

SUPPORTING INFORMATION

A new antimony-based organic-inorganic hybrid material as electron extraction layer for efficient and stable polymer solar cells

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Table S1: Crystallographic data for [C₅H₈N₃]₂SbCl₅

Chemical formula	[C ₅ H ₈ N ₃] ₂ SbCl ₅
Molecularweight (g/mol)	519.30
Crystal system	Monoclinic
Space group	P2 ₁ /c
Temperature	293K
Cell constants	
a,b,c(Å°)	9.11(5),20.39(5), 10.32(5)
α, β, γ (°)	90, 97.43(5),90
Cell volume(Å ³)	1895(15)
Z	4
Radiation type,λ (Å)	Mo/K _a , 0.71073
crystal size (mm ³)	0.4×0.4 × 0.9
Crystal colorBrown	
Diffractometer	KCCD
ρ _{calc} (g cm ⁻³)	1.820
θ min, /θ max (°)	3.349/27.540
Measured reflections	17445
Independent reflections	3869
F(000)	1016
Goof S(F ²)	0.809
Δρ max (eÅ ⁻³) /Δρ min (eÅ ⁻³)	0.68/-0.89
R[F ² > 2σ(F ²)]	0.038
wR(F ²)	0.138

The total number of measured reflections was 17445 and we noted 3281 which had an intensity of $I > 2\sigma(I)$. The positional parameters for the heavy atoms were obtained from Patterson method by SHELXS-2013 program,^[1] while the non-hydrogen atoms were found from successive difference Fourier Maps using the SHELXL-2013 program.^[2]

The hydrogen atoms were fixed geometrically by the appropriate instructions of the SHELXL-2013 (HFIX).^[2] The final cycle of refinement lead to the final discrepancy factors $R1 = 0.03$ and $wR2 = 0.13$. Crystallographic data and refinement details are given in **Table S1** and the final atomic coordinates are reported in **Table S2**. The structure graphics were made with Diamond.^[3]

¹ G. M. Sheldrick, SHELXS-2013, Programs for Crystal Solution, University of Gottingen, Germany, (2013).

² G. M. Sheldrick, SHELXL-2013, Programs for Crystal Structure Refinement, University of Göttingen, Germany, (2013).

³ K. Brandenburg; Diamond Version 2.0 Impact GbR, Bonn, Germany, (1998).

Table S2: Atomic coordinates and equivalent isotropic displacement parameters for the
[C₅H₈N₃]₂SbCl₅

	x	y	z	Uiso*/Ueq
Sb01	1.11240 (4)	0.43212 (2)	0.39730 (4)	0.03680 (15)
Cl02	1.06988 (19)	0.36210 (8)	0.21092 (15)	0.0488 (4)
Cl03	1.1872 (2)	0.32266 (9)	0.53143 (18)	0.0563 (4)
Cl04	1.02747 (19)	0.52930 (8)	0.24099 (18)	0.0533 (4)
Cl05	1.37925 (18)	0.45134 (10)	0.34932 (18)	0.0547 (4)
Cl06	0.82601 (18)	0.41952 (9)	0.42802 (18)	0.0513 (4)
N007	0.7807 (6)	0.1691 (2)	0.2035 (5)	0.0382 (11)
H007	0.8244	0.1426	0.1560	0.046*
N008	0.7922 (7)	0.0676 (3)	0.5030 (6)	0.0621 (17)
H00A	0.8259	0.0433	0.4453	0.074*
H00B	0.8515	0.0831	0.5673	0.074*
N009	1.0135 (7)	0.1991 (3)	0.3023 (7)	0.0595 (16)
H00C	1.0708	0.2213	0.3591	0.071*
H00D	1.0507	0.1722	0.2511	0.071*
N010	0.5597 (7)	0.1306 (3)	0.0937 (5)	0.0505 (14)
H0C	0.6091	0.1044	0.0502	0.061*
H01D	0.4646	0.1309	0.0795	0.061*
N011	0.5600 (6)	0.0550 (2)	0.3882 (5)	0.0366 (10)
H011	0.6013	0.0313	0.3341	0.044*
N012	0.3392 (6)	0.0356 (3)	0.2573 (6)	0.0509 (13)
H01A	0.3873	0.0127	0.2068	0.061*
H01B	0.2449	0.0403	0.2392	0.061*
C013	0.8677 (8)	0.2063 (3)	0.2938 (6)	0.0435 (14)
C014	0.6311 (7)	0.1709 (3)	0.1839 (5)	0.0360 (12)
C015	0.4109 (7)	0.0639 (3)	0.3642 (6)	0.0386 (13)
C016	0.6483 (7)	0.0811 (3)	0.4927 (6)	0.0415 (13)
C017	0.3441 (8)	0.1023 (3)	0.4519 (7)	0.0488 (15)
H017	0.2426	0.1100	0.4389	0.059*
C018	0.5589 (8)	0.2139 (3)	0.2593 (7)	0.0479 (15)
H018	0.4562	0.2172	0.2479	0.057*
C019	0.6435 (10)	0.2513 (4)	0.3510 (8)	0.063 (2)
H019	0.5960	0.2801	0.4020	0.076*
C020	0.5827 (9)	0.1190 (4)	0.5797 (6)	0.0531 (17)
H020	0.6395	0.1376	0.6519	0.064*
C021	0.7967 (9)	0.2480 (3)	0.3710 (7)	0.0572 (18)
H021	0.8507	0.2735	0.4352	0.069*
C022	0.4315 (9)	0.1289 (4)	0.5585 (7)	0.0579 (19)
H022	0.3872	0.1541	0.6178	0.070*

