

## SUPPORTING INFORMATION

### Impact of P3HT Regioregularity and Molecular Weight on the Efficiency and Stability of Perovskite Solar Cells

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## Experimental section

**Materials:** TiO<sub>2</sub> 30N-RD Titania paste was purchased from dyesol, Lead(II) iodide (PbI<sub>2</sub>) and lead(II) bromide (PbBr<sub>2</sub>) were purchased from TCI chemicals company; formamidine iodide (FAI) and methylammonium bromide (MABr) were purchased from Greatcell Solar company; N,N- dimethylformamide (DMF), dimethyl sulfoxide (DMSO) chlorobenzene (CB, 99.9%), 4-tert- Butylpyridine (TBP), bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI), cobalt (III) tris(bis(trifluoromethylsulfonyl)imide) (FK-209), acetylacetonate (ACAC) and disopropoxytitaniumbis(acetylacetonate) (TAA) were purchased from Sigma-Aldrich. Cesium iodide (CsI) was purchased from ABCR GmbH Chemicals were used as received. All glassware for synthesis was dried in an oven at 175 °C and assembled and closed rapidly and purged with argon.

## Synthesis

### P3HT-223-kDa/79%

A three necked round bottom flask and a dropping funnel were assembled rapidly and purged with argon. The 3-hexylthiophene (2g, 11.88 mmol, 1 eq.) and the anhydrous chloroform (120 ml) were added with a syringe and the suspension was stirred at room temperature. The FeCl<sub>3</sub> (5.78 g, 35.7 mmol, 3 eq.) was added into a vial kept under argon and chloroform (15 ml) was added. The suspension was added into the dropping funnel, rinsing the vial with a few small portions of chloroform (total 70 ml). The suspension was slowly added dropwise, over 6h. In the case of FeCl<sub>3</sub> re deposition into the dropping funnel, it was resuspended by bubbling argon briefly into it. When the addition was finished the reaction was left to stir at room temperature for 18 h. At the end, the suspension was poured into methanol (500 ml) and the polymer precipitated. The polymer was filtered on a Hirsch funnel under vacuum, giving a black powder, which was washed with methanol. The powder was stirred overnight with 180 ml of methanol containing 10 ml of hydrazine hydrate, filtered on Hirsch and washed with methanol. The polymer was purified by Soxhlet extraction with methanol, hexane, and chloroform. The final chloroform solution was concentrated and precipitated with methanol, giving a dark powder: 854 mg (42.7%). The regioregularity, measured by <sup>1</sup>H-NMR is 79.4%.

UV-Vis (CHCl<sub>3</sub>): λ<sub>max</sub>: 440 nm; logε: 3.93; ε: 8551 M<sup>-1</sup> cm<sup>-1</sup>.

<sup>1</sup>H-NMR 600 MHz, (CDCl<sub>3</sub>), (50°C) δppm: 7.05 (s), 7.03 (s), 7.00 (s), 6.98 (s), 2.81 (t), 2.56 (t), 1.71 (m, 2H), 1.44 (m, 2H), 1.37 (m, 4H), 0.92 (t, 3H).

SEC (35°C, THF): M<sub>n</sub> = 54957 Da; M<sub>w</sub> = 223430 Da; PDI = 4.06.

### P3HT-338-kDa/76%

The same procedure reported for P3HT-004 was used, but slightly modified due to the use of cobalt salts.[1,2]

The glassware was kept in the oven at 175°C overnight and was assembled rapidly and purged with argon. A three necked 500 ml round bottom flask and a 100 ml dropping funnel, were properly assembled, closed with stoppers and purged five times with argon. The CoCl<sub>2</sub> (154 mg, 1.19 mmol, 0.1 eq) was introduced from a lateral neck and the apparatus was flushed with argon 3 times. Chloroform (30 ml) was added in the dropping funnel and in the flask (20 ml).

The FeCl<sub>3</sub> (5.78 g, 35.7 mmol, 3 eq.) was rapidly weighed and transferred into the dropping funnel. Further 20 ml of CHCl<sub>3</sub> were introduced into the dropping funnel. The apparatus was flushed with argon 3 times, after which 100 ml of CHCl<sub>3</sub> were introduced into the flask, followed by the 3-hexylthiophene (2g, 2.137 ml, 23.8 mmol, 1 eq.). The solution was stirred fast and further 20 ml of CHCl<sub>3</sub> were introduced into the dropping funnel. The FeCl<sub>3</sub> suspension was added dropwise over 6 h and, from time to time (15-30 min), argon was bubbled into the suspension to avoid re-deposition of FeCl<sub>3</sub>. At the end of the FeCl<sub>3</sub> addition, the reaction was left to run for 18 h. At the end the suspension was poured into methanol and stirred for a while, after which the solid material was filtered on Hirsch. The solid was stirred overnight into 180 ml of methanol and 10 ml of hydrazine hydrate and finally filtered again. This solid was extracted with Soxhlet with methanol, hexane and chloroform. The extraction with chloroform was continued for 3 days, until the extracting solvent in the Soxhlet was clear. The solvent was removed under vacuum and the concentrated solution was precipitated into methanol giving a black powder: 819 mg (41.4%). The regioregularity, measured by <sup>1</sup>H-NMR, is 76.0%.

UV-Vis (CHCl<sub>3</sub>): λ<sub>max</sub>: 446 nm, logε: 3.82; ε: 6607 M<sup>-1</sup> cm<sup>-1</sup>.

<sup>1</sup>H-NMR 600 MHz, (CDCl<sub>3</sub>), (50°C) δ ppm: 7.05 (s), 7.03 (s), 7.00 (s), 6.98 (s), 2.81 (t), 2.56 (t), 1.72 (m, 2H), 1.45, (m, 2H), 1.36 (m, 4H), 0.92 (t, 3H).

SEC (35°C, THF): M<sub>n</sub> = 60867 Da; M<sub>w</sub> = 338963 Da; PDI = 5.6.

