Supporting information

**The impact of side chain elongation from the Y6 to Y6-12 acceptor in organic solar cells: a fundamental study from molecules to devices**

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Supporting information 1 (S1):
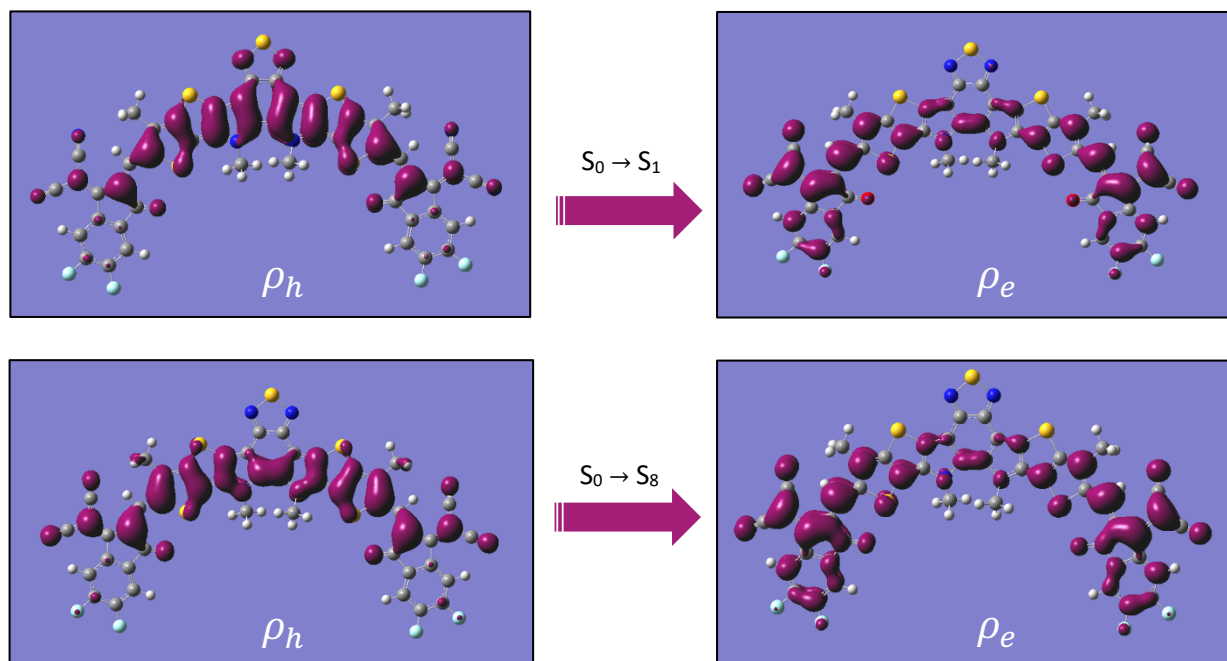
Figure S1: *Natural Transition Orbitals (NTO)s for the $S_0 \rightarrow S_1$ (upper figure) and $S_0 \rightarrow S_8$ (lower figure) transition. Hole density (ρ_h) and electron density (ρ_e) are represented on the left and right side respectively for both optical transitions.*

Supporting information 2 (S2):

UV-vis absorption analysis

All solutions dedicated to spectroscopic analysis were prepared under inert atmosphere (nitrogen glovebox) by dissolving in a vial the powder of each compound (PM7, Y6 and Y6-12), as purchased from the company Brilliant Matters. Each material was dissolved in the two host solvents (i.e., chlorobenzene and chloroform) to obtain a concentration of 6.25×10^{-3} mg/mL. These samples were then placed on a hot plate and heated at 50°C under magnetic stirring for 4h to ensure a homogeneous dissolution. The absorbance measurements were performed with a Perkin Elmer Lambda 650S spectrometer.

The thin films of PM7, Y6 and Y6-12 were prepared from solution of 12.5 mg/mL in chloroform and 20 mg/mL in chlorobenzene under inert atmosphere. After a complete dissolution of the compounds (50°C hot plate and stirring for 4h), each solution was filtered and spin-coated with a rotation speed of 1500 rpm (rotation per minutes) for 60 seconds on a 4 cm^2 glass substrate previously cleaned with soap (RBS), rinsed with distilled water, washed with acetone and isopropanol before being dried under a nitrogen flow and placed in an oxygen plasma for 5 minutes. The thermal annealing of the films was carried out by placing the sample under inert atmosphere on a hot plate heated at 100°C for 10 minutes.

The absorbance measurements on films were also performed with the Perkin Elmer Lambda 650S spectrometer.

The PM7:Y6 and PM7:Y6-12 blend with a (1:1) weight ratio was prepared following the same protocol as for pure thin films and deposited on a cleaned 4 cm^2 glass substrate under inert atmosphere via spin coating at 1500 rpm for 60 seconds. In this case, both PM7:Y6 and PM7:Y6-12 solutions in chloroform had a total concentration of 10 mg/mL while the blend solutions in chlorobenzene had a concentration of 20 mg/mL. This concentration modification was done in order to obtain the desired 100 nm thickness for the blend films. The thermal annealing of the films was carried out by placing the samples under inert atmosphere on a hot plate heated at 100°C for 10 minutes.

