

Supplementary Information

Moisture resistance in perovskite solar cells attributed to a water-splitting layer

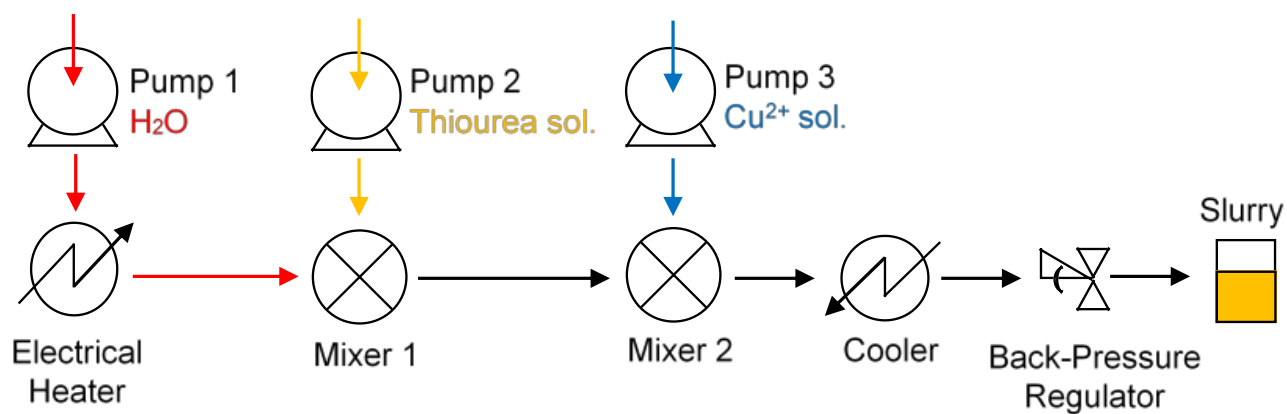
Min Kim,^{1,2#} Antonio Alfano,^{1,3#} Giovanni Perotto,⁴ Michele Serri,⁵ Nicola Dengo,⁶ Alessandro Mezzetti,¹ Silvia Gross,^{6,7} Mirko Prato,⁸ Marco Salerno,⁸ Antonio Rizzo,⁹ Roberto Sorrentino,¹ Enrico Cescon,⁶ Gaudenzio Meneghesso,^{7,9} Fabio Di Fonzo,¹ Annamaria Petrozza,¹ Teresa Gatti^{10*}
Francesco Lamberti^{6,7*}