### **P3HT-19-kDa/95%**

A three-necked Schlenk round bottom flask was connected with a bubble condenser, closed on the top with a balloon for gases. The apparatus was purged with argon 3 times. The K<sub>2</sub>CO<sub>3</sub> (0.4197 g, 3.04 mmol, 1.2 eq) was introduced in the flask through a lateral arm and the apparatus was purged with argon for 10 minutes. Two vials were taken from the oven, closed with rubber stopper and purged with argon. The neodecanoic acid (0.1 g, 0.58 mmol, 0.231 eq.) and anhydrous dimethylacetamide (DMA) (5 ml) were introduced in a vial. In the second vial the Pd(OAc)<sub>2</sub> (3.5 mg, 0.0052 mmol, 0.02eq, 2%) and 15 ml of DMA were introduced, purging with argon for 10 minutes. The 2-bromohexylthiophene (0.62 g, 0.5 ml, 2.51 mmol, 1eq.) and DMA were introduced in the reaction flask and the flask was purged with argon for 10 minutes. The solutions were transferred from the vials into the reaction flask and further DMA (20 ml) for a total of 50 ml of solvent.

The solution was warmed to 70°C. The colour of the solution changed rapidly to orange and, after, to deep red after 3 h. The reaction was run for 48 h, after which the solution was cooled to room temperature and poured into methanol to precipitate the polymer under stirring. After 20 minutes the polymer was filtered on Hirsch under vacuum. The crude solid was extracted with Soxhlet with methanol, hexane and chloroform. The solvent was concentrated and the polymer was further precipitated with methanol, giving a dark red powder, 0.386 g (91%). The regioregularity, measured by <sup>1</sup>H-NMR, is 95%.

UV-Vis (CHCl<sub>3</sub>): λ<sub>max</sub>: 444 nm; logε: 3.921; ε: 8327 M<sup>-1</sup> cm<sup>-1</sup>.

<sup>1</sup>H-NMR 600 MHz, (CDCl<sub>3</sub>), (50°C) δ ppm: 6.98 (s, 1H), 2.82 (t), 2.58 (t), 1.72 (m, 2H), 1.45 (m, 2H), 1.36 (m, 4H), 0.92 (t, 3H).

SEC (35°C, THF): M<sub>n</sub> = 8.190 Da; M<sub>w</sub> = 18.880 Da; PDI = 2.30.

### P3HT-194-kDa/100%

A 20 ml vial and a 10 ml vial were kept in the oven at 175°C overnight and was closed rapidly with stoppers and purged with argon for 15 minutes. THF was introduced in the 20 ml vial, followed by the 2-bromo-3-hexyl-5-iodothiophene (0.256 g, 0.15 ml, 0.686 mmol, 1eq) under stirring. A 2M iPrMgCl solution in THF (0.34 ml, 0.68 mmol, 1 eq) was introduced, followed by a 0.5 M LiCl solution in THF (1.4 ml, 0.7 mmol, 1.1 eq.). the reaction was left to run for 1 h at room temperature. A 10 mmol/L solution of Ni(iPr)(acac)<sub>2</sub> (3.34 micromol, 0.34 ml, 0.6%) in THF. The reaction was run for 30 min. The solution turned immediately to orange and to red and in 6 minutes it became turbid, due to precipitation of P3HT. at 30 minutes of reaction, 5 M HCl was added (2.28 ml) and the suspension was left to stir for 10 minutes, when the suspension was poured into 70 ml of hexane. After a few minutes of stirring, the polymer was filtered on Hirsch and washed with water and acetone, giving about 500 mg of crude product. The crude was dissolved in chloroform and precipitated in methanol, giving 91.2 mg (81.8%) of a dark powder. The regioregularity, measured by <sup>1</sup>H-NMR, is 100%.

UV-Vis (CHCl<sub>3</sub>): λ<sub>max</sub>: 455 nm, logε: 3.85; ε: 7079 M<sup>-1</sup> cm<sup>-1</sup>.

<sup>1</sup>H-NMR 600 MHz, (CDCl<sub>3</sub>), (50°C) δ ppm: 6.98 (s, 1H), 2.82 (t, 2H), 1.72 (m, 2H), 1.45 (m, 2H), 1.36 (m, 4H), 0.92 (t, 3H).

SEC (145°C, o-dichlorobenzene): M<sub>n</sub> = 68367 Da; M<sub>w</sub> = 193894 Da; PDI = 2.8.

