

Supplementary Information

Pyrrolidino [60] and [70]Fullerene Homo and Heterodimers as electron acceptors for OPV.

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SYNTHESIS AND CHARACTERIZATION

General. NMR spectra were recorded at room temperature on a Bruker DPX 300 MHz. High resolution mass spectrometry measurements were performed at the Unidad de Espectrometría de Masas of Universidad Complutense de Madrid. Infrared spectrum was recorded on a Bruker TENSOR FTIR. Column Chromatography was performed by Size Exclusion Chromatography, SEC, (Bio-Rad Bio-Beads S-XI). UV-vis spectra were recorded in a Shimadzu UV-Vis-NIR 3200 spectrometer at a constant temperature of 25 °C in toluene solution. HPLC studies was performed using a *Buckyprep-M Waters* ($\varnothing 4.6 \times 250 \text{ mm}$) column at room temperature.

MASS SPECTROMETRY

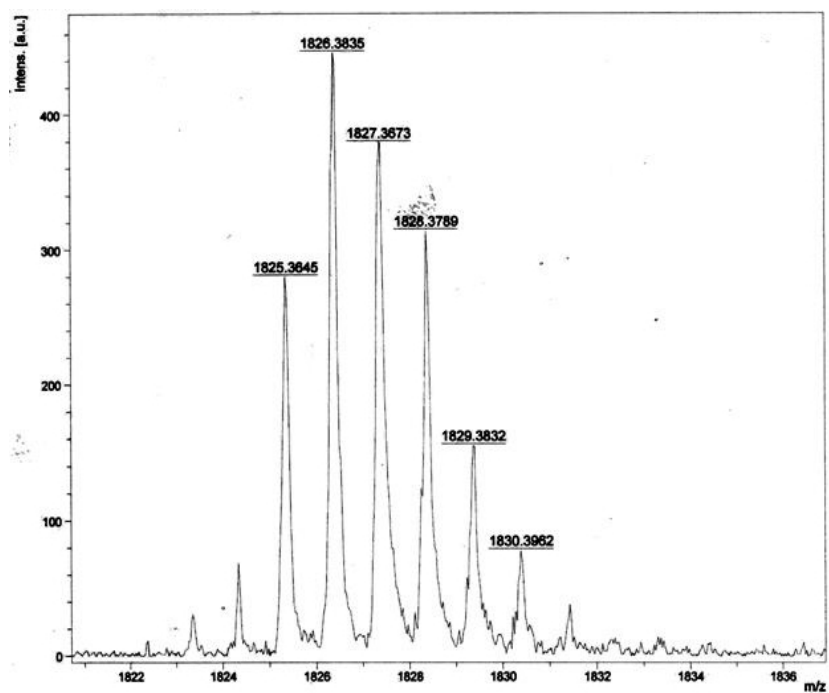


Figure S1: HRMS (MALDI-) of **4a**.