Morphological analysis

The morphological analyses of all pure films and blends were performed under inert conditions with a nanoscope 8 multimode atomic force microscope (AFM) in tapping mode configuration using a PPP-NCHR-50 positively doped silicon tip from Nanosensors^{TM} at a scan rate of 0.4 Hz.

AFM was also used to measure the thickness of the films by making a small scratch with a thin razor blade to remove a small portion of the film and reveal the glass substrate. By performing a topography measurement on both sides of this scratch, the height difference between the deposited layer and the glass substrate gives the thickness of the film analyzed.

Supporting information 3 (S3):

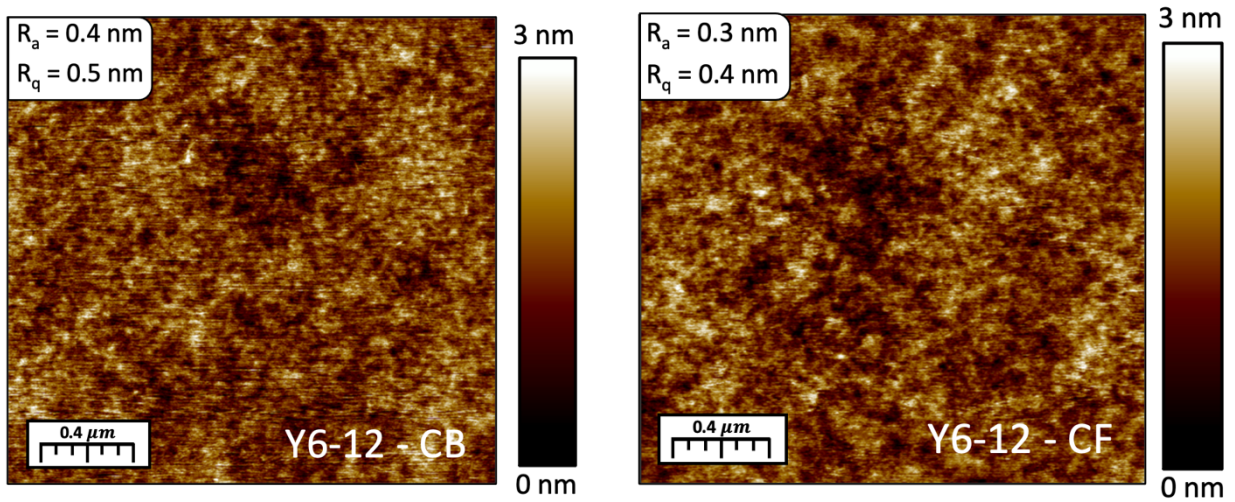*Morphology of annealed pure neat films*
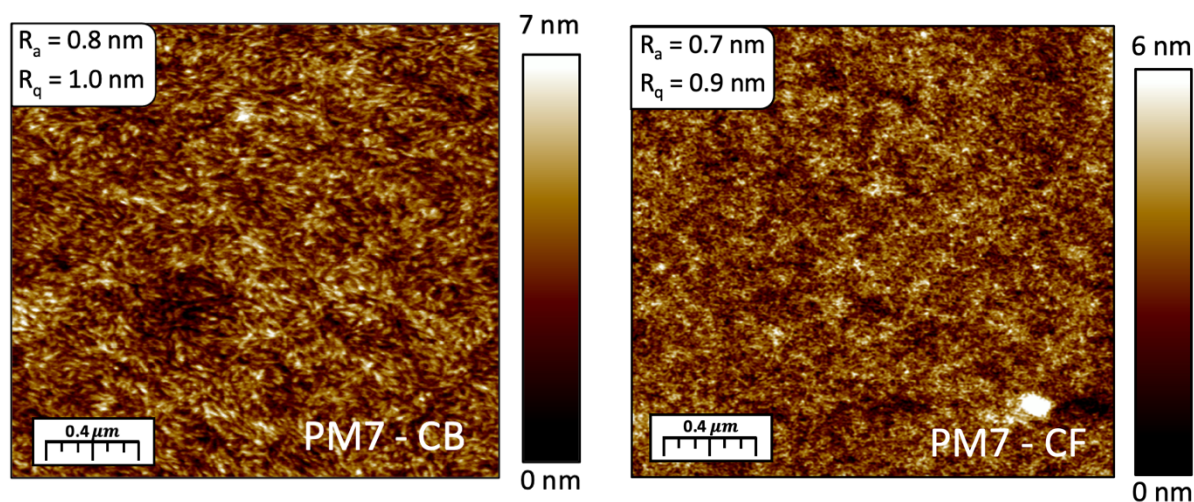
Figure S3-A*: AFM images (2x2 μm^2) for PM7 annealed pure films prepared from chlorobenzene (left figure) and chloroform (right figure). Their thickness are 150 nm and 170 nm, respectively.*
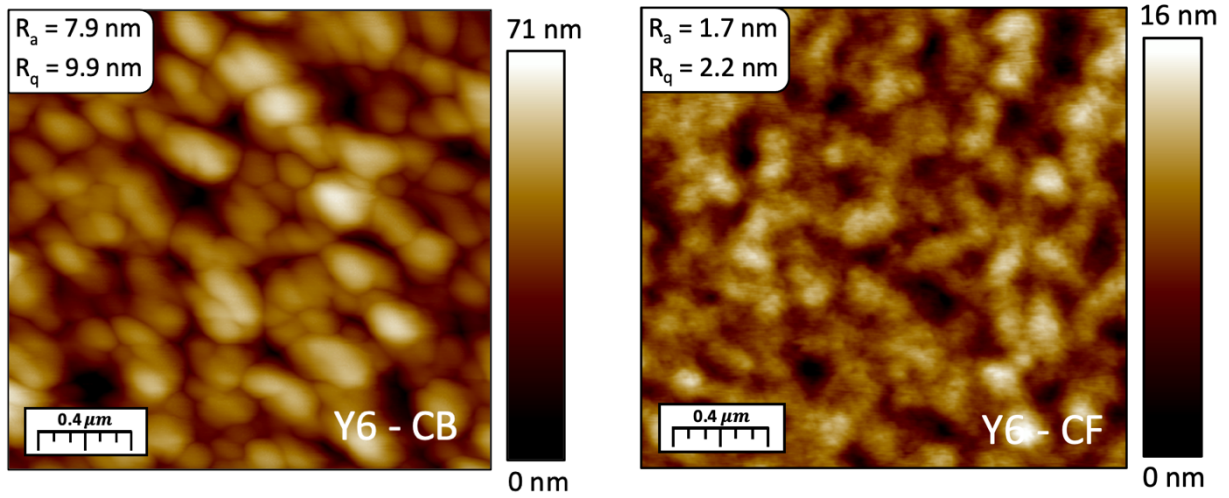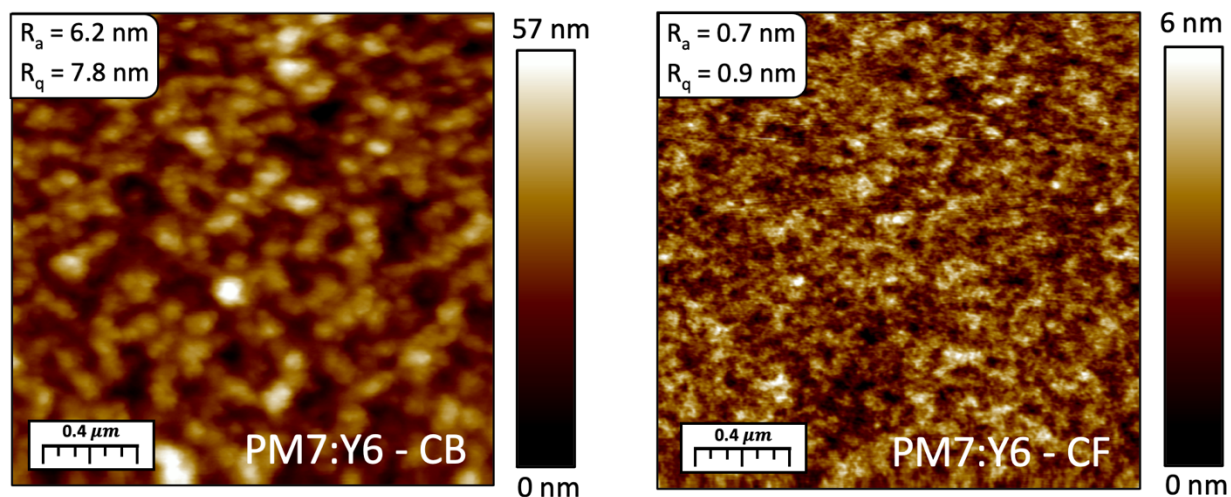
Figure S3-B*: AFM images (2x2 μm²) for Y6 annealed pure films prepared from chlorobenzene (left figure) and chloroform (right figure). Their thickness are 60 nm and 90 nm, respectively.*