Table S3a: Geometry of anions in [C₅H₈N₃]₂SbCl₅

Bond lengths (Å)	
Sb01—Cl02	2.384 (8)
Sb01—Cl05	2.572 (13)
Sb01—Cl04	2.604 (6)
Sb1—Cl03	2.662 (6)
Sb1—Cl06	2.681 (14)

Bond angles (°)	
Cl02—Sb01—Cl05	89.68 (18)
Cl02—Sb01—Cl04	87.1 (3)
Cl05—Sb01—Cl04	88.7 (2)
Cl02—Sb01—Cl03	85.7 (3)
Cl05—Sb01—Cl03	92.43 (19)
Cl04—Sb01—Cl03	172.63 (6)
Cl02—Sb01—Cl06	88.81 (17)
Cl05—Sb01—Cl06	174.58 (6)
Cl04—Sb01—Cl06	85.99 (18)
Cl03—Sb01—Cl06	92.64 (16)

Table S3b: Geometry of the organic cations in [C₅H₈N₃]₂SbCl₅

Bond lengths (Å)			
N007—C014	1.352 (11)	C013—C021	1.380 (10)
N007—C013	1.371 (9)	C014—C018	1.391 (9)
N008—C016	1.330 (12)	C015—C017	1.393 (10)
N009—C013	1.328 (12)	C016—C020	1.376 (10)
N010—C014	1.343 (9)	C017—C022	1.382 (11)
N011—C015	1.361 (11)	C018—C019	1.371 (11)
N011—C016	1.367 (9)	C019—C021	1.386 (14)
N012—C015	1.337 (9)	C020—C022	1.381 (13)

Bond angles (°)			
C014—N007—C013	124.7 (5)	N007—C014—C018	118.3 (6)
C015—N011—C016	124.3 (6)	N012—C015—N011	117.6 (6)
N009—C013—C021	124.7 (7)	N012—C015—C017	124.7 (7)
C016—C020—C022	119.1 (7)	N011—C015—C017	117.8 (6)
N009—C013—N007	118.0 (6)	N008—C016—N011	117.1 (6)
C021—C013—N007	117.3 (7)	N008—C016—C020	124.7 (7)
N010—C014—N007	118.4 (6)	N011—C016—C020	118.1 (7)
N010—C014—C018	123.3 (7)	C022—C017—C015	118.7 (7)
C019—C018—C014	118.1 (7)	C018—C019—C021	122.8 (7)
C020—C022—C017	122.0 (7)		