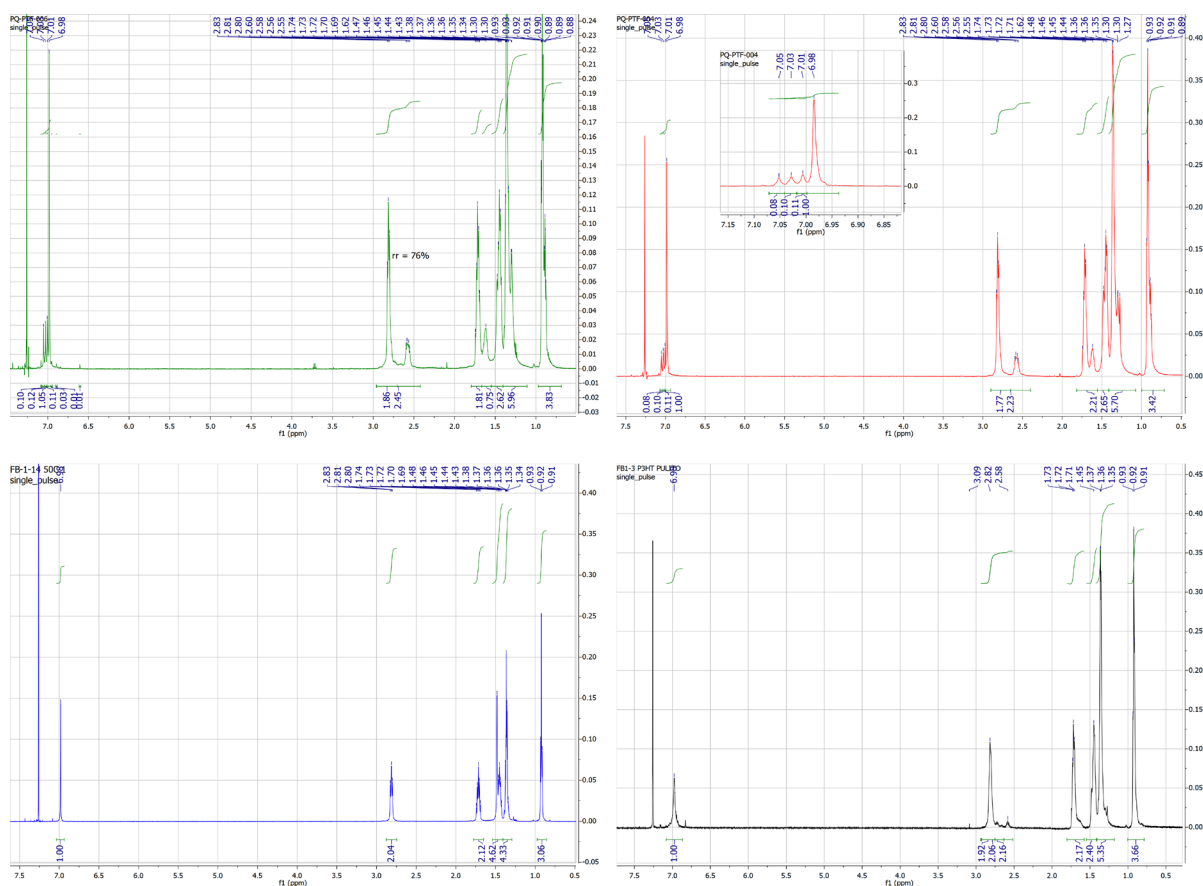


Figure S1. NMR spectra of <sup>1</sup>H-NMR of compounds: P3HT-338-kDa/76%, (green, top left), P3HT\_223-kDa/79% (red, top left), P3HT\_194 KDa (blue, bottom left), P3HT\_19KDa (black, bottom right).

## **Polymer Characterization**

### **Spectroscopic Measurements**

<sup>1</sup>H-NMR spectra were recorded in CDCl<sub>3</sub>, either on a Bruker AVANCE 200 working at 200 MHz or a JEOL ECZ-R 600, working at 600 MHz.

UV-Vis spectra were recorded in dichlorobenzene (o-DCB) with a Shimadzu UV-1700 spectrophotometer. Fluorescence spectra have been acquired o-dichlorobenzene (o-DCB) with a Perkin Elmer LS55 spectrofluorimeter.

### **SEC – Molecular weight measurement**

SEC measurements on low regioregular and highly soluble polymers, were performed with Waters SEC chromatographic system refractometer with a guard column and three columns in series (Styregel HR2,HR4 and HR6). The analyses were performed at 35°C and THF was used as the mobile phase at a flow rate of 1 ml min<sup>-1</sup>. SEC measurements on highly regioregular and low soluble polymers, were performed with a Waters SEC chromatographic system equipped with DRI, UV-Vis diode array, and DV detectors. Three columns in series (Shodex HT 806M, 805, 804, from Showa Denko - Japan) were used. The measurements were performed with DCB (o-dichlorobenzene) as solvent, at 145°C and 0.8 ml/min flow rate. In both cases, a calibration curve was prepared with a series of polystyrenes of different molecular weight (575 -3848000 g mol<sup>-1</sup> for normal SEC and 162 -3280000 g mol<sup>-1</sup> for high temperature SEC).

### **Cyclic Voltammetry Measurement:**

Cyclic voltammetry analysis has been performed with SP-300 BIOLOGIC using DCM and/or DCB as solvent and tetrabutylammonium hexafluorophosphate (TBAP) as support electrolyte. Scan rate was set to 50 mV/s and the scan was performed from -1.2 to 1.5 V using Ag/AgCl as reference electrode and Fc/Fc<sup>+</sup> as internal reference.

### **Thermal Analysis:**

Thermogravimetric analysis (TGA) has been performed with a TGA TAQ 600 (TA Instruments) in nitrogen atmosphere with a heating gradient of 30°C/min from 30°C to 1000°C. Calorimetric analysis (DSC) has been performed with a DSC TAQ 200 (TA Instruments) in nitrogen atmosphere with a heating gradient of 30°C/min from -70°C to 250°C.

### **SEM measurement:**

Microstructural analysis was carried out by using a field emission scanning electron microscope (FE-SEM, SUPRA™ 35, Carl Zeiss SMT, Oberkochen, Germany). For cross section view the samples were broken in liquid nitrogen to preserve the layered structure.

### **XRD and GIWAXS analysis:**

A Panalytical Empyrean diffractometer was used to perform Bragg-Brentano X-ray diffraction (XRD) measurements, with divergent slits as incident optical pathway. A Cu-anode lamp was used to produce the X-rays probe and detection was accomplished by means of a PIXcel 3D

detector set for 1D acquisition mode. A flat sample holder was used for thin film structural investigation and the  $7^\circ < 2\theta < 70^\circ$  angular range was explored. Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) measurements were performed on the same apparatus however on the incident beam path a PreFIX module (Beta- filter Nickel, Soller slits 0.04rad, fixed divergence slits  $2^\circ$ , anti-scatter slit  $1^\circ$ ) was used, while a parallel plate collimator  $0.27^\circ$  was allocated on the diffracted beam path. The PIXcel 3D detector was set on 0D mode (active length 1.815 mm, number of active channels 33) to accomplish the acquisition.