Figure S3-C*: AFM images (2x2 μm²) for Y6-12 annealed pure films prepared from chlorobenzene (left figure) and chloroform (right figure). Their thickness are 60 nm and 150 nm, respectively.*
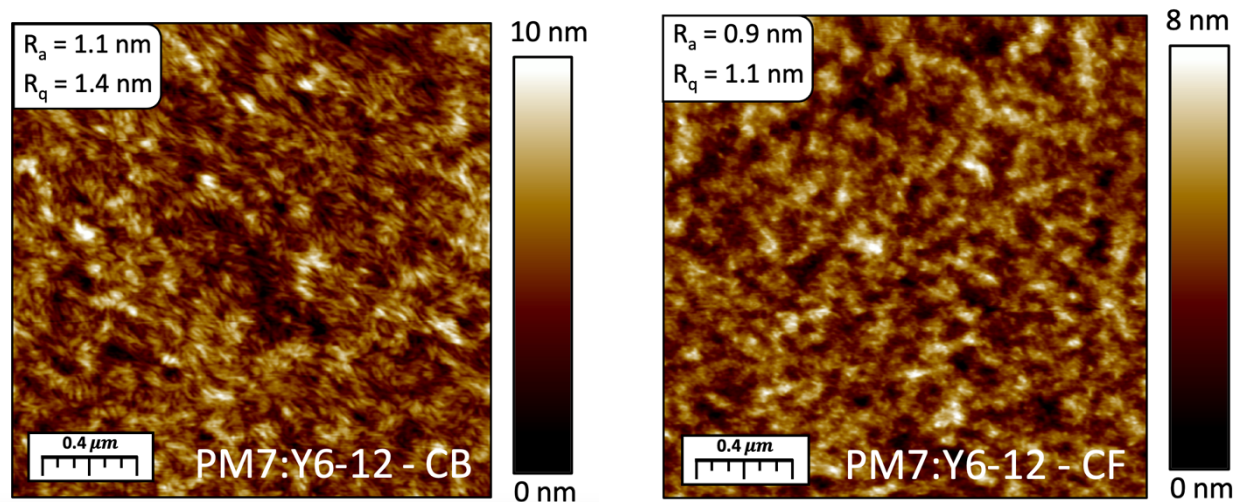
Morphology of annealed blend films