Table of contents

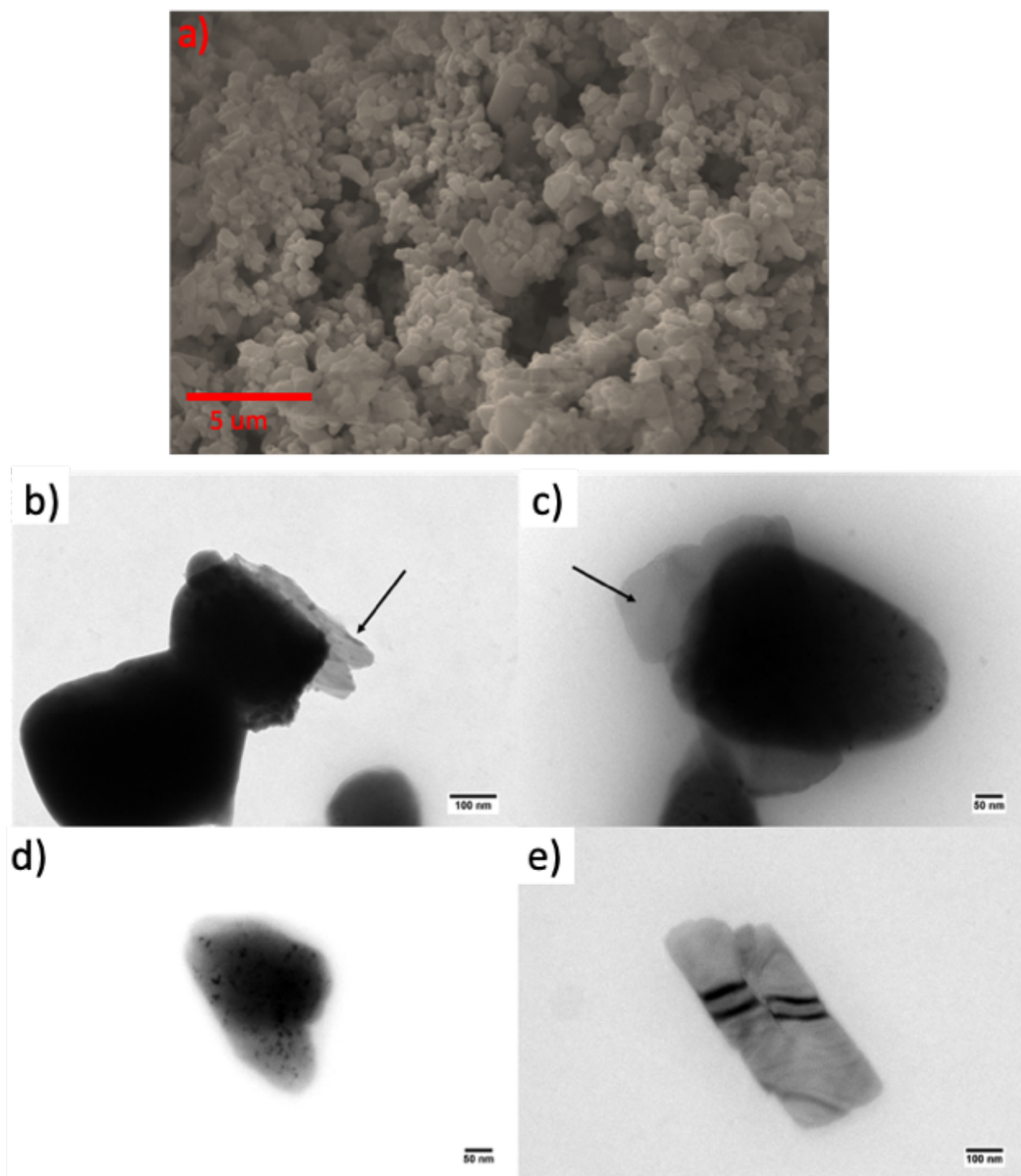
- Supplementary Methods

- **Supplementary Figure 1.** Scheme of the continuous flow hydrothermal synthesis setup employed for the production of CuSCN-NP
- **Supplementary Figure 2.** Electron microscopy characterization of CuSCN-NP
- **Supplementary Figure 3.** Various physico-chemical characterizations of CuSCN-NP: optical, XRD and EDX characterizations
- **Supplementary Figure 4.** KP microscopy characterization of CuSCN-NP and time-resolved EPR characterization of CuSCN@P3HT and pristine P3HT
- **Supplementary Figure 5.** SEM characterization of PSC containing P3HT and 5% CuSCN@P3HT HTM
- **Supplementary Figure 6.** HTM wettability characterization
- **Supplementary Figure 7.** Summary of PSC figures of merit at different control times
- **Supplementary Figure 8.** Statistical data on Jsc and FF variations during 28 days in a water-saturated atmosphere
- **Supplementary Figure 9.** TR-PL decays of perovskite/HTM junctions after 28 days in a water-saturated atmosphere
- **Supplementary Figure 10 and Supplementary Table 1.** Further TR-PL characterization of perovskite/HTM junctions
- **Supplementary Figure 11.** IPCE for fresh and aged samples in humid conditions

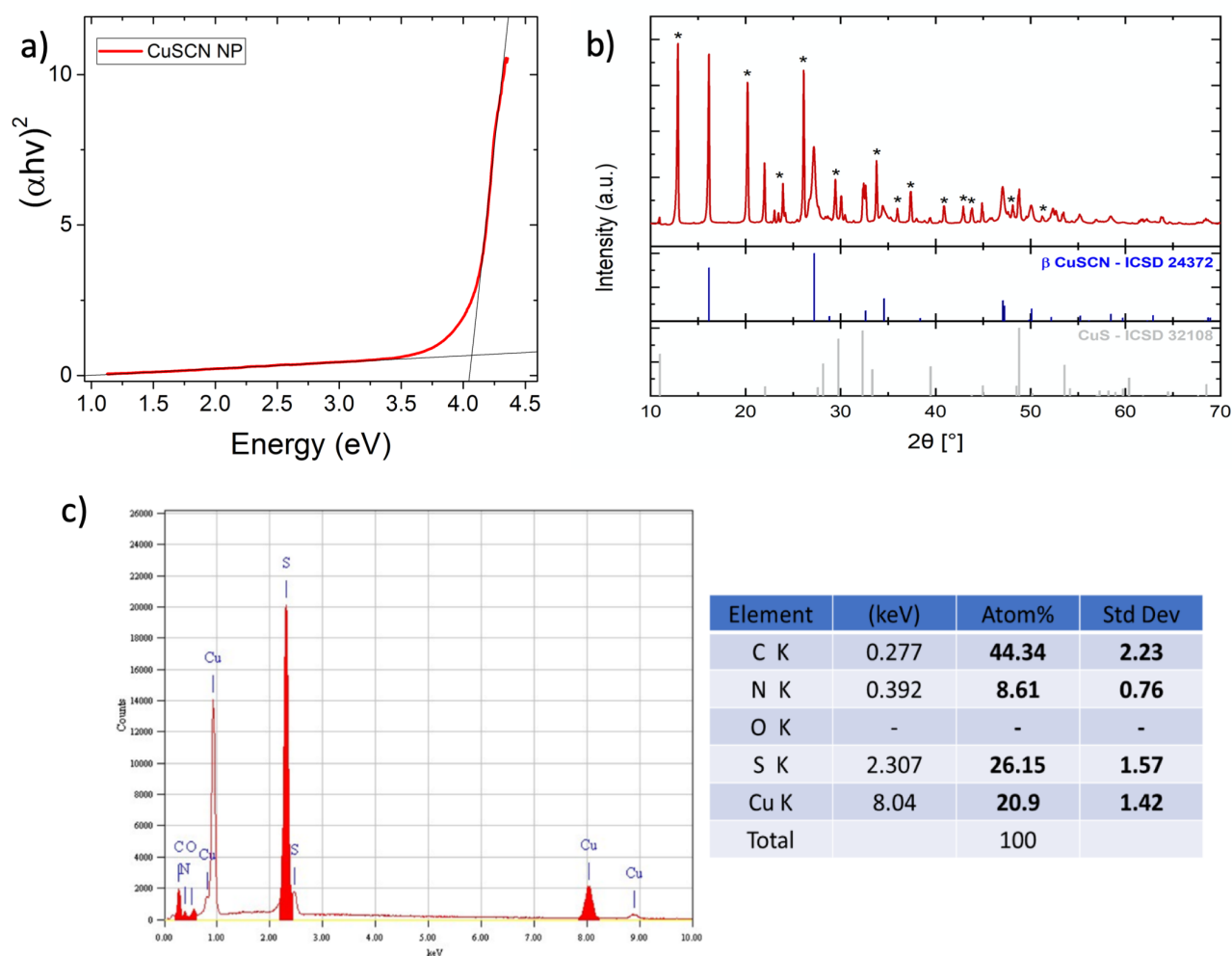
- **Supplementary Figure 12.** AFM imaging of the CuSCN lamellae
- **Supplementary Figure 13.** LSV analysis.



