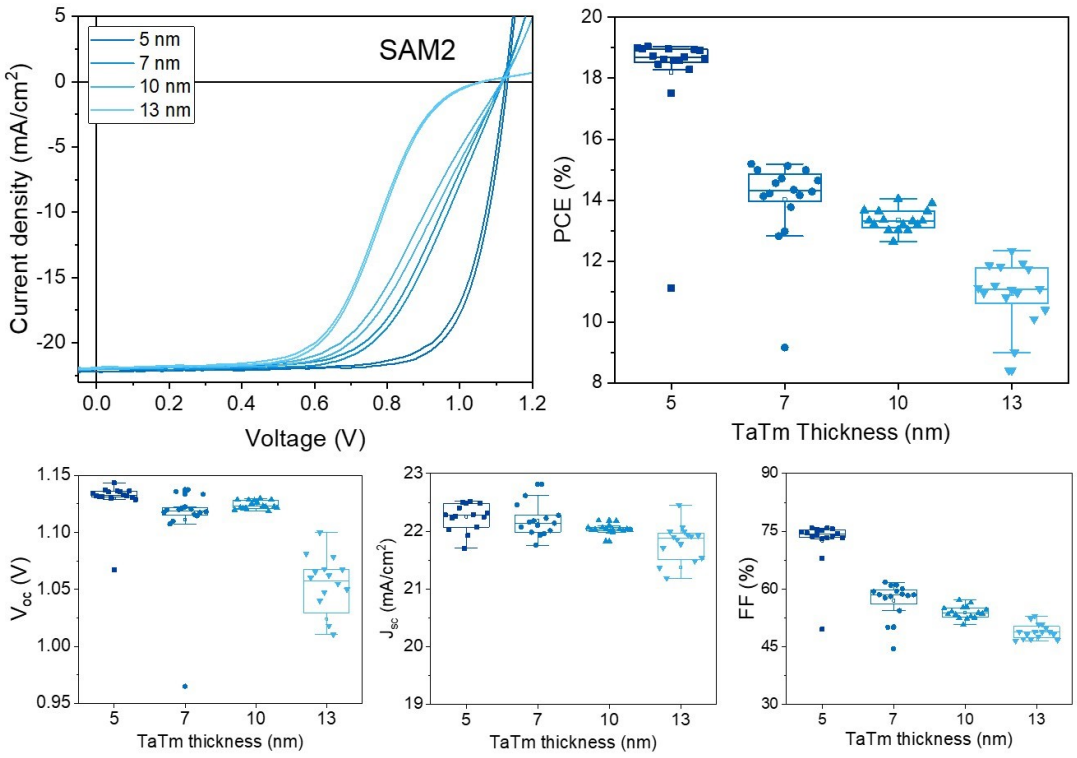

Figure S5. Thickness optimization for TaTm using SAM 2 as interlayer. The data include typical *J–V* curves obtained for each condition, including the forward and reverse scans. It also contains statistical data for *PCE, V_{oc}, J_{sc}* and *FF* obtained from more than 60 cells (at least 16 cells per condition). The top bar shows the maximum value, the bottom bar shows the minimum value, and the rectangle shows the region containing 25–75% of the data, obtained for each condition. The total device area is 0.0825 cm², with an illuminated area of 0.05 cm².