### Device Fabrication:

A raster scanning laser (Nd:YVO4 pulsed at 30 kHz average output power  $P = 10$  W) was used to etch the FTO/ glass substrates (Pilkington,  $15\Omega\text{cm}^{-1}$ ,  $25\text{ mm} \times 25\text{ mm}$ ). The patterned substrates were cleaned in an ultrasonic bath, using detergent with de-ionized water, and 2-propanol, 5 min for each step. A compact  $\text{TiO}_2$  (c- $\text{TiO}_2$ ) layer was deposited onto the patterned FTO by spray pyrolysis deposition using a previously reported procedure [3] Briefly, the temperature of the substrate was fixed at  $450^\circ\text{C}$ ; the distance between the substrate and the autograph (tilted about  $45^\circ$  with respect to the substrate) was fixed to 20 cm. Around 15 successive spray cycles were made to reach a final thickness of 50 nm. Patterning of the c- $\text{TiO}_2$  was achieved using a screen-printed metal mask which was removed after the c- $\text{TiO}_2$  deposition using an acidic solution, de-ionized water, and ethanol. A nano-crystalline mesoporous  $\text{TiO}_2$  layer (18NR-Paste, Dyesol paste, Dyesol), diluted with ethanol, with w/w ratio of 1:6, was spin coated 4000 rpm 20 second onto the c- $\text{TiO}_2$  surface and sintered using annealing program (see **Figure S2(a)**). Then, Li-salt treatment was performed on the mesoporous layer as reported in our previous work [4], this layer was annealed the same as mesoporous layer and once the temperature reached at  $150^\circ\text{C}$  immediately transferred to the glove box to not absorb any water and humidity on the surface before perovskite deposition (if this layer absorb water the white dots will be appear in the interface of perovskite and scaffold Layer). Then, the perovskite layer was deposited on the scaffold layer. The perovskite solution was made as reported in Ref [4]. Briefly the perovskite solution was prepared by mixing the solutions of  $\text{MAPbBr}_3$  (0.18 M) and  $\text{FAPbI}_3$  (1.47 M) precursor complexes in 1 ml of mixed DMF/DMSO (4:1/v:v) solvents. 5 mole% CsI solution (stock solution: 389.71 mg CsI powder in 1 ml DMSO) was added to the mixed solution before deposition of the perovskite layer. The final composition of the mixed cation/anion solution can be defined as  $(\text{FAPbI}_3)_{0.81}(\text{MAPbBr}_3)_{0.14}(\text{CsI})_{0.05}$ . The perovskite solution was stirred for 1 hour at  $70^\circ\text{C}$  and then cold solution was spin-coated in a two-step program, for 10 s at 1000 rpm with a ramp of 200 and 5000 rpm with a ramp of 2000 rpm for 20 s, respectively. During the last 10 second of the second step, the chlorobenzene was poured on the spinning substrate to form the perovskite nuclei. Then, the substrates were annealed at  $100^\circ\text{C}$  for 60 min.

P3HT (20 mg) was dissolved in 1 ml chlorobenzene (CB) and the solutions were doped with Li-TFSI (1.8 M in acetonitrile), TBP and FK209-Co(III)-TFSI (0.14 M in acetonitrile) with ratio of 20:78:2 mol%. as mentioned in our previous work [4], considering that all pristine P3HT polymers were dissolved completely in CB solvent (clear solution) while doped P3HT polymers need stirring and heating at temperature around  $60^\circ\text{C}$  on the hotplate to prevent any gelification and having very clear solution especially for high RR polymers. Final solutions

were deposited via spin-coating method. Finally, 100 nm gold was deposited via evaporation method as a back contact.

### Device characterization

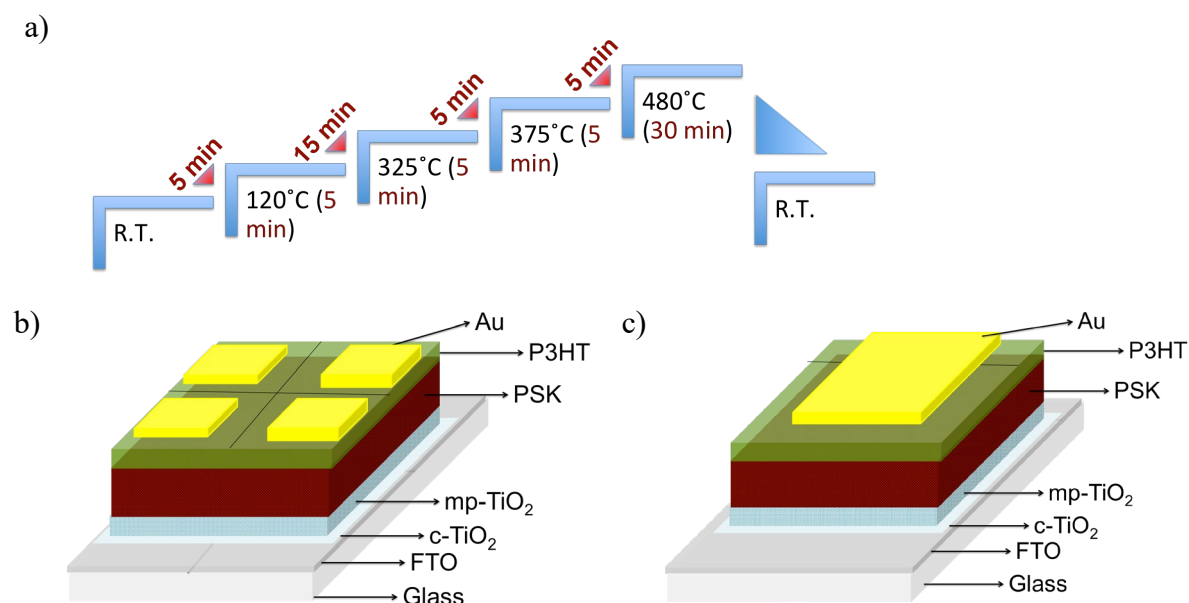
Current density-voltage (J-V) curves of masked devices were recorded using a solar simulator (ABET Sun 2000, class A(Newport)) under one-sun illumination conditions AM 1.5 ( $100 \text{ mWcm}^{-2}$ ), calibrated with a certified reference Si cell (RERA Solutions RR-1002).

The electrochemical impedance spectroscopy (EIS) measurements were performed with an Eco-ChemieAutolab PGSTAT 302N electrochemical workstation controlled with NOVA software in the frequency range of 0.01 to 100 kHz, under  $100 \text{ mWcm}^{-2}$  solar simulator at a bias voltage ranging from 0.7 to 1.0 V.

Incident Photon-to-electron Conversion Efficiency (IPCE) was measured with a commercial apparatus (ArkeoAriadne, Cicci Research s.r.l.) based on a 300 W xenon lamp and was able to acquire spectrum from 300 to 1100 nm with 2 nm of resolution.