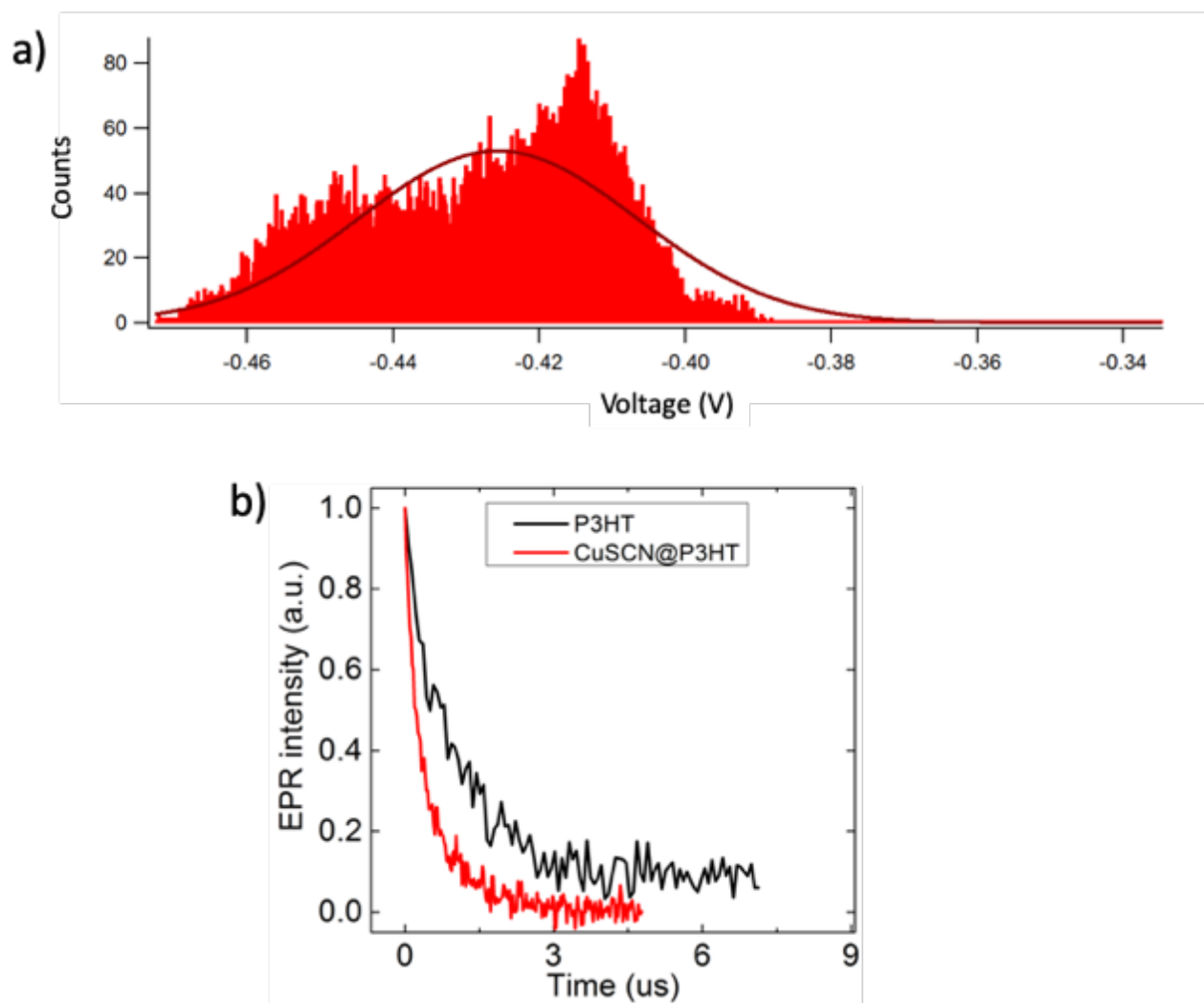
Supplementary Figure 1. Scheme of the continuous flow hydrothermal synthesis setup employed for the production of CuSCN-NP.



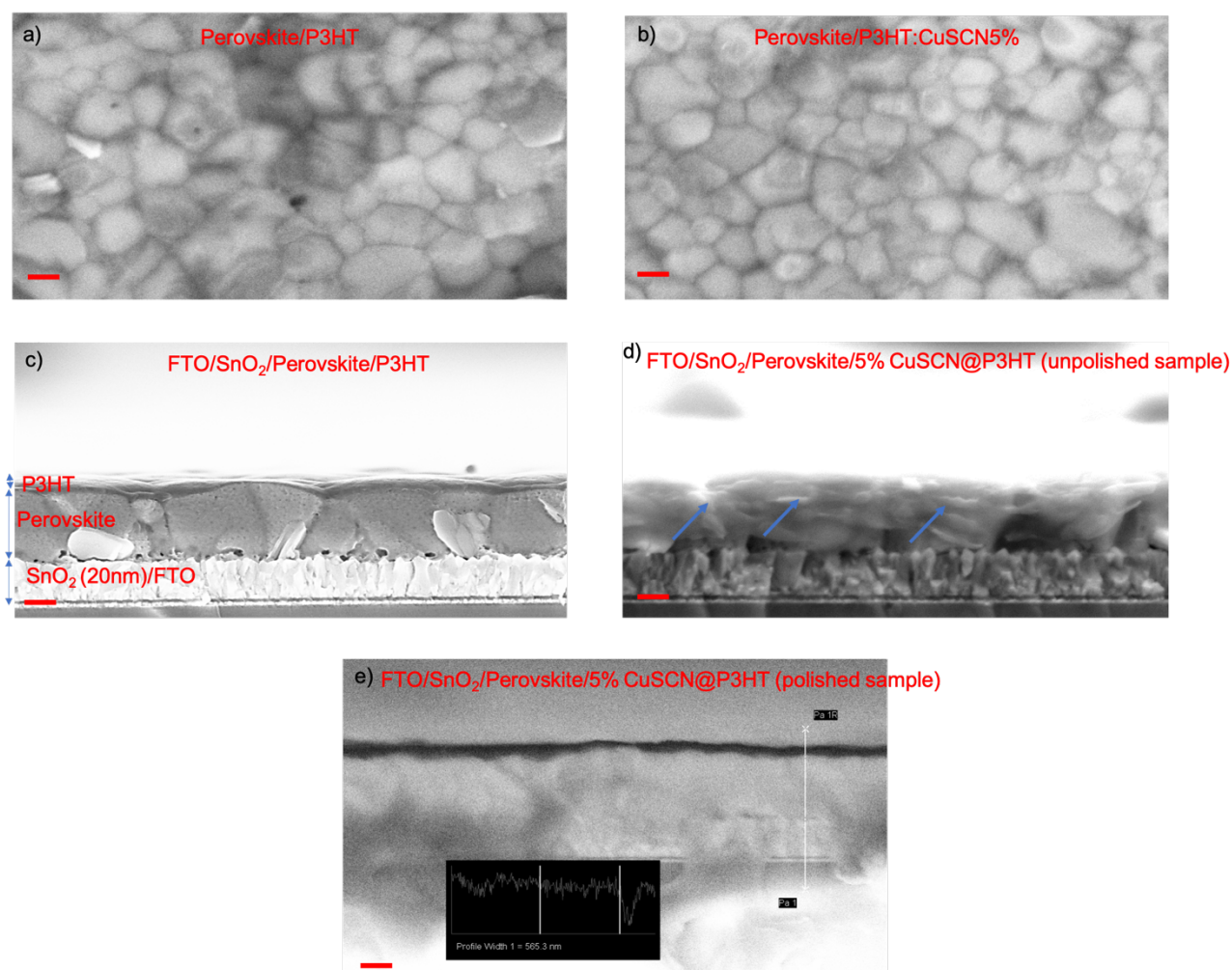
Supplementary Figure 2. Electron microscopy characterization of CuSCN-NP. a) SEM image of CuSCN-NP. b) to e) TEM images of CuSCN-NP. b) and c) Thin lamellae structures seen next to solid CuSCN particles. Surfactant in b) was keratin and in c) was PVP; d) CuSCN-NP image with increased contrast/brightness that highlights the presence of darker particles inside the structure; e) example of isolated lamellae.