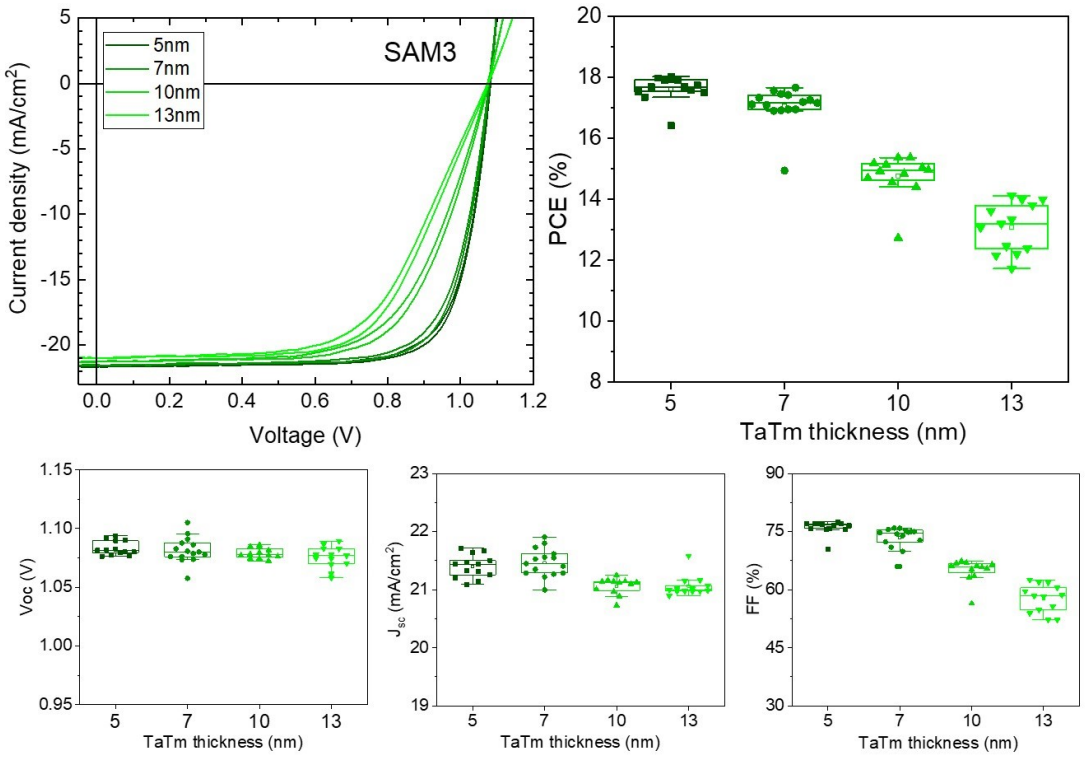

Figure S6. Thickness optimization for TaTm using SAM 3 as interlayer. The data include typical *J–V* curves obtained for each condition, including the forward and reverse scans. It also contains statistical data for *PCE, V_{oc}, J_{sc}* and *FF* obtained from more than 50 cells (at least 12 cells per condition). The top bar shows the maximum value, the bottom bar shows the minimum value, and the rectangle shows the region containing 25–75% of the data, obtained for each condition. The total device area is 0.0825 cm², with an illuminated area of 0.05 cm².

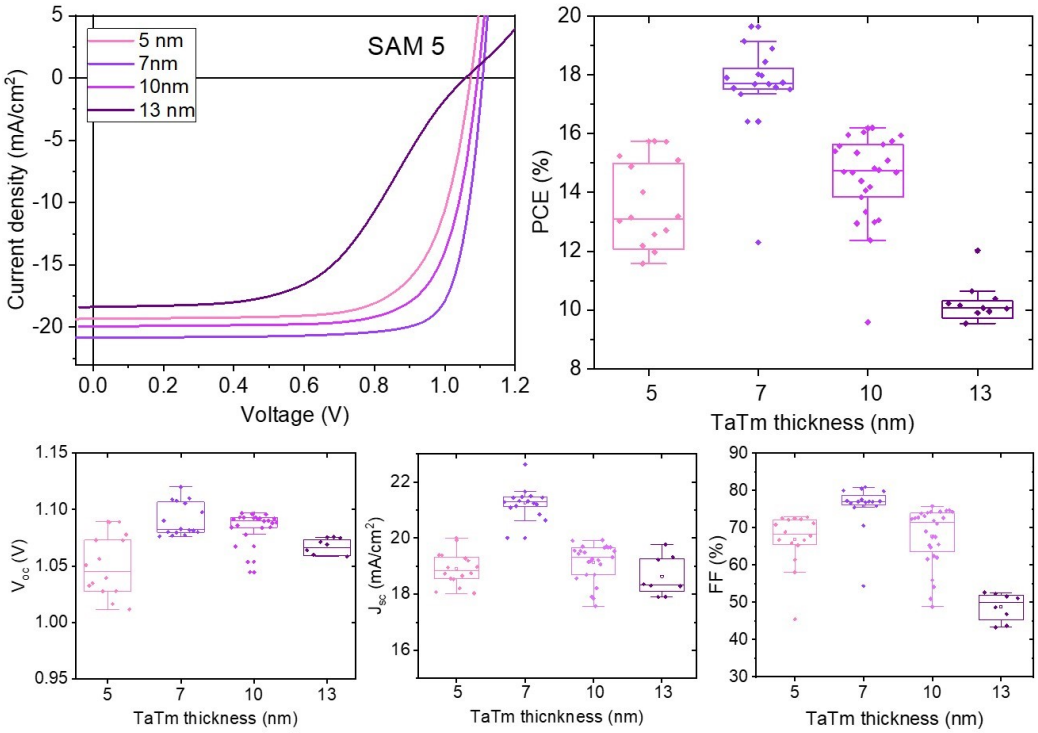

Figure S7. Thickness optimization for TaTm using SAM 3 as interlayer. The data include typical *J–V* curves obtained for each condition, including the forward and reverse scans. It also contains statistical data for *PCE, V_{oc}, J_{sc}* and *FF* obtained from more than 70 cells (at least 13 cells per condition). The top bar shows the maximum value, the bottom bar shows the minimum value, and the rectangle shows the region containing 25–75% of the data, obtained for each condition. The total device area is 0.0825 cm², with an illuminated area of 0.05 cm².