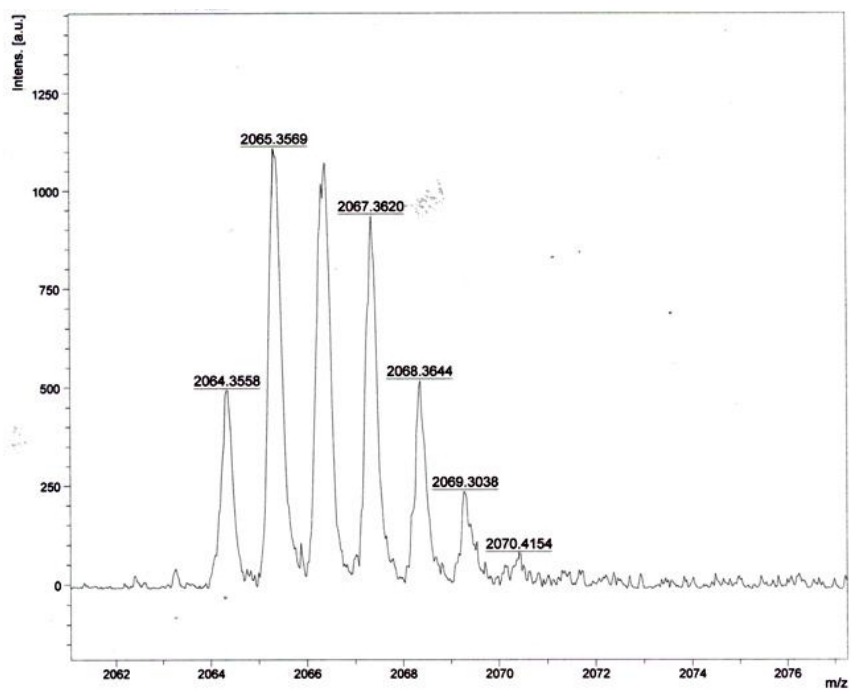


Figure S2: HRMS (MALDI-) of **5a**.

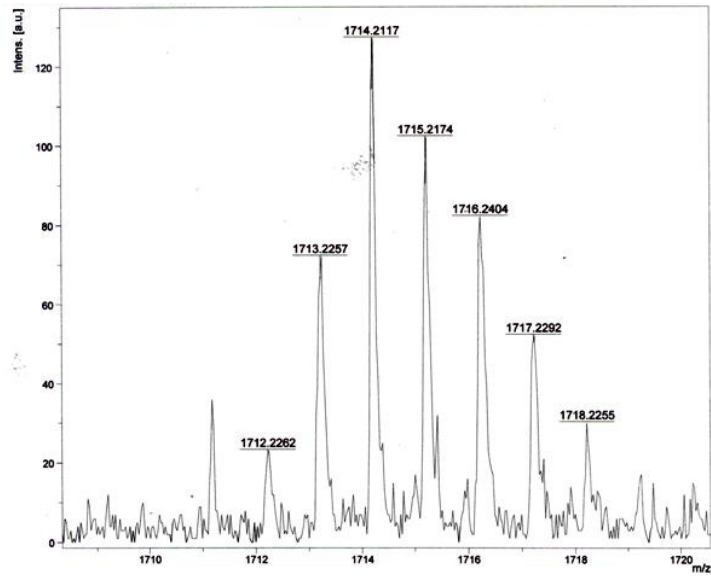


Figure S3: HRMS (MALDI+) of **4b**.

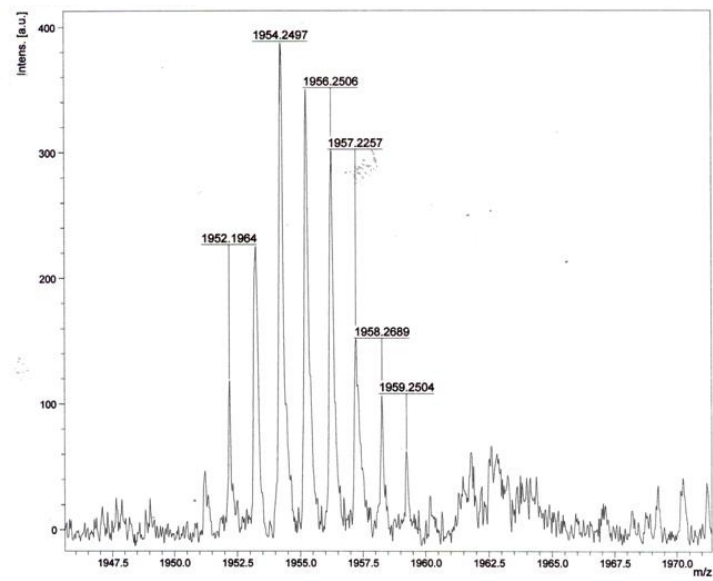


Figure S4: HRMS (MALDI+) of **5b**.