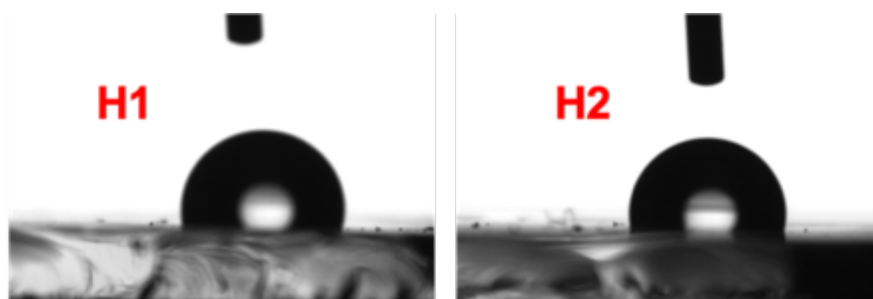
Supplementary Figure 3. Various physico-chemical characterizations of CuSCN-NP. a) Tauc Plot of the CuSCN-NP. b) Experimental XRD pattern of the CuSCN-NP powder sample with indication of the retrieved crystalline phases (stick plots). (*) unknown reflection. c) EDX analysis of CuSCN-NP.



Supplementary Figure 4. a) Kelvin Probe analysis of CuSCN NPs. An average voltage of 0.43 mV is found for CuSCN NP. This value is consistent with a Fermi level of the material of 4 eV (assuming 4.4 eV for the reference used as reported in the Experimental section of the main manuscript). b) Normalized transverse relaxation magnetization decays of bare P3HT and CuSCN@P3HT.



Supplementary Figure 5. SEM characterization of PSC containing P3HT and 5% CuSCN@P3HT HTM: a,b) top view images and c,d) cross-sectional images, in which no polishing was performed; e,f) cross-sectional images of polished samples exploiting higher contrast for better highlighting the top layer. The blue arrows indicate the CuSCN-NP emerging from the composite HTM in the unpolished sample. Scale bar is 200 nm.



Sample	C.A. 1	C.A.2	C.A.3	Average
H1: P3HT	100,3°	106,1°	108,1°	104,8°
H2: CuSCN@P3HT	101,2°	102,5°	102,3°	102,0°

Supplementary Figure 6. Water contact angle measurements on bare P3HT HTM and on 15% CuSCN@P3HT HTM.

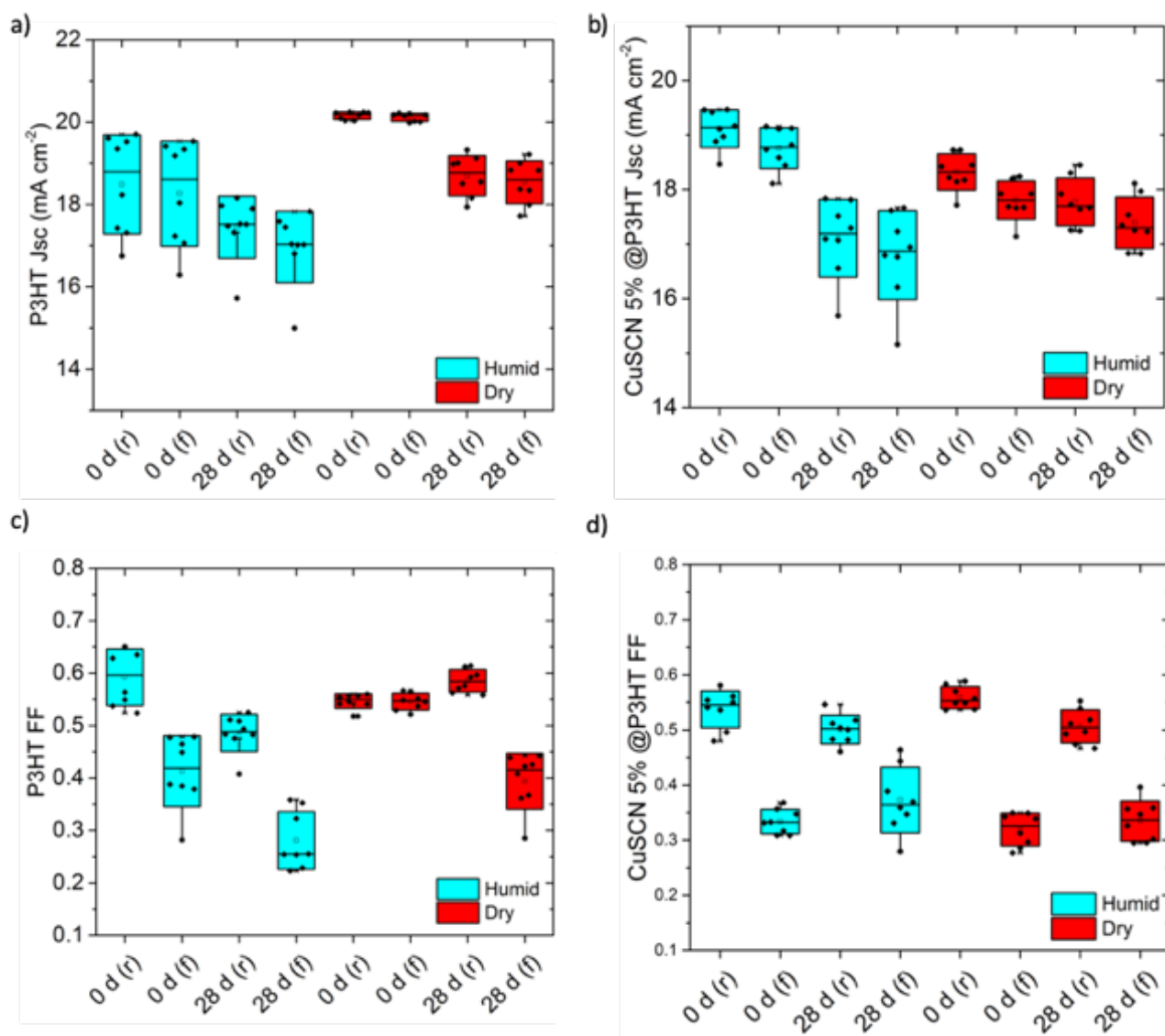
* Average device parameters (best 4 pixels from each) / two devices are duplicates.