Table S4: Hydrogen Bonding systems

N-H...Cl	H...Cl (Å)	N...Cl (Å)	N-H...Cl(°)
N007-H007...Cl04	2.808	3.346	122.17
N007-H007 ...Cl06	2.672	3.435	148.36
N008-H00A...Cl04	2.495	3.273	150.83
N008-H00B...Cl02	2.575	3.412	164.68
N009-H00C...Cl03	2.836	3.665	162.33
N009-H00D...Cl03	2.724	3.414	138.20
N010-H0C...Cl06	2.524	3.304	151.22
N010-H01D...Cl03	2.683	3.503	159.78
N011-H011...Cl05	2.519	3.332	158.17
N012-H01A...Cl05	2.595	3.385	153.12
N012-H01B...Cl04	2.525	3.344	159.44
C021-H021...Cl06	2.978	2.540	120.34

[-x+2, y-1/2, -z+1/2] ; [x, -y+1/2, z-1/2] ; [x, -y+1/2, z+1/2] ; [x-1, -y+1/2, z-1/2]

[-x+2, y-1/2, -z+1/2] ; [-x+1, y-1/2, -z+1/2]

Figure S1: ^1H -NMR spectra of organic part: diaminopyridin $\text{C}_5\text{H}_7\text{N}_3$ (bottom) and the hybrid material H-NMR $[\text{C}_5\text{H}_8\text{N}_3]_2\text{SbCl}_5$ (HM) (top)