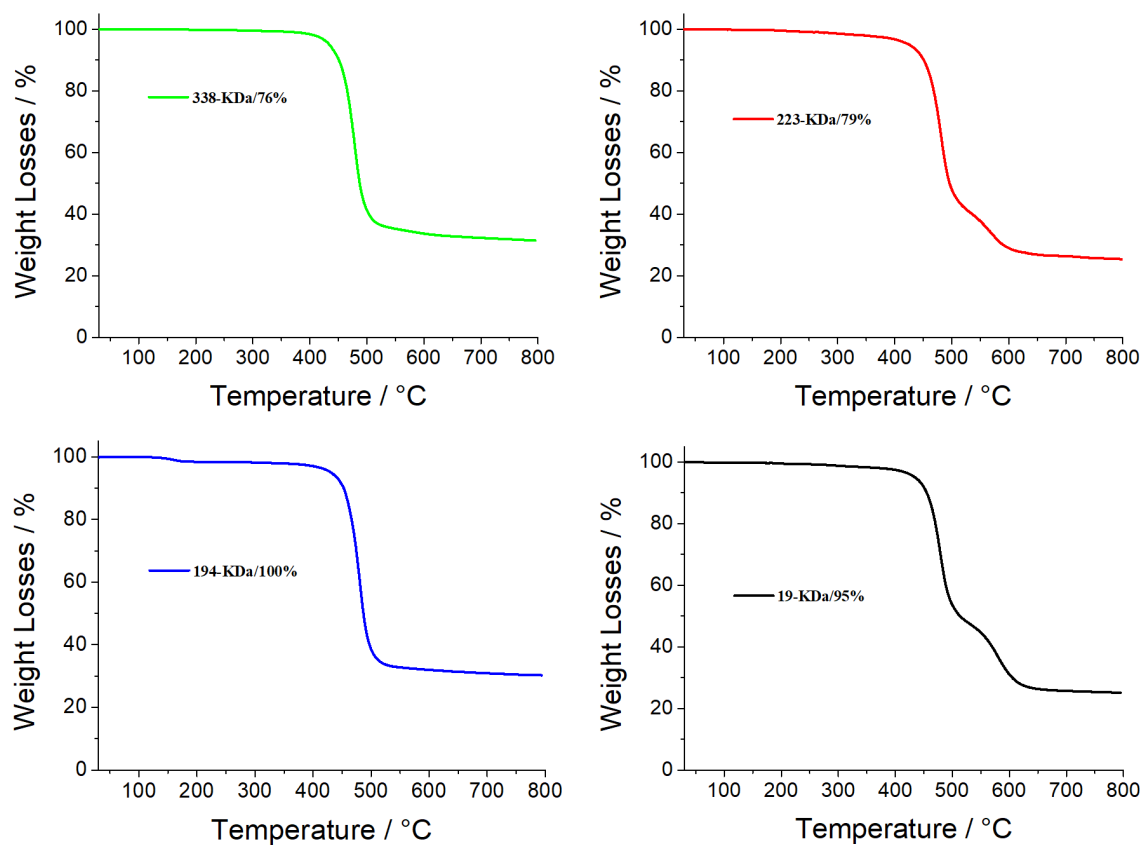
Dark JV measurement from fabricated PSCs structure was done using cyclic voltammetry module of AUTOLAB potentiostat at instrument. Electrochemical impedance spectroscopy was done by AUTOLAB. TPV and TPC were measured with a commercial apparatus (Arkeo, Cicci Research s.r.l.) based on a high-speed waveform generator that drives a high speed LED (5000Kelvin)

Photoluminescence (PL) test was performed with a commercial platform (ARKEO Ariadne - Cicci Research s.r.l). Details about this measurement is reported in our previous work [5].