Time	0d												3d												5d												7d																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
HUMID degradation	Jsc				Voc				PCE				FF				Jsc				Voc				PCE				FF				Jsc				Voc				PCE				FF																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																											

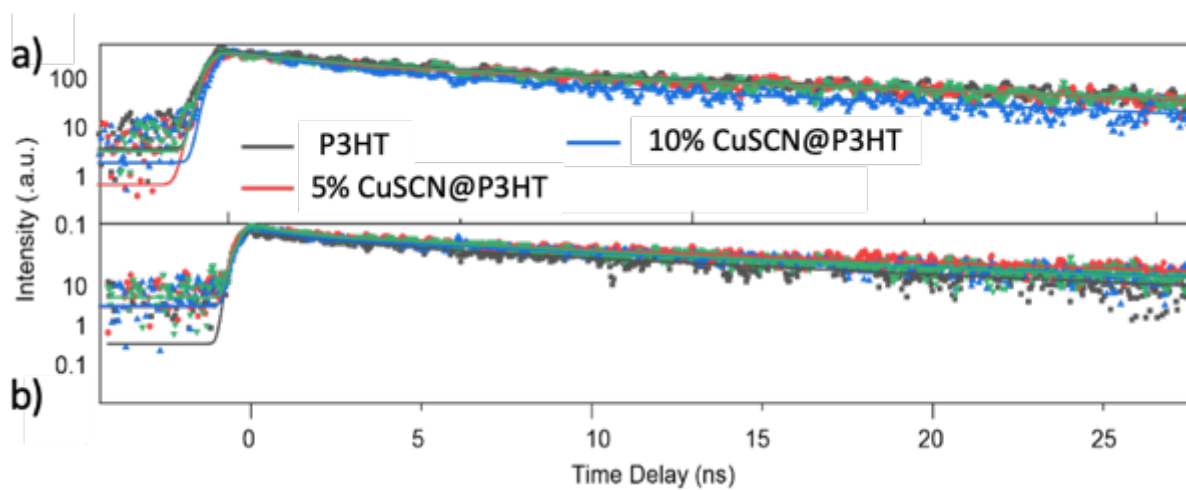
(continues)

Time	17d						21d						23d						25d					
	Jsc	Voc	PCE	FF			Jsc	Voc	PCE	FF			Jsc	Voc	PCE	FF			Jsc	Voc	PCE	FF		
HUMID degradation																								
5-P3HT	r	18.607	0.941	11.310	0.637		r	16.400	0.729	5.722	0.474		r	17.772	0.847	7.608	0.500		r	17.460	0.853	7.552	0.497	
	f	18.379	0.839	5.616	0.360		f	16.162	0.611	2.924	0.293		f	17.306	0.747	3.425	0.262		f	16.971	0.747	3.203	0.248	
	r	19.232	0.877	9.738	0.569		r	13.965	0.681	4.688	0.487		r	18.462	0.787	7.368	0.502		r	17.438	0.688	5.980	0.475	
a5-P3HT	f	19.016	0.758	4.553	0.312		f	13.441	0.509	1.825	0.262		f	18.141	0.642	4.328	0.369		f	16.965	0.566	3.214	0.314	
6-P3HT-CuSCN5%	r	19.044	0.861	9.188	0.553		r	16.762	0.793	6.558	0.488		r	17.411	0.947	8.304	0.498		r	16.601	0.881	7.214	0.482	
	f	18.807	0.766	5.733	0.393		f	16.587	0.647	3.666	0.341		f	17.109	0.860	5.367	0.361		f	16.233	0.770	4.213	0.329	
	r	19.105	0.862	9.533	0.571		r	16.424	0.868	7.460	0.518		r	18.270	0.943	9.115	0.523		r	17.613	0.921	8.606	0.519	
a6-P3HT-CuSCN5%	f	18.907	0.768	5.931	0.403		f	16.240	0.708	4.561	0.394		f	18.063	0.823	6.549	0.435		f	17.363	0.786	5.817	0.416	
7-P3HT-CuSCN10%	r	19.364	0.844	9.207	0.555		r	14.999	0.802	5.469	0.449		r	16.979	0.916	7.477	0.474		r	15.780	0.839	6.110	0.448	
	f	19.152	0.791	5.888	0.387		f	14.686	0.601	2.731	0.308		f	16.597	0.871	4.478	0.305		f	15.314	0.732	3.396	0.294	
	r	18.900	0.869	9.348	0.562		r	16.889	0.855	7.093	0.486		r	18.416	0.946	9.145	0.519		r	17.752	0.905	8.262	0.503	
a7-P3HT-CuSCN10%	f	18.704	0.764	6.163	0.426		f	16.701	0.680	4.459	0.388		f	18.202	0.833	6.446	0.420		f	17.451	0.789	5.321	0.378	
Dry degradation																								
1-P3HT	r	19.516	0.857	9.583	0.565		r	17.818	0.937	10.295	0.611		r	18.286	0.922	10.307	0.599		r	18.568	0.918	10.166	0.590	
	f	19.283	0.722	5.683	0.403		f	17.663	0.750	6.131	0.476		f	18.104	0.765	5.743	0.406		f	18.380	0.749	5.761	0.413	
	r	19.476	0.899	9.938	0.557		r	17.300	0.774	6.861	0.507		r	19.108	0.900	10.045	0.572		r	19.314	0.917	10.428	0.583	
a1-P3HT	f	19.365	0.876	8.287	0.481		f	17.026	0.567	3.212	0.329		f	18.969	0.793	5.808	0.382		f	19.195	0.771	6.359	0.424	
2-P3HT-CuSCN5%	r	17.817	0.893	8.502	0.527		r	18.330	0.874	9.040	0.558		r	18.029	0.791	7.719	0.530		r	18.437	0.814	8.066	0.532	
	f	17.278	0.826	4.267	0.295		f	18.136	0.754	5.834	0.422		f	17.669	0.683	4.279	0.349		f	18.114	0.740	4.794	0.354	
	r	18.234	0.866	8.219	0.514		r	16.027	0.799	6.526	0.505		r	17.521	0.790	6.824	0.482		r	17.873	0.808	7.096	0.486	
a2-P3HT-CuSCN5%	f	17.745	0.731	4.627	0.352		f	15.705	0.657	3.237	0.310		f	17.106	0.701	3.921	0.320		f	17.515	0.725	4.240	0.330	
3-P3HT-CuSCN10%	r	17.265	0.868	7.794	0.510		r	17.154	0.862	7.970	0.532		r	17.831	0.766	6.858	0.491		r	17.850	0.746	6.403	0.465	
	f	16.689	0.728	3.786	0.306		f	16.957	0.732	5.073	0.404		f	17.408	0.696	3.911	0.315		f	17.481	0.706	4.001	0.317	
	r	18.383	0.825	8.734	0.580		r	15.010	0.822	6.382	0.512		r	17.227	0.780	6.299	0.457		r	17.354	0.818	6.717	0.465	
a3-P3HT-CuSCN10%	f	17.908	0.774	4.708	0.336		f	14.743	0.679	3.278	0.324		f	16.852	0.676	3.747	0.321		f	16.985	0.738	4.010	0.315	