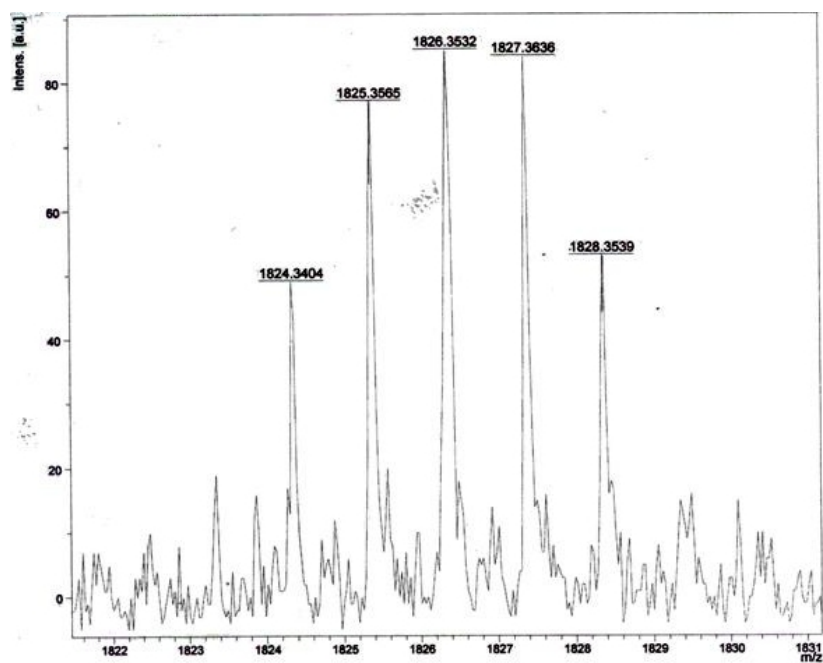


Figure S5. HRMS (MALDI+) of 4c.

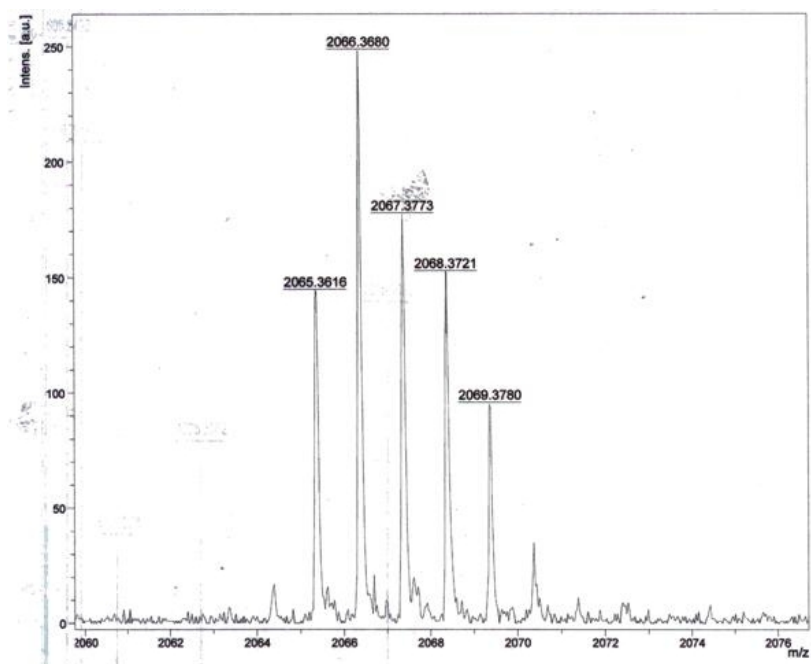


Figure S6: HRMS (MALDI+) of 5c.