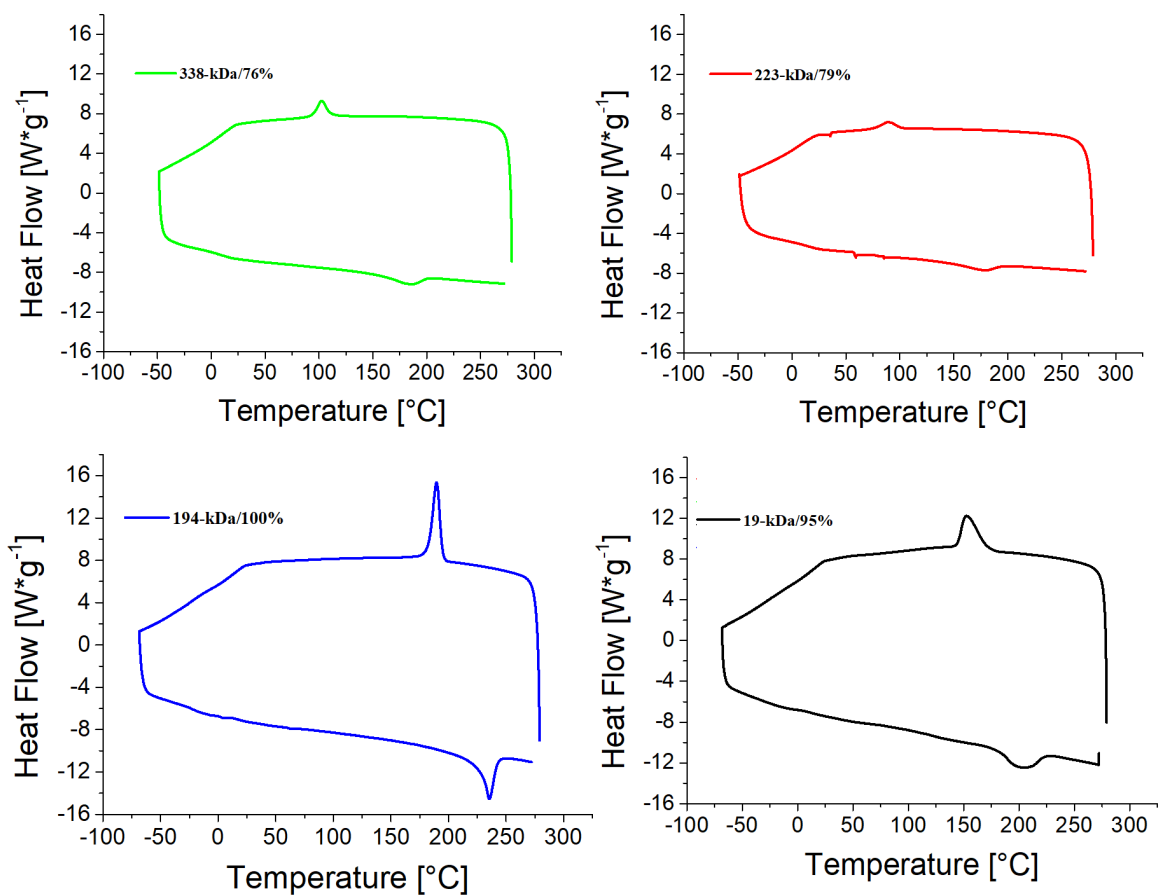


**Figure S2.** Sintering program of the mp-TiO<sub>2</sub> layer (a), Stack configuration of the 4-pixel small area ( $0.1 \text{ cm}^2 \text{ a.a.}$ ) (b) and one pixel large area ( $1.0 \text{ cm}^2 \text{ a.a.}$ ) (c) of the PSCs.

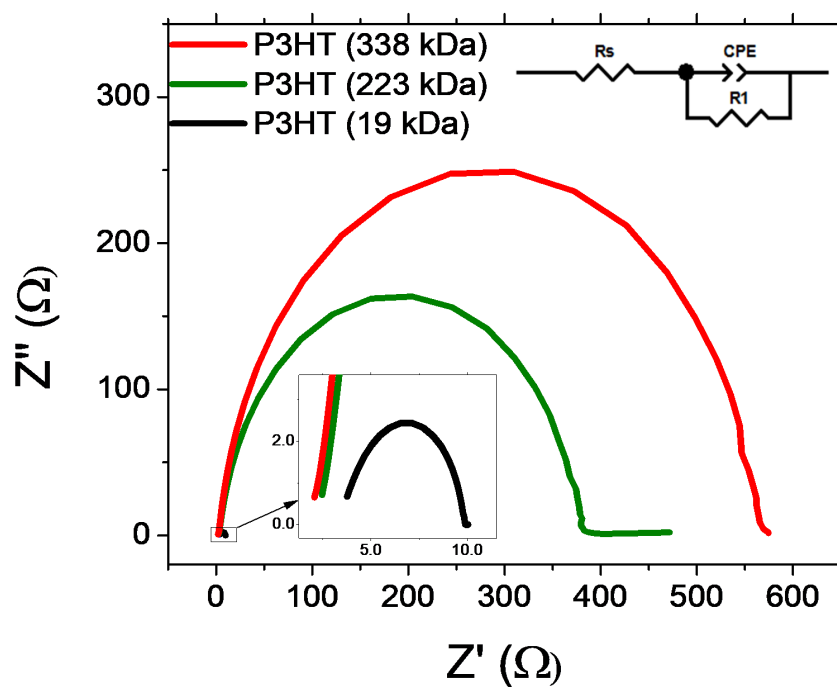




**Figure S3.** ThermoGravimetric Analyses of P3HT-338-kDa/76%, (green, top left), P3HT-223-kDa/79% (red, top left), P3HT-19-kDa/95% (blue, bottom left), P3HT-194-kDa/100% (black, bottom right).



**Figure S4.** Differential Scanning Calorimetry of P3HT-338-kDa/76%, (green, top left), P3HT-223-kDa/79% (red, top left), P3HT-19-kDa/95% (blue, bottom left), P3HT-194-kDa/100% (black, bottom right).



**Figure S5.** Nyquist plots and equivalent circuit.

**Table S1.** Fitting parameters for EIS data of the Schottky diodes containing different MWs of P3HT.

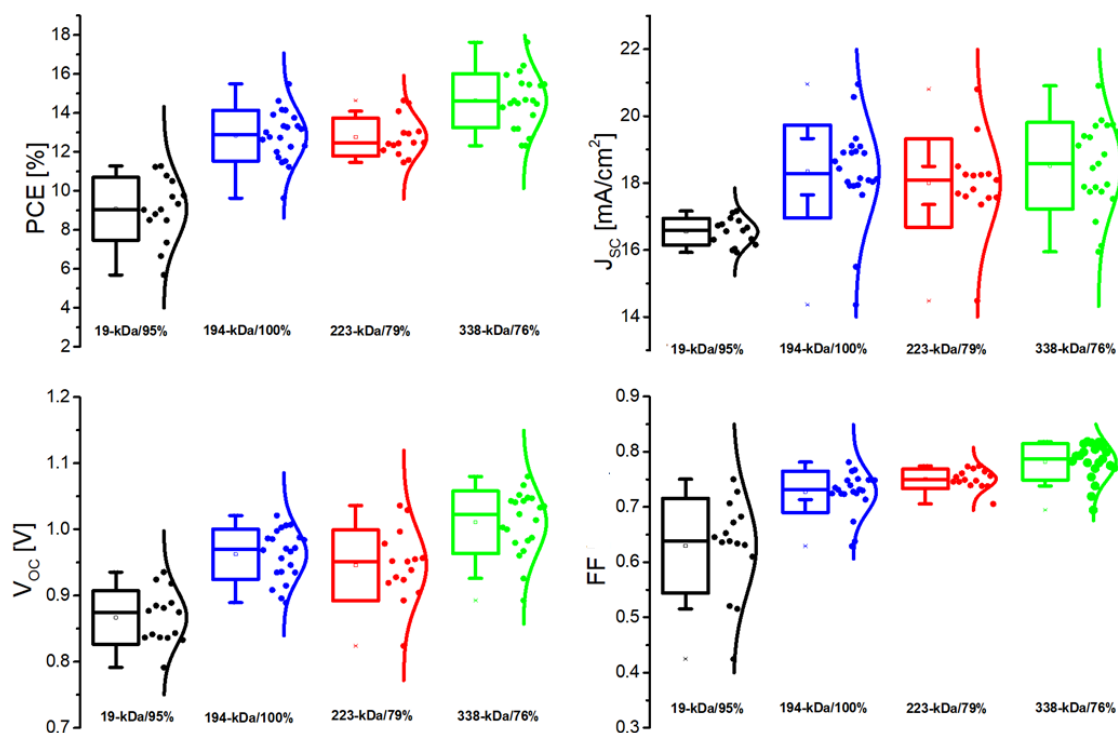
P3HT MW	EIS fitting parameters				
	$R_s$ ( $\Omega/\text{cm}^2$ )	$\text{CPE-T}$ ( $\Omega^{-1}\text{s}^{\text{CPE-P}}$ )	$\text{CPE-P}$	$R_p$ ( $\Omega/\text{cm}^2$ )	$C_\mu$ ( $\mu\text{F}$ )
338 kDa	2.239	1.2329E-5	0.901	570.6	7.147
223 kDa	2.567	1.1897E-5	0.892	381.7	6.192
19 kDa	3.594	2.0479E-5	0.834	6.317	3.459