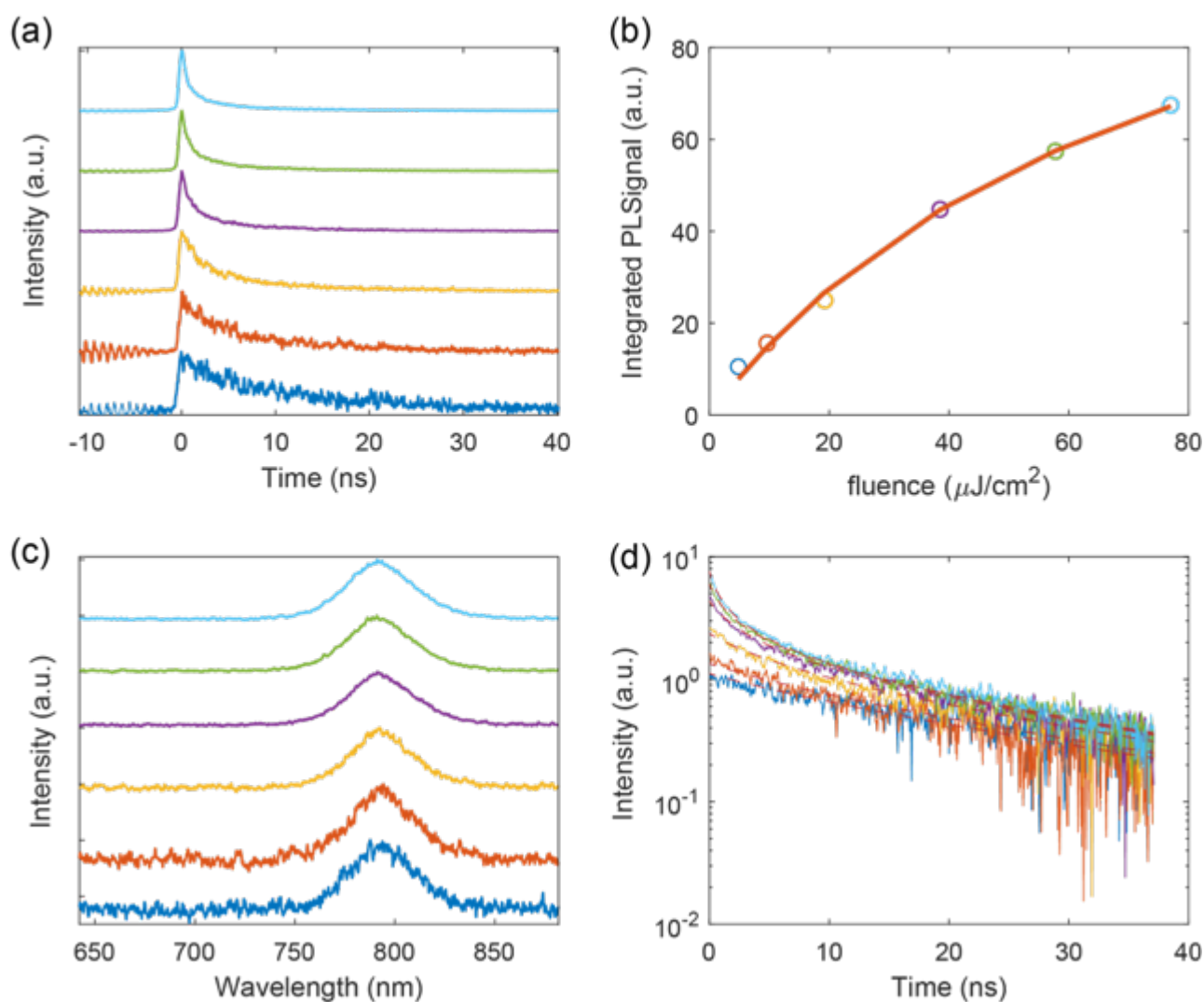
Supplementary Figure 7. Chart summarizing photovoltaic figures of merit for the PSC prepared in this work at different time points.