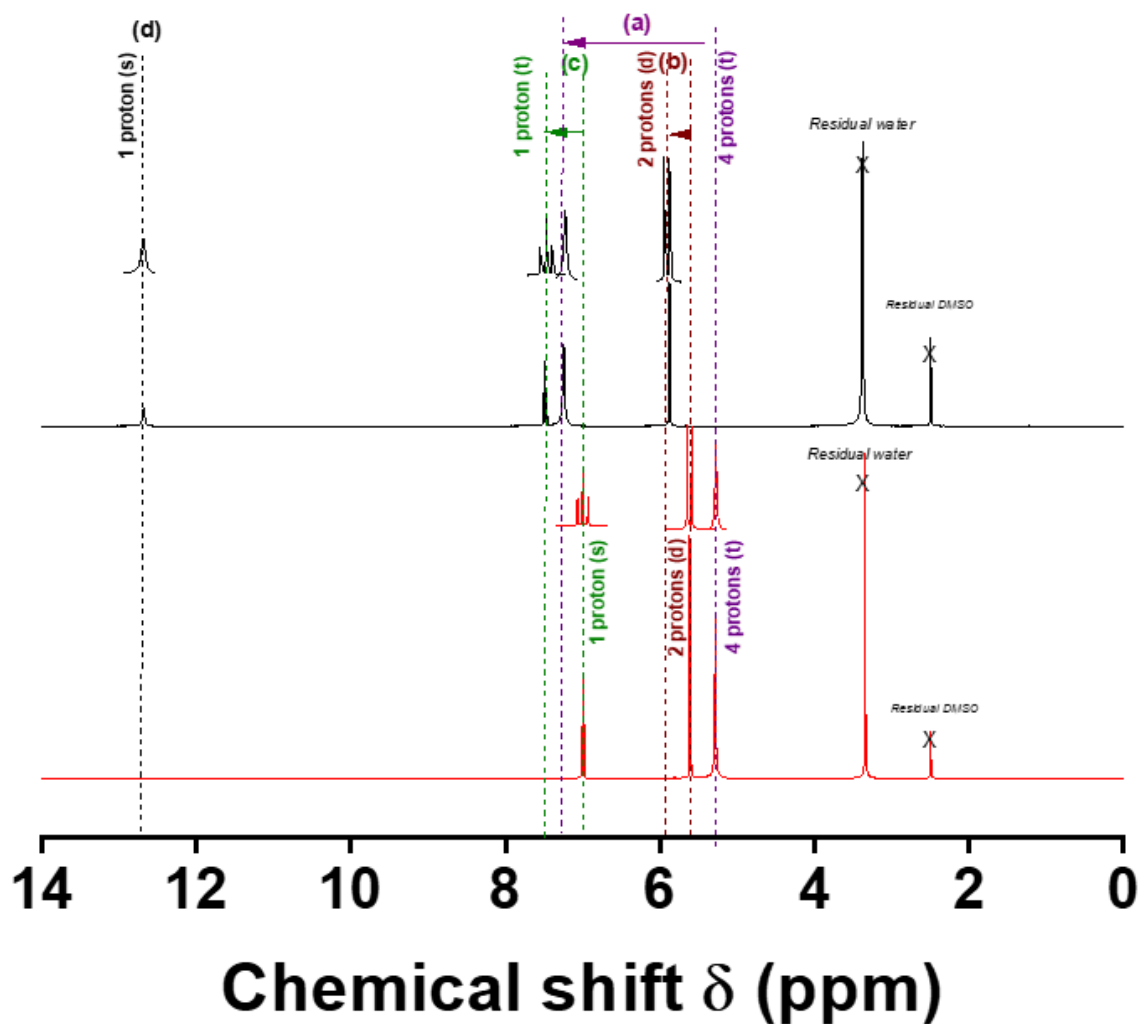


Figure S2: Thermogravimetric TGA (a) and DTA (b) scans for $[\text{C}_5\text{H}_8\text{N}_3]_2\text{SbCl}_5$ (the scans were performed in flowing nitrogen).

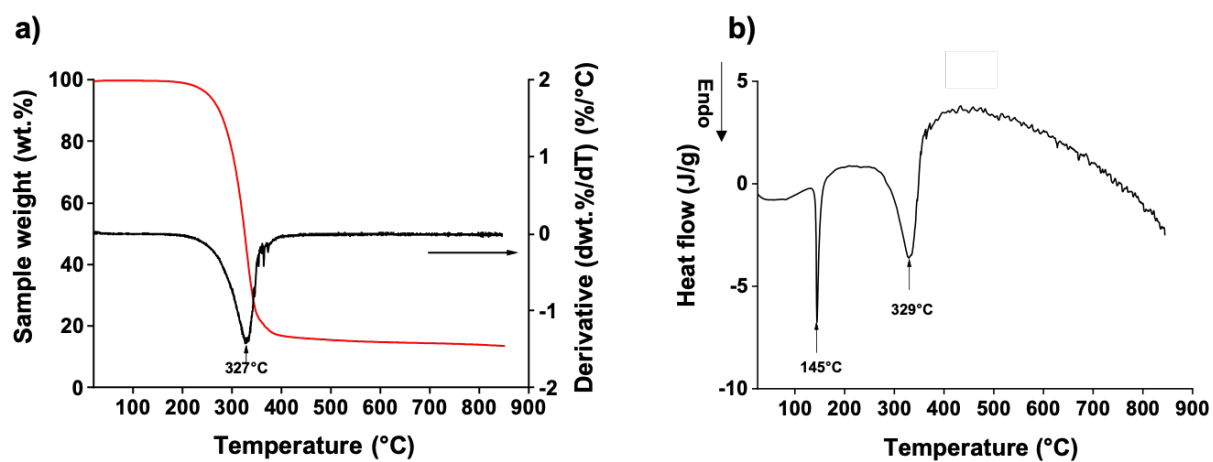


Figure S3: Projection of the atomic arrangement in plane (b, c) (a) and in plane (a, b) (b)