**Table S2.** Fitting parameters for dark JV of the Schottky diodes containing different MWs of P3HT.

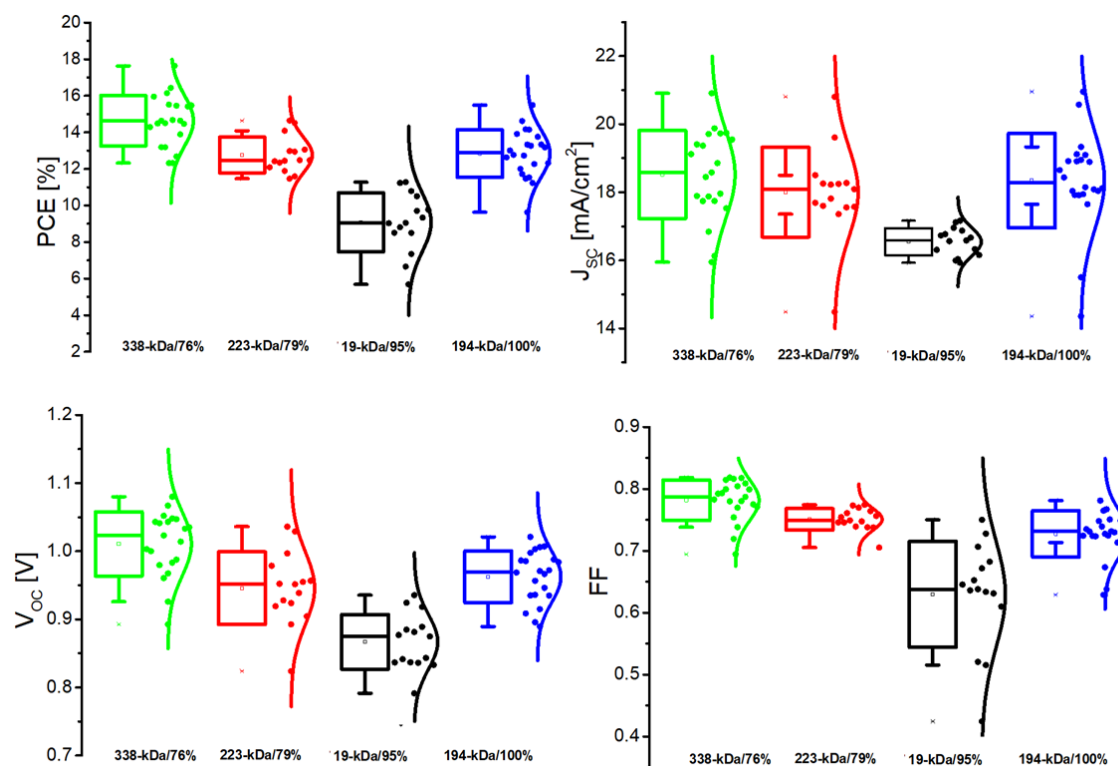
<b>P3HT MW</b>	<b>J<sub>01</sub> (fA/cm<sup>2</sup>)</b>	<b>J<sub>02</sub> (nA/cm<sup>2</sup>)</b>	<b>R<sub>sh</sub> (kΩ/cm<sup>2</sup>)</b>	<b>V<sub>TFL</sub> (V)</b>	<b>μ (cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>)</b>
19-kDa	3.4	95.1	110.7	0.90	<b>1.0 x 10<sup>-3</sup></b>
223-kDa	2.7	253.9	26.2	0.85	<b>3.0 x 10<sup>-3</sup></b>
338-kDa	5.0	127.4	460.0	0.72	<b>2.0 x 10<sup>-3</sup></b>