Supplementary Figure8. Statistical data on Jsc and FF variations during 28 days in a water-saturated atmosphere (humid, pale blue) and in a dry atmosphere (dry, red) for PSC containing a,c) the reference P3HT and b,d) the 5% CuSCN@P3HT HTM.



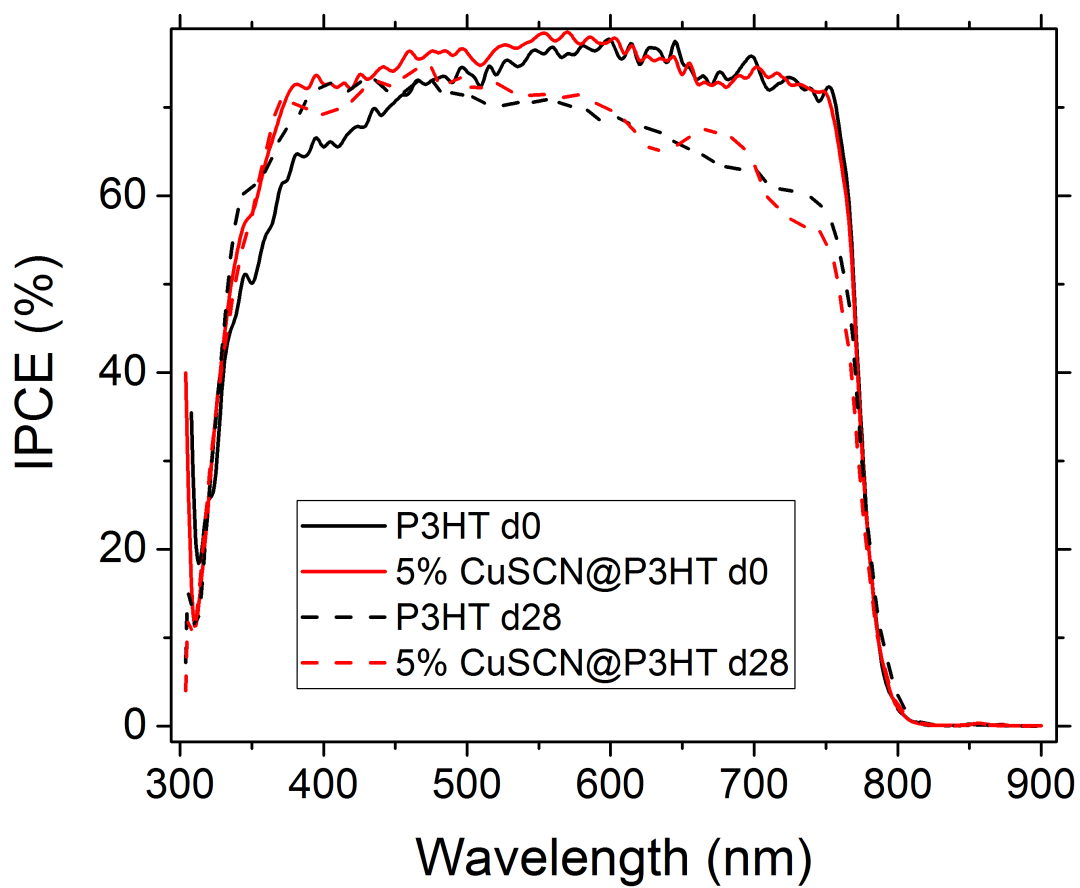
Supplementary Figure9. Comparison between PL decay kinetics of perovskite emission (780 nm) for a) "dry" and b) "humid" aged samples.



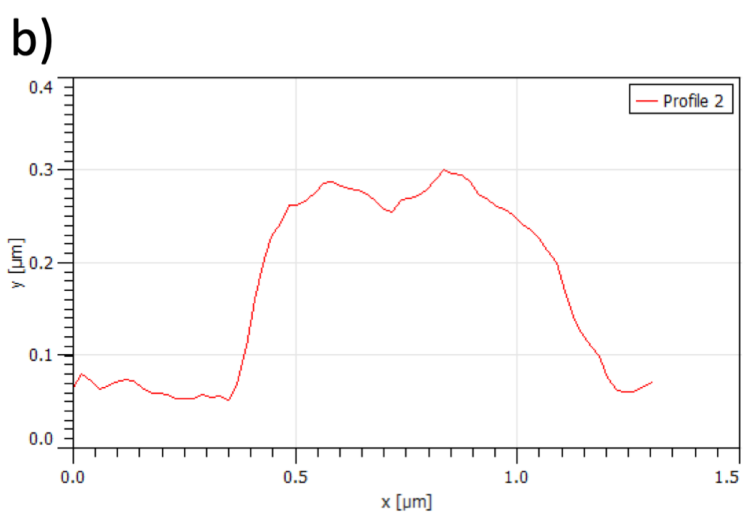
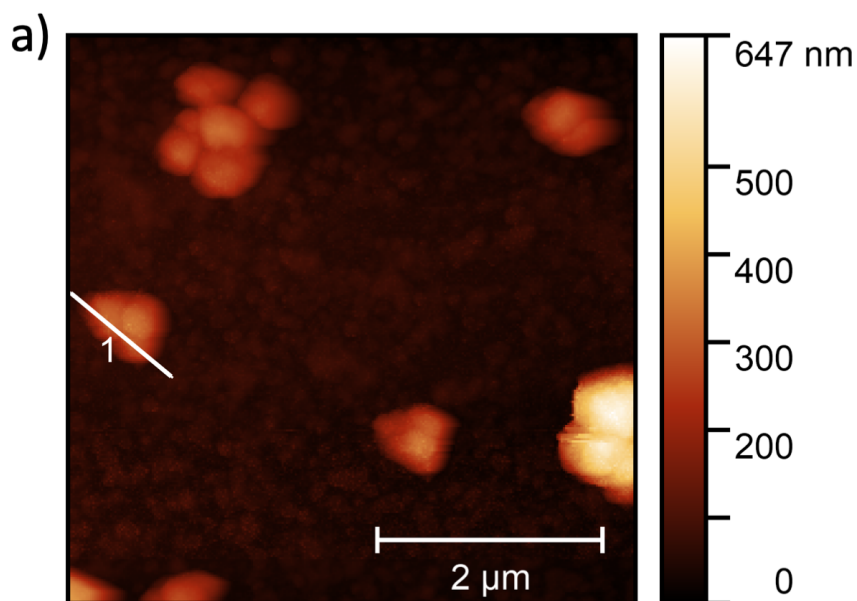
Supplementary Figure10. TR-PL characterization of perovskite/HTM junctions. a) Excitation fluence dependent TRPL measurements on 5% CuSCN@P3HT/perovskite junction after 28 days of humid storage. The excitation fluence is indicated by colored dots in panel b) and color correspondence is maintained throughout the four panels. c) Time integrated PL intensity at different pump fluences. d) PL decay (solid line) and model fit (dashed line) for different powers.