Figure S3-D: *AFM images (2x2 μm^2) for blend films of PM7:Y6 prepared from chlorobenzene (left figure) and chloroform (right figure). Their thickness is 105 nm and 98 nm in chlorobenzene and chloroform, respectively.*

Figure S3-E: *AFM images (2x2 μm^2) for blend films of PM7:Y6-12 prepared from chlorobenzene (left figure) and chloroform (right figure). Their thickness is 110 nm and 103 nm in chlorobenzene and chloroform, respectively.*

Each organic solar cell involved in our study has been manufactured following the main six steps described below.

(I) A commercially Indium Tin Oxide (ITO) electrode (2.0 cm x 1.5 cm) purchased from Ossila has been cleaned with soap (RBS), rinsed with distillated water, washed with acetone and isopropanol before being dried under a nitrogen flow and placed in an oxygen plasma for 5 minutes. The resistances of the pre-patterned ITO glass substrates is around 20 Ohm/square.

(II) A thin aluminium bus of 100 nm was deposited by thermal evaporation (SPECTROS^{TM} 150 deposition system from the Kurt J. Lesker Company®) on the rotating substrate at a rate of 0.40 Å/s under high vacuum (P ~ 5.0 10^{-6} mbar). Such an Al layer allows for a reduction of the series resistances (R_s) of the devices, as experienced in our laboratory.

(III) A 10 nm-thick hole blocking layer (HBL) made of SnO_2 was deposited from a solution containing 0.5 mL of ink solution (2.5 wt% of crystalline SnO_2 diluted in butanol, viscosity 3.5 cP) added to 2.6 mL of butanol. This solution was spin-coated (SPIN150 wafer spinner) at a rotation speed of 3000 rpm for 30 seconds and an annealing step was performed by placing the sample on a hot plate for 30 min at 150°C. The ink solution was purchased from Sigma-Aldrich Company.

(IV) The 100 nm-thick PM7:Y6 and PM7:Y6-12 blends with (1:1) weight ratio was spin-coated (POLOS coater) from chloroform or chlorobenzene under inert conditions (nitrogen glovebox) at a speed of 1500 rpm during 60 sec and annealed at 100°C for 10 minutes on a hot plate. Note that the powders of these compounds, purchased from the company Brilliant Matters, were initially stored inside an argon glovebox.

(V) A 10 nm-thick electron blocking layer (EBL) made of MoO_3 was deposited on the rotating sample by thermal evaporation at a speed of 0.25 Å/s via SPECTROS^{TM} 150 thermal evaporation equipment (P ~ 5.0 10^{-6} mbar).

(VI) A 100 nm-thick aluminium counter-electrode was also deposited with the same equipment by thermal evaporation at a speed of 0.40 Å/s to obtain the final inverted device architecture Glass/ITO/Al/SnO_2/Active layer/MoO_3/Al.