HPLC

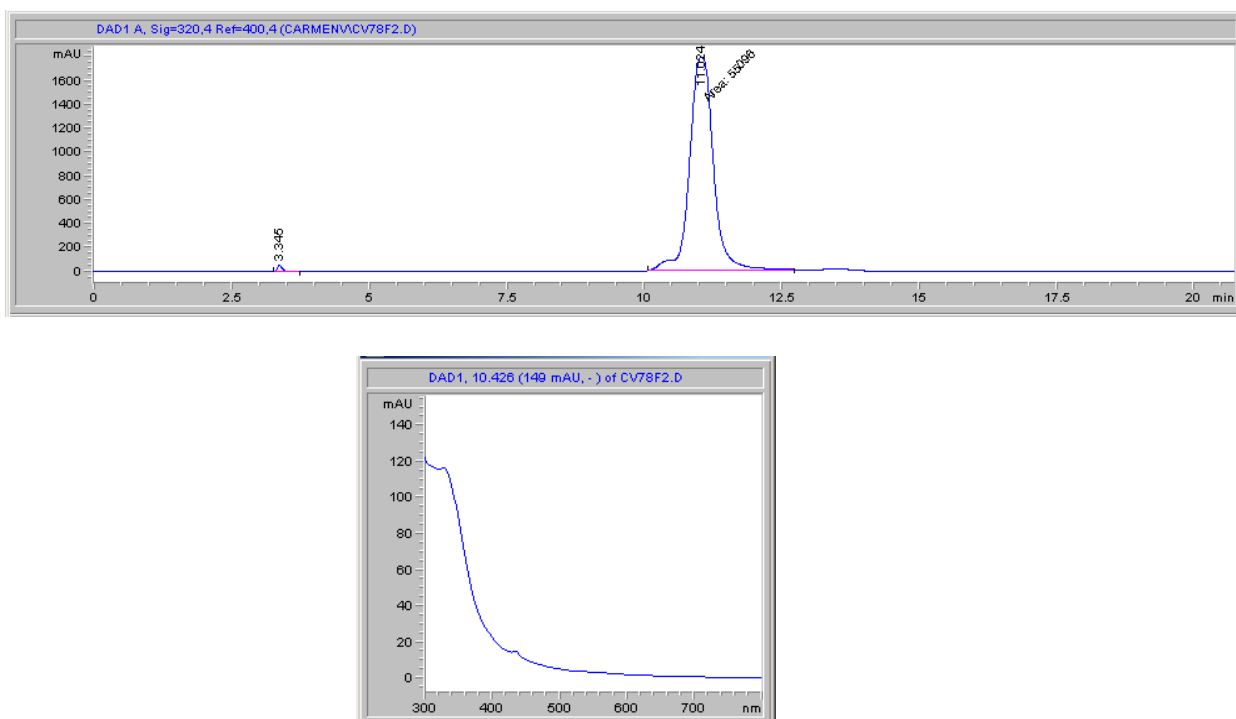


Figure S7: HPLC of compound **4a**, peak at 11.02 min; toluene, 1 ml/min (top). UV-Vis of the peak at 11.02 min (bottom).

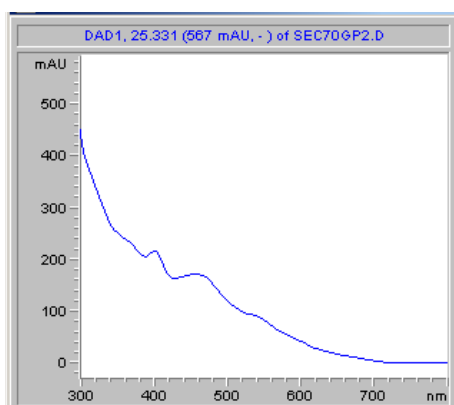
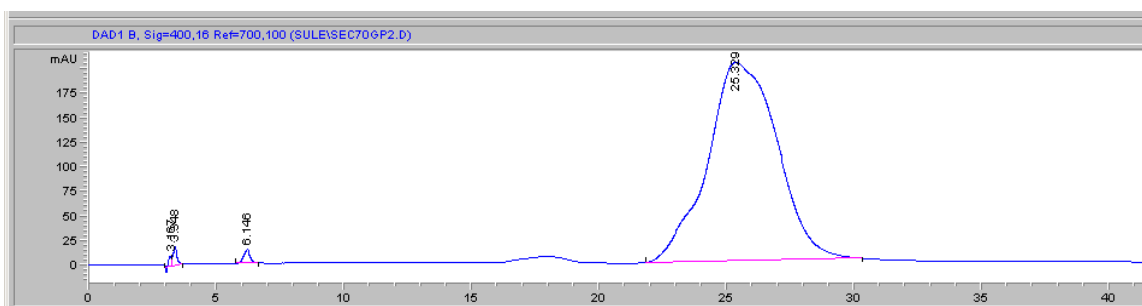


Figure S8: HPLC of compound **5b**, broad peak at 25.32 min; toluene, 1 ml/min (top). UV-Vis of the peak at 25.32 min (bottom).

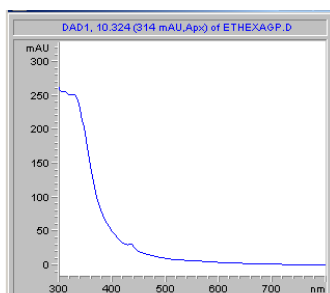