Supplementary Table S1. Carrier recombination rates extracted from model fitting of PL decay kinetics for PSC kept in the two opposite ageing conditions.

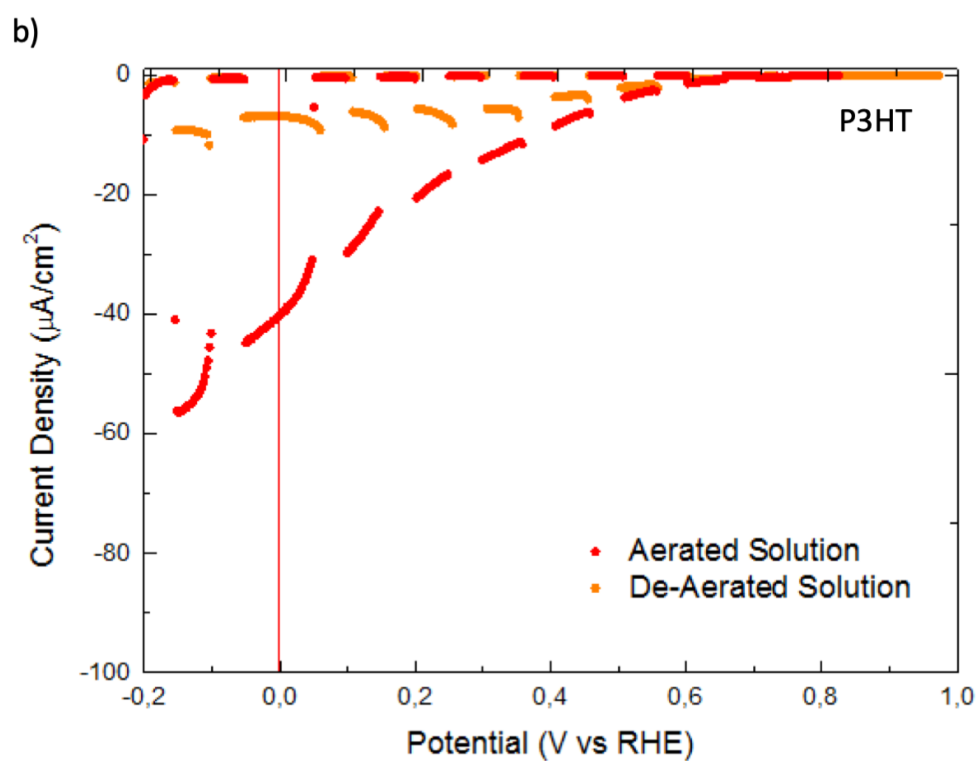
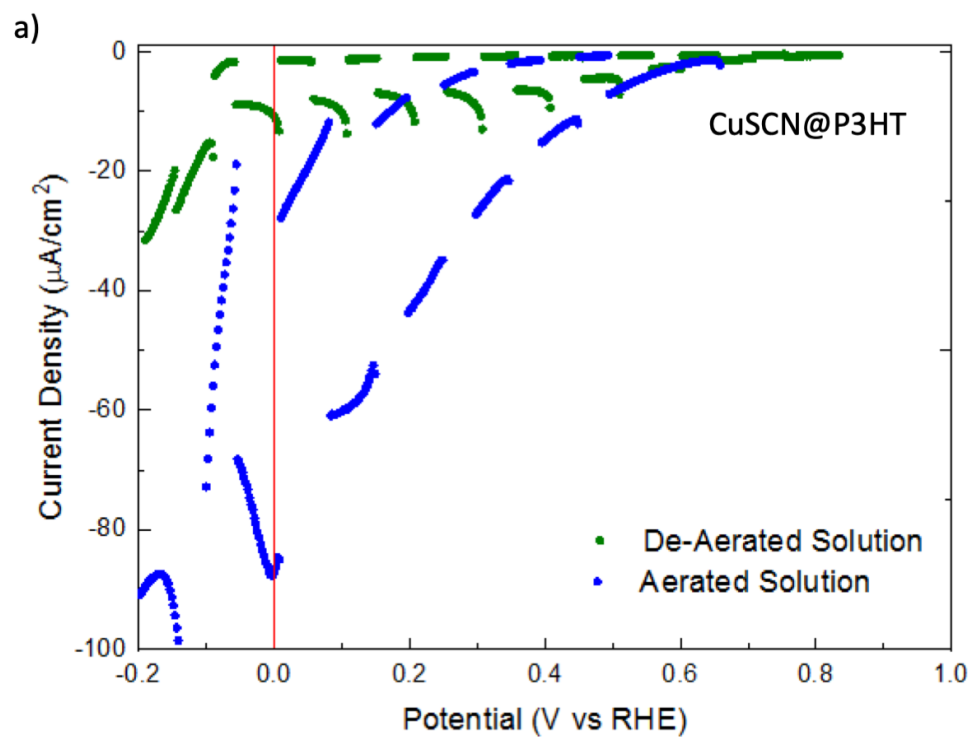
Device	k1 (10^7 s^{-1})		k2 ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$)	
	Dry	Humid	Dry	Humid
P3HT	2.89	3.14	1.12	1.44
5% CuSCN@P3HT	2.72	3.39	1.17	0.05
10% CuSCN@P3HT	2.28	3.40	4.34	0.15



Supplementary Figure11. IPCE analysis for P3HT and 5% CuSCN@P3HT samples in humid conditions.



Supplementary Figure12. AFM imaging of CuSCN lamellae. a) topography image in tapping mode, b) line profile related to isolated particles.



Supplementary Figure13. LSV showing the cathodic behavior of different HTM used in the study, alternating light and dark steps as described in Experimental Section of the main manuscript.