The characterization of each solar cell was performed under inert conditions (nitrogen glovebox) with a Newport^{TM} ABA LED LSH-7320 solar simulator. This model incorporates an AM 1.5 filter and was configured at 1 Sun output power (~100 mW/cm^2). The cells were placed under the LED lamp on a Push-Fit Test Board Substrates support sold by Ossila and electrically connected to a current-voltage generator (Keithley's Standard Series 2400 Source Measure Unit (SMU) Instrument). The current measurement was performed on each device (D_X, with x = 1 to 8) under a voltage range varied from -1.5 V to +1.5 V by 0.04 V steps. The software IGOR Pro (version 6.3.4.1) was used to analyzes the data and obtain directly exploitable J(V) curves as well as the J_{SC}, V_{OC}, FF, R_S, R_{Sh} and PCE parameters of the manufactured solar cells. Average cell parameter values and their respective standard deviation have been calculated for 5 devices (D_X) excluding short-circuited or S-shaped curves.
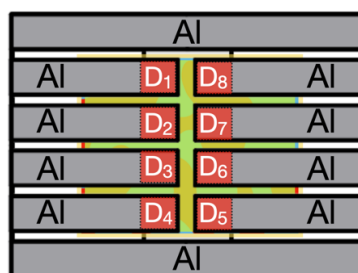
Figure S4: Illustration of each device (in red) characterized from the same OSC active layer
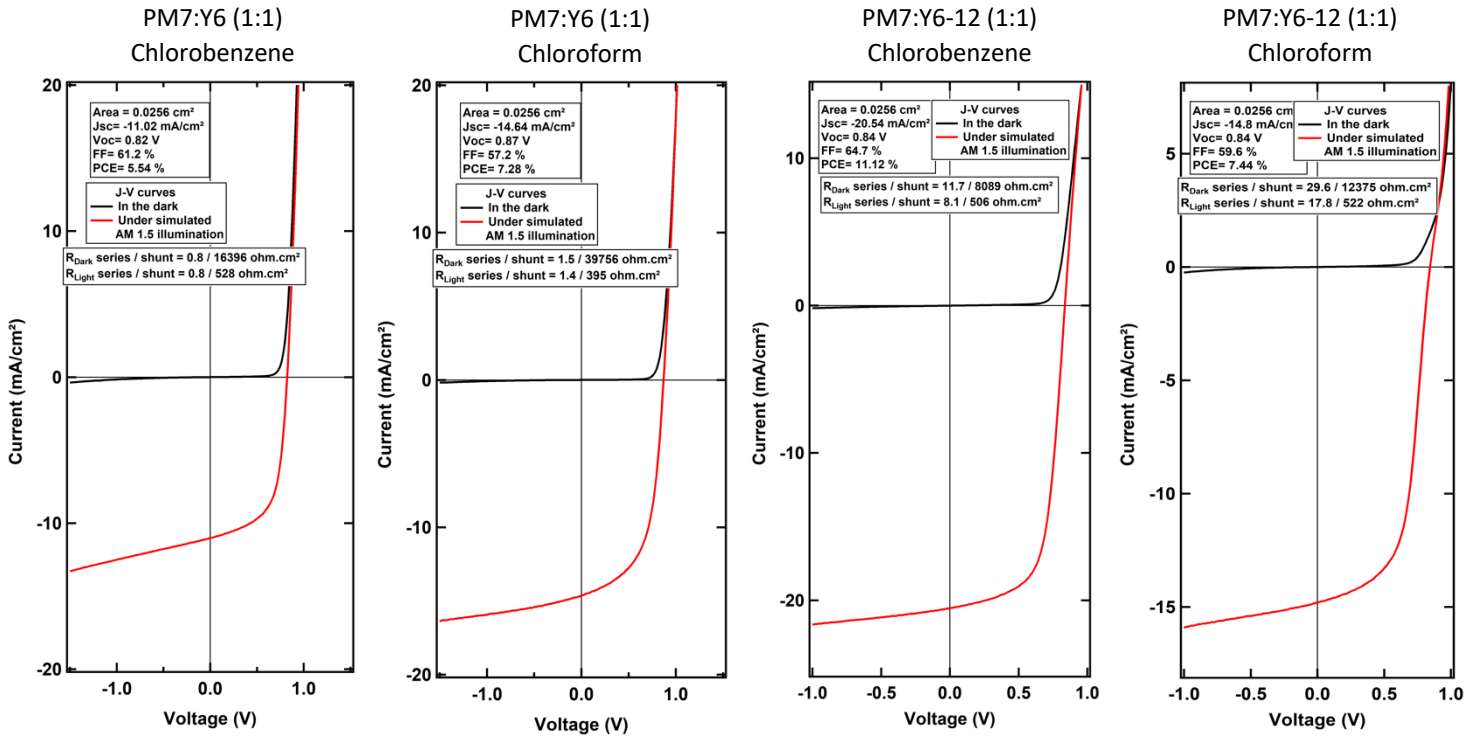
Supporting information 5 (S5):

Figure S5: *Best current density-voltage (J-V) curves obtained for each type of device manufactured in this study (ITO/Al/SnO$_2$/active layer/MoO$_3$/Al). The active layer are from left to right: PM7:Y6 (chlorobenzene), PM7:Y6 (chloroform), PM7:Y6-12 (chlorobenzene) and PM7:Y6-12 (chloroform), each with a weight ratio of (1:1).*

Supporting information 6 (S6):

J-V curves for PM7:Y6 blend from chlorobenzene

Figure S6-A: *J-V curves obtained from 5 devices on the same substrate (ITO/Al/SnO$_2$/active layer/MoO$_3$/Al) including the PM7:Y6 (1:1) blend prepared from chlorobenzene as active layer.*