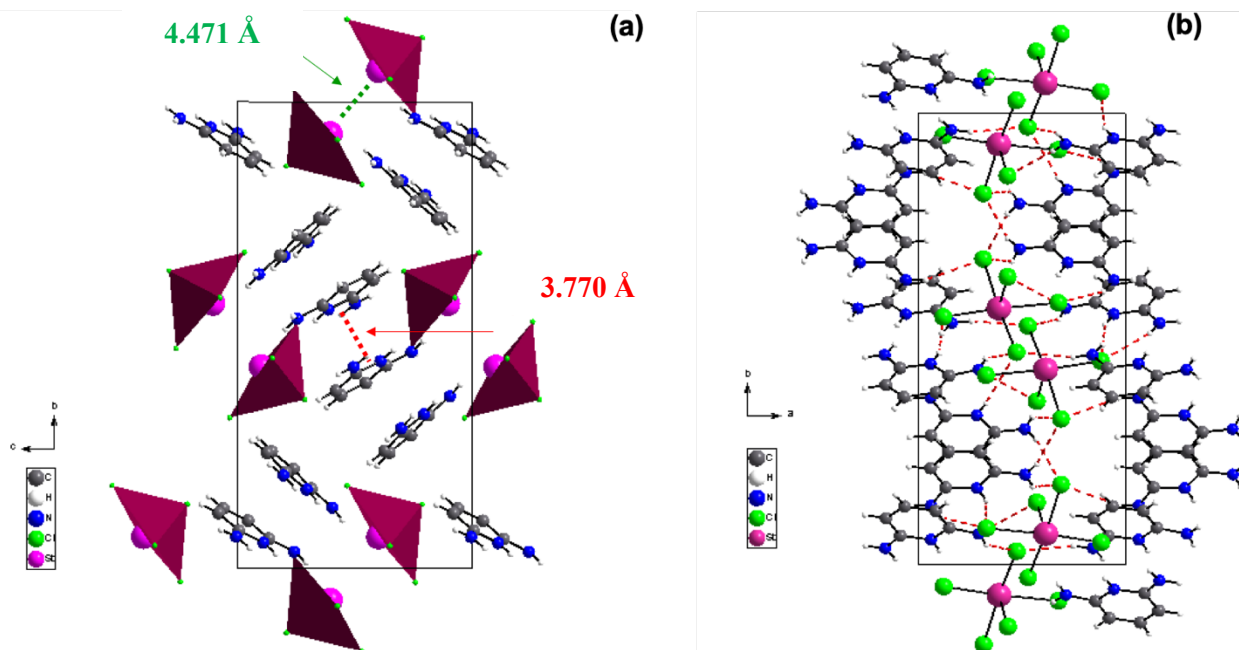


Table S5: Tentative assignments of IR and Raman wavenumbers

FT-IR	FT-Raman	Assignment			
3388w, 3308 s, 3256 w		$\nu(NH_2)$	1167 w	1120 w	$\beta(CH)$
3193 s		$\nu(NH_2) + \nu(C-H)$	1107 w		$\beta(CH)$
3086 w, 2992 w		$\nu(C-H)$	1057 w	1061 w 1021	$\rho(NH_2) + \beta(CH)$
2351 w	-	$\nu(NH_2)$	981 w	999 s	$\rho(NH_2) + \beta(CH)$
2099,2108 w, 1960 w		$\nu(N-H \dots Cl)$	833 w	870 w	$\beta(CCN)$
1737 w	1606w	$\delta(NH_2)$	767 s 730 w	759 s	$\beta_{aromatic} -C=C-C-$
1636 s	1526 w	$\nu(CCN)$	679 s		$\delta(CCN)$
1488 s 1416 w	1444 w	$\nu(C=C) + \nu(CN)$	616, 609, 602 w	569s	$\delta(CCC)$
1366 s	1345 w	$\nu(C=C) + \nu(CN)$		538 w	$\delta(CCC) + \delta(CCN)$
1315 w		$\nu(CC) + \nu(CN)$		346 s	$\delta(CCC) + t(NH_2)$
1303 w		$\nu(CC) + \nu(CN)$		319 s	$\delta(CCC) + t(NH_2)$ + $\beta(CNC)$
	1224 w	$\nu(CC) + \nu(CN)$	-	245 w	$\nu(Sb-Cl) + \beta(CNC)$

Abbreviations: s: strong, w: weak.

 ν : stretching; β : bending; δ : scissoring; ω : wagging; ρ : rocking; t: twisting

Figure S4: UPS spectra of HM films taken with HeI ($h\nu = 21.22$ eV) photons.