**Table S3.** Crystallographic orientations of polycrystalline perovskite are reported.

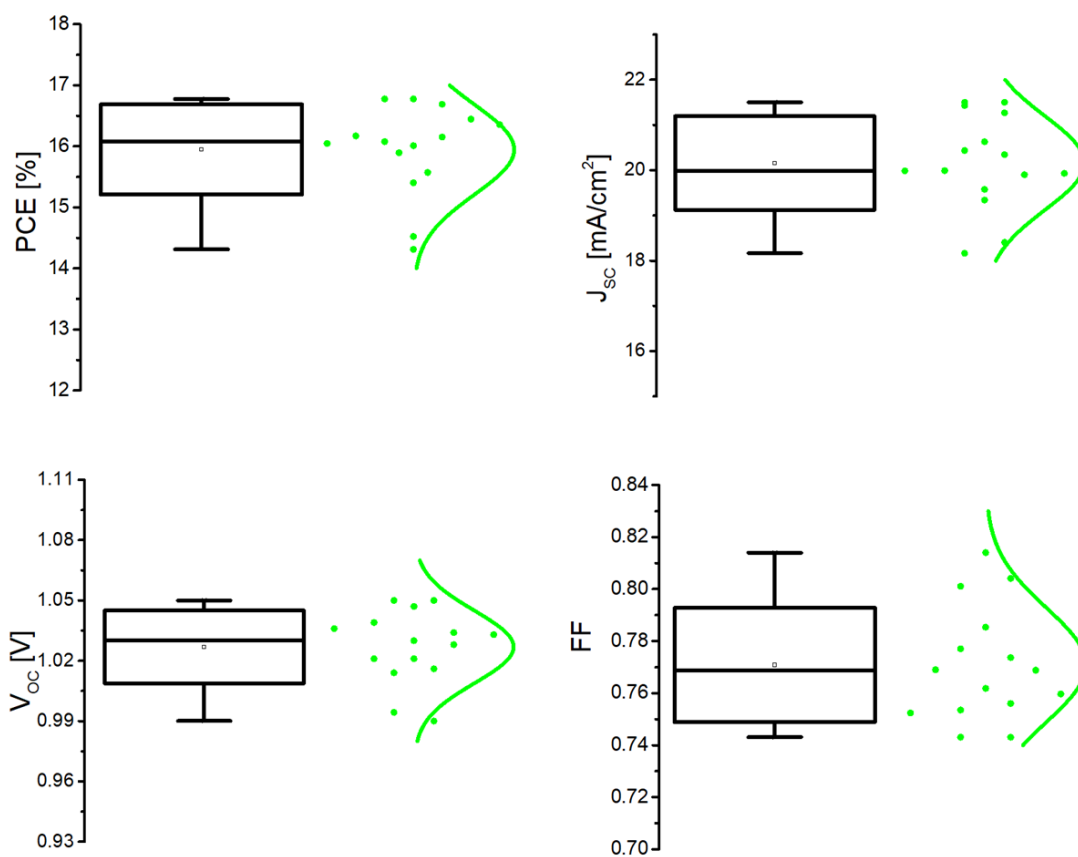
<b>2θ (degrees)</b>	<b>Miller indexes (hkl)</b>
13.95°	(001)
20.00°	(011)
24.32°	(111)
27.90°	(002)
31.95°	(012)
35.15°	(112)
40.90°	(022)
43.70°	(122)
13.95°	(001)
20.00°	(011)



**Figure S6.** Statistical photovoltaic parameters of the small area PSCs containing P3HT as HTM with different Mw: PCE (top left),  $J_{sc}$  (top right),  $V_{oc}$  (bottom left) and FF (bottom right).



**Figure S7.** Statistical photovoltaic parameters of the small area PSCs containing P3HT as HTM with different RR: PCE (top, left),  $J_{sc}$  (top, right),  $V_{oc}$  (bottom, left) and FF (bottom, right).



**Figure S8.** Statistical photovoltaic parameters of the large area PSCs containing 338-kDa/76%, P3HT as HTM: PCE (top, left),  $J_{sc}$  (top, right),  $V_{oc}$  (bottom, left) and FF (bottom, right).

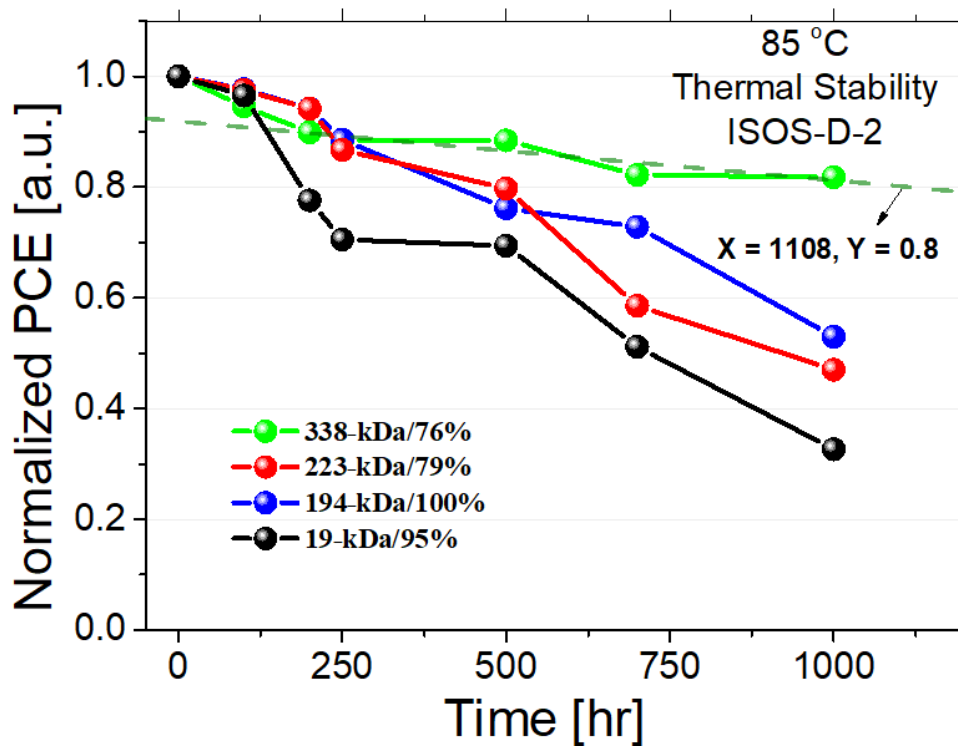


Figure S9. Extracted T80 lifetime.

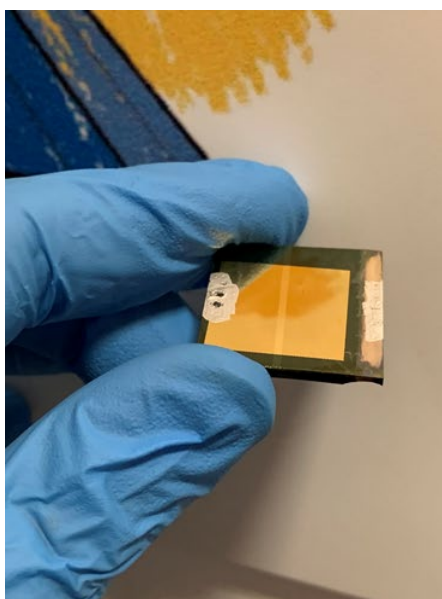


Figure S10. Picture of Large area P3HT-based PSCs

## SI References:

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