J-V curves for PM7:Y6 blend from chloroform

Figure S6-B: *J-V curves obtained from 5 devices on the same substrate (ITO/Al/SnO₂/active layer/MoO₃/Al) including the PM7:Y6 (1:1) blend prepared from chloroform as active layer.*
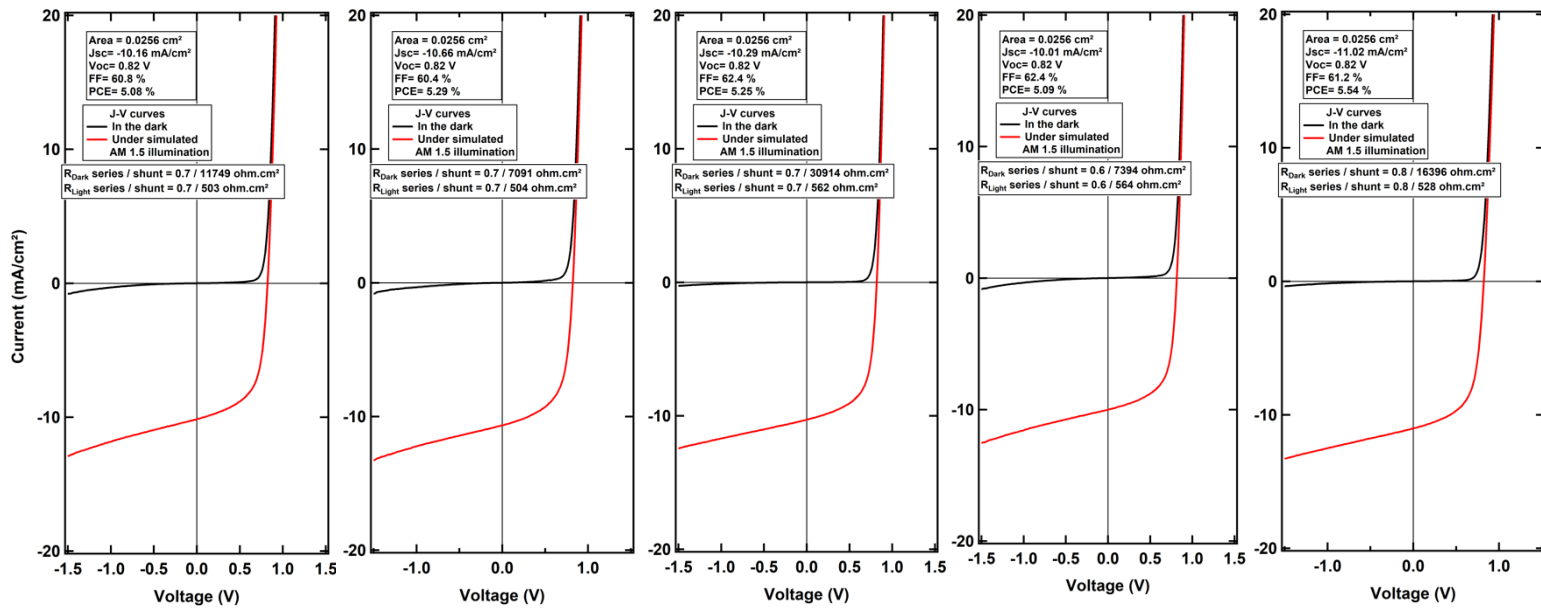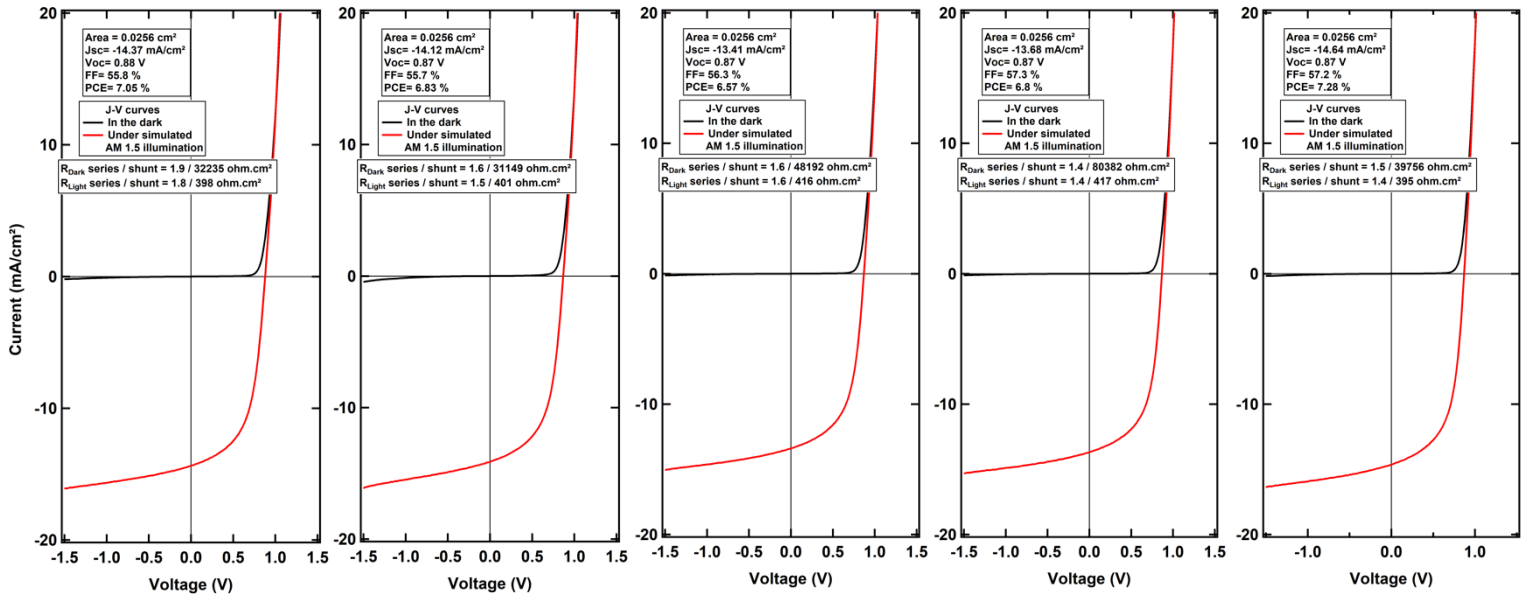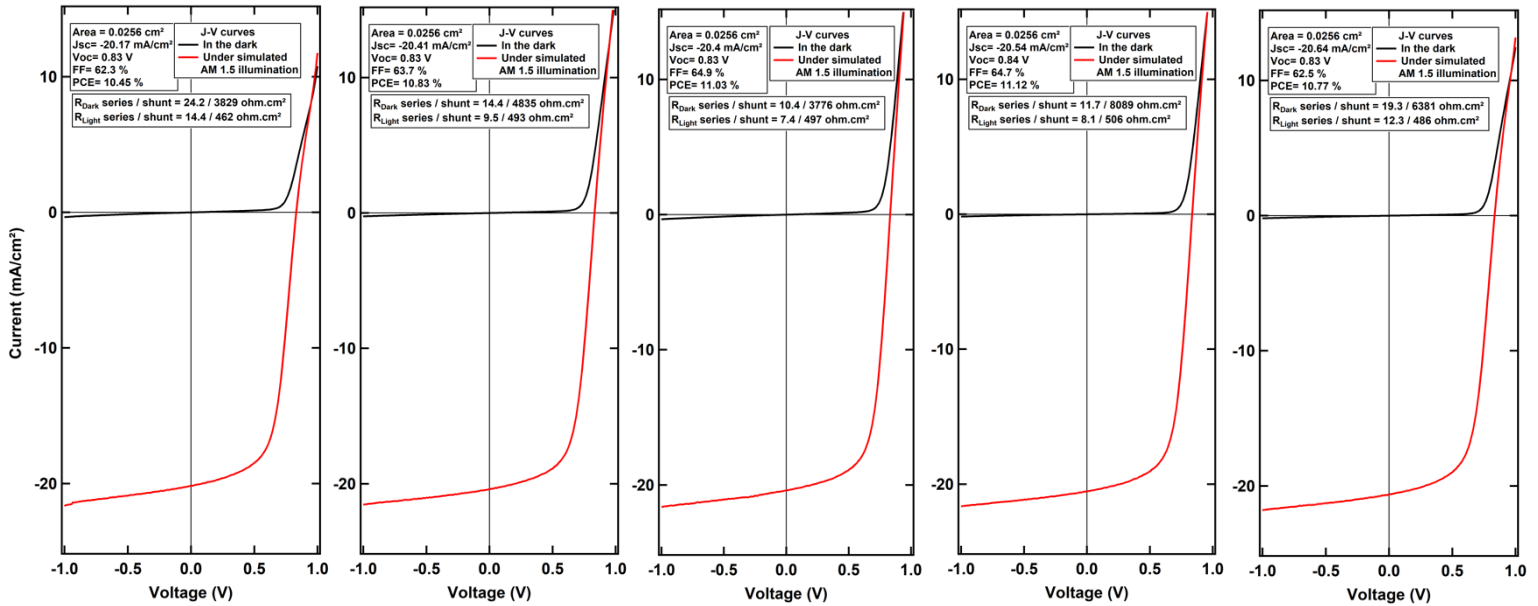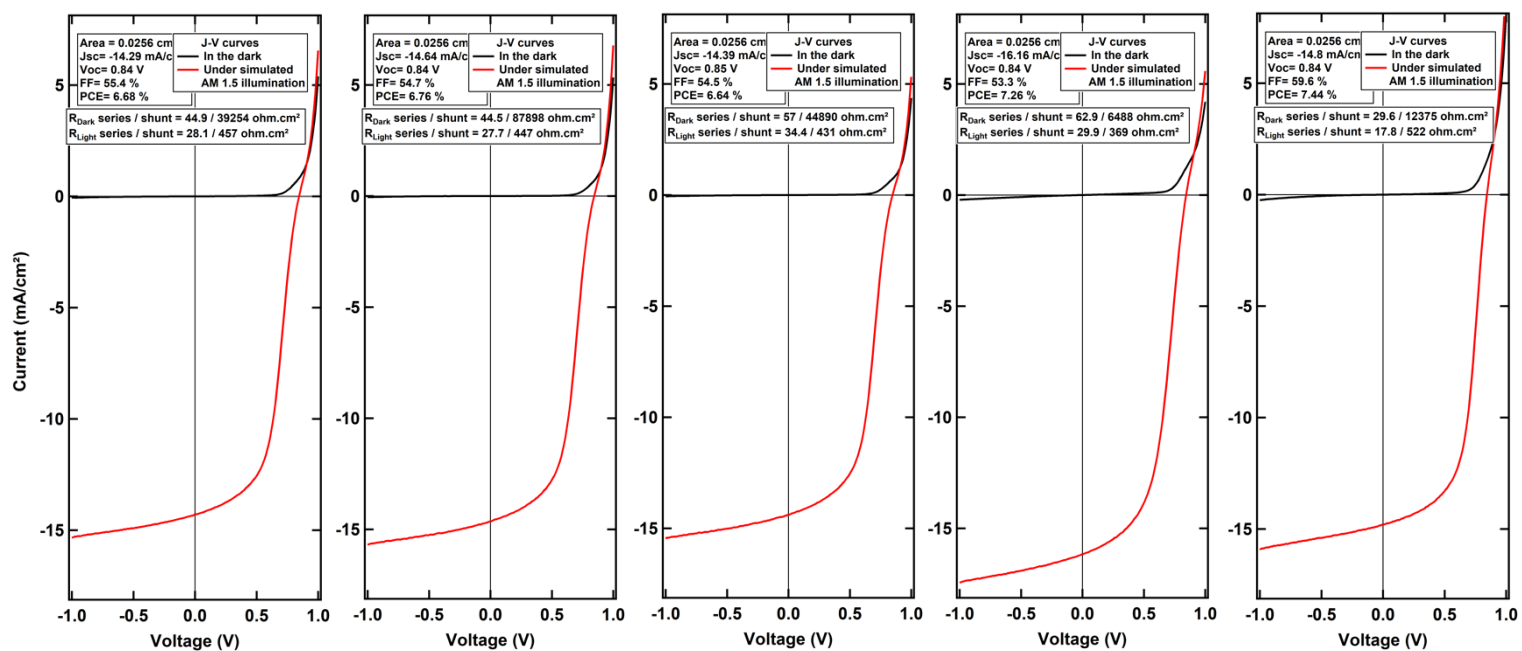
J-V curves for PM7:Y6-12 blend from chlorobenzene