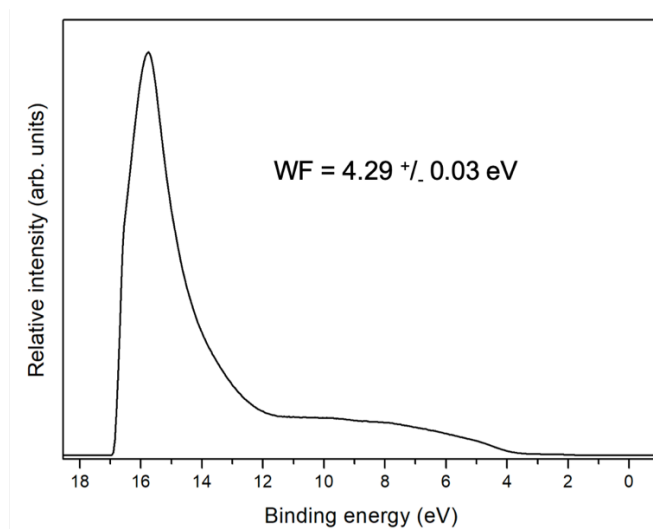


Figure S5: $J(V)$ curves of ITO/PEDOT:PSS/PTB7-Th:PC₇₀BM/HM/Al devices structures for various HM annealing temperatures.

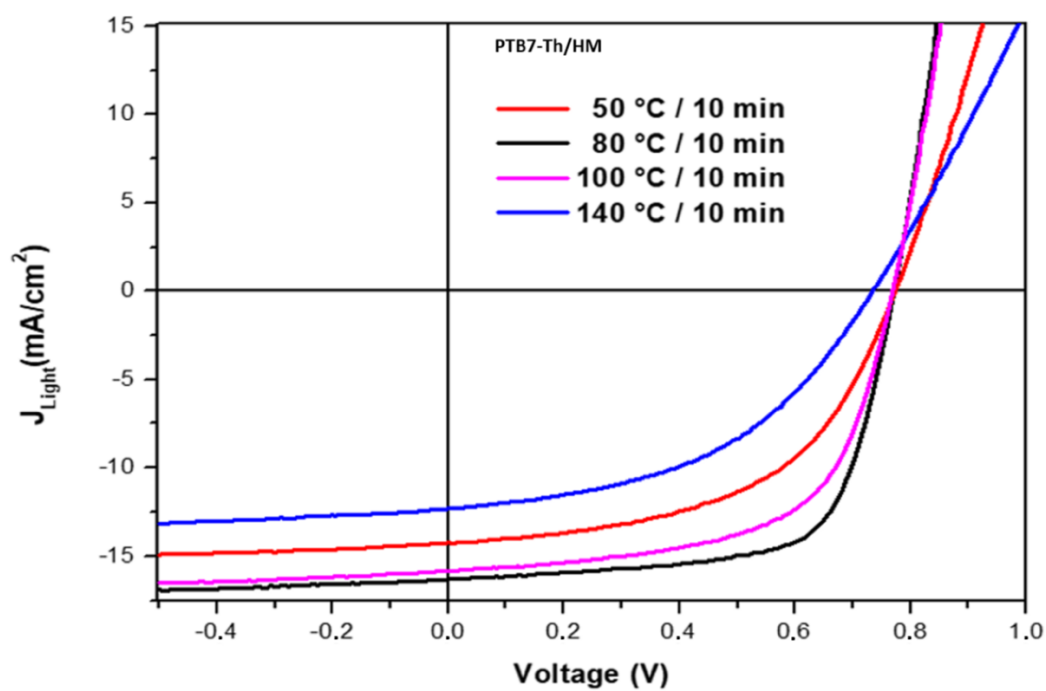


Table S6: Photovoltaic parameters (PCE, V_{OC} , J_{SC} and FF) of ITO/PEDOT:PSS/PTB7-Th:PC₇₀BM/HM/Al devices structures for various HM annealing temperatures.

Annealing temperature (°C)	PCE (%)	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF(%)	Average PCE (± std. dev)
50	5.84	773	14.26	53	5.59 ± 0.14
80	8.42	771	16.31	67	8.27 ± 0.11
100	7.40	768	15.80	61	7.26 ± 0.09
140	4.24	734	12.30	47	4.06 ± 0.12

Figure S6: AFM images of the active layer as deposited (a), after 10mn annealing at 140°C (b) and 10h annealing at 140°C (c).

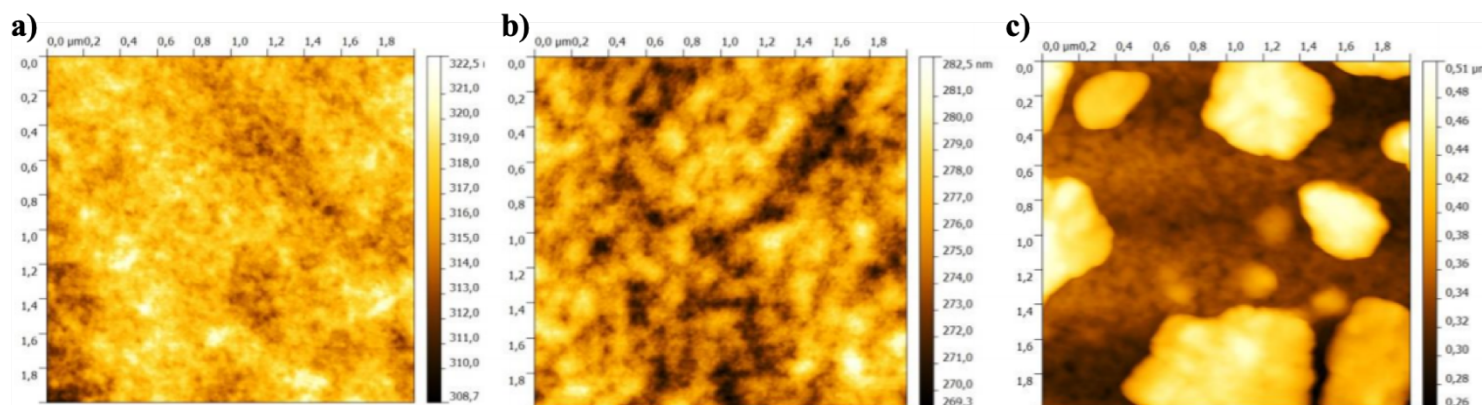


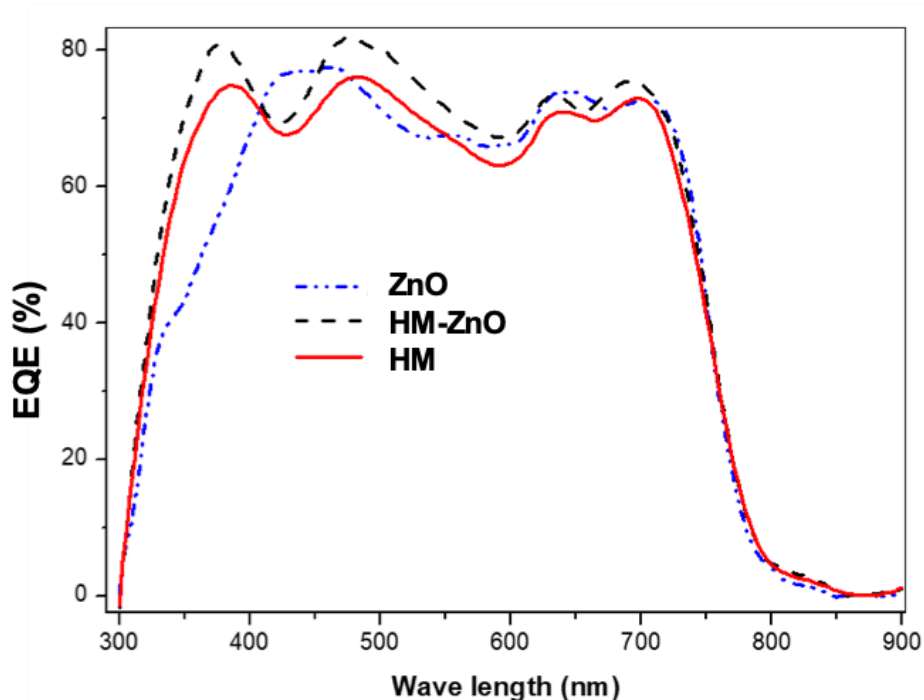
Table S7: Series resistance fitted from the J(V) curves of ITO/PEDOT:PSS/PTB7-Th:PC70BM/EEL/Al devices structures using the different optimized EEL.

Electron extraction layer	Rs ($\Omega \text{ cm}^2$)
Bismuth-based hybrid material ^[4]	8.1
HM	3.7
ZnO	4.3
HM-ZnO	1.6

Table S8: Series resistance fitted from the J(V) curves of ITO/PEDOT:PSS/PTB7-Th:PC70BM/HM/Al devices structures using different HM thicknesses.

Thickness of the HM layer (nm)	Rs ($\Omega \text{ cm}^2$)
20	4.3
40	3.7
60	3.9
80	4.4

Figure S7: External quantum efficiency (EQE) analysis of ITO/PEDOT:PSS/PTB7-Th:PC₇₀BM/EEL/Al devices structures using either ZnO, HM or HM-ZnO as interfacial layer.



⁴ D. Fredj, F. Pourcin, R. Alkarsifi, V. Kilinc, X. Liu, S. Ben Dkhil, N. C. Boudjada, M. Fahlman, C. Videlot-Ackermann, O. Margeat, J. Ackermann, M. Boujelbene, *ACS Appl. Mater. Interfaces* **2018**, 10, 17309.

Table S9: Photovoltaic parameters (PCE, V_{oc} , J_{sc} and FF) of ITO/PEDOT:PSS/PTB7-Th:PC₇₀BM/EEL/Al devices as a function of storage time for the HM (top) and HM-ZnO (bottom) interfacial layers.

<u>EEL</u> : HM	PCE (%)	$V_{oc}(mV)$	$J_{sc}(mA/cm^2)$	FF(%)	Average PCE (\pm std. dev)
As prepared	8.43	770	16.11	68	8.32 ± 0.09
1 day	8.14	768	15.82	67	8.03 ± 0.08
3 days	7.63	766	15.33	65	7.45 ± 0.14
7 days	6.94	755	14.60	63	6.66 ± 0.16

<u>EEL</u> : HM-ZnO	PCE (%)	$V_{oc}(mV)$	$J_{sc}(mA/cm^2)$	FF(%)	Average PCE (\pm std. dev)
As prepared	9.63	783	16.98	72.5	9.5 ± 0.10
1 day	8.93	774	16.49	70	8.7 ± 0.17
3 days	8.32	772	15.86	68	8.12 ± 0.13
7 days	6.79	758	14.94	60	6.61 ± 0.11

Table S10: Photovoltaic parameters (PCE, V_{OC} , J_{SC} and FF) of ITO/PEDOT:PSS/PTB7-Th:PC₇₀BM/EEL/Al devices as a function of illumination time for the ZnO (top), HM (center) and HM-ZnO (bottom) interfacial layers.

<u>EEL</u> : ZnO	PCE (%)	V_{OC}(mV)	J_{SC}(mA/cm²)	FF(%)	Average PCE (± std. dev)
As prepared	9.16	799	16.39	70	8.94 ± 0.14
10 hours	8.18	798	14.86	69	8.01 ± 0.13
1 day	7.24	797	13.77	66	7.04 ± 0.11
3 days	5.81	787	12.32	60	5.55 ± 0.19
6 days	4.15	772	10.98	49	3.84 ± 0.22
15 days	2.81	679	9.64	43	2.61 ± 0.14

<u>EEL</u> : HM	PCE (%)	V_{OC}(mV)	J_{SC}(mA/cm²)	FF(%)	Average PCE (± std. dev)
As prepared	8.32	770	16.39	66	8.10 ± 0.16
10 hours	8.19	769	16.15	66	7.97 ± 0.13
1 day	7.87	769	15.75	65	7.71 ± 0.10
3 days	7.44	768	15.39	63	7.26 ± 0.13
6 days	7.19	766	15.15	62	6.98 ± 0.14
15 days	6.74	756	14.87	60	6.48 ± 0.16

<u>EEL</u> : HM-ZnO	PCE (%)	V_{OC}(mV)	J_{SC}(mA/cm²)	FF (%)	Average PCE (± std. dev)
As prepared	9.58	784	16.86	72.5	9.45 ± 0.11
10 hours	8.93	774	16.50	70	8.68 ± 0.15
1 day	8.57	772	16.10	69	8.37 ± 0.10
3 days	8.52	772	16	69	8.34 ± 0.11
6 days	7.90	764	15.68	66	7.69 ± 0.15
37 15 days	6.76	762	15.30	58	6.49 ± 0.17