Table S3. Photovoltaic parameters of the *J–V* scans under forward and reverse bias obtained for the champion cells shown in Figure 4.

		PCE	Voc	Jsc	FF
SAM2	FWD	19.19	1.11	22.62	76.63
	Rev	19.50	1.12	22.80	76.46
SAM3	FWD	17.63	1.08	21.66	75.30
	Rev	18.02	1.08	21.66	76.83
SAM5	FWD	19.65	1.12	22.63	77.24
	Rev	19.71	1.12	22.54	78.13

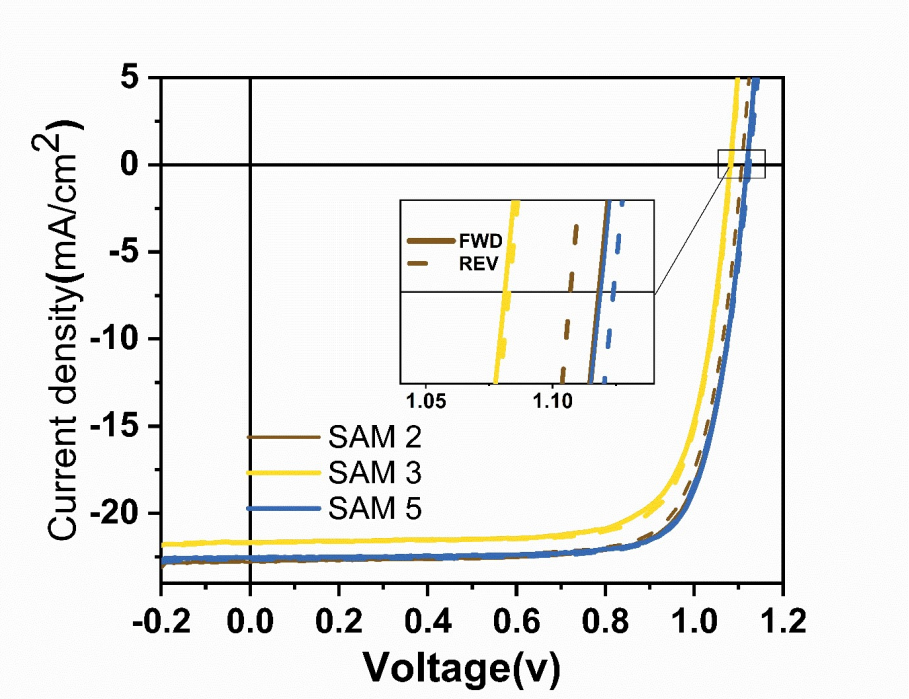

Figure S8. J-V scans obtained under forward and reverse bias, for the champion cells containing SAM 2, SAM 3 and SAM 5 as interlayers. The total device area is 0.0825 cm², with an illuminated area of 0.05 cm². The cells, measured in air, are encapsulated with 30nm of Al_2O_3.

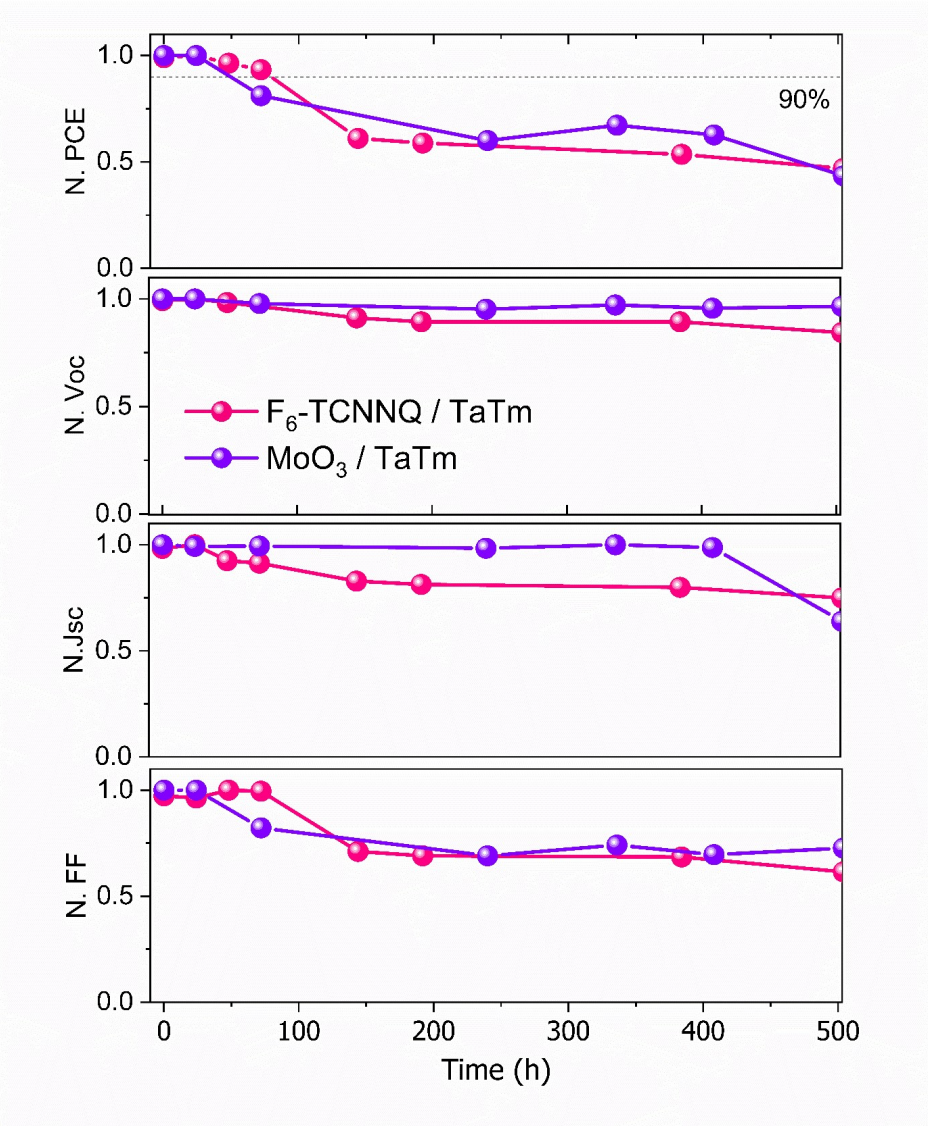

Figure S9. Thermal stability test of $MAPbI_3$ PSCs at 85 °C containing the reference interlayers, MoO_3 and F6-TCNNQ (dopant). The dashed line indicates the value for 90 % drop of initial efficiency. The devices were encapsulated with 30 nm of Al_2O_3 (total device area 0.0825 cm², illuminated area 0.05 cm²).

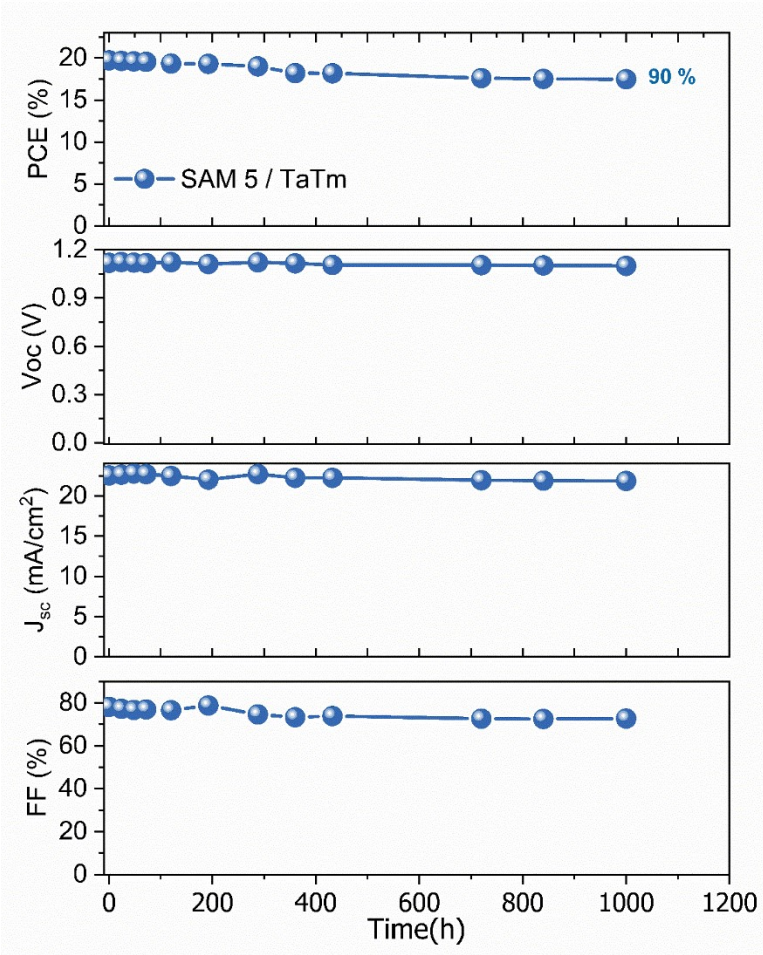

Figure S10. Evolution of the photovoltaic parameters of the champion cell prepared using SAM 5 as interlayer. The device was tested for 1000h under thermal stress of 85C in N_2 atmosphere after encapsulation with 30 nm of Al_2O_3 (total device area 0.0825 cm^2, illuminated area of 0.05 cm^2).