Figure S6-C: *J-V curves obtained from 5 devices on the same substrate (ITO/Al/SnO₂/active layer/MoO₃/Al) including the PM7:Y6-12 (1:1) blend prepared from chlorobenzene as active layer.*

J-V curves for PM7:Y6-12 blend from chloroform

Area = 0.0256 cm	J-V curves
Jsc= -14.29 mA/c	In the dark
Voc= 0.84 V	Under simulated
FF= 55.4 %	AM 1.5 illumination
PCE= 6.68 %	

R$_{Dark}$ series / shunt = 44.9 / 39254 ohm.cm²
R$_{Light}$ series / shunt = 28.1 / 457 ohm.cm²

Area = 0.0256 cm	J-V curves
Jsc= -14.64 mA/c	In the dark
Voc= 0.84 V	Under simulated
FF= 54.7 %	AM 1.5 illumination
PCE= 6.76 %	

R$_{Dark}$ series / shunt = 44.5 / 87898 ohm.cm²
R$_{Light}$ series / shunt = 27.7 / 447 ohm.cm²

Area = 0.0256 cm	J-V curves
Jsc= -14.39 mA/c	In the dark
Voc= 0.85 V	Under simulated
FF= 54.5 %	AM 1.5 illumination
PCE= 6.64 %	

R$_{Dark}$ series / shunt = 57 / 44890 ohm.cm²
R$_{Light}$ series / shunt = 34.4 / 431 ohm.cm²

Area = 0.0256 cm	J-V curves
Jsc= -16.16 mA/c	In the dark
Voc= 0.84 V	Under simulated
FF= 53.3 %	AM 1.5 illumination
PCE= 7.26 %	

R$_{Dark}$ series / shunt = 62.9 / 6488 ohm.cm²
R$_{Light}$ series / shunt = 29.9 / 369 ohm.cm²

Area = 0.0256 cm	J-V curves
Jsc= -14.8 mA/cn	In the dark
Voc= 0.84 V	Under simulated
FF= 59.6 %	AM 1.5 illumination
PCE= 7.44 %	

R$_{Dark}$ series / shunt = 29.6 / 12375 ohm.cm²
R$_{Light}$ series / shunt = 17.8 / 522 ohm.cm²

Figure S6-D: *J-V curves obtained from 5 devices on the same substrate (ITO/Al/SnO$_2$/active layer/MoO$_3$/Al) including the PM7:Y6-12 (1:1) blend prepared from chloroform as active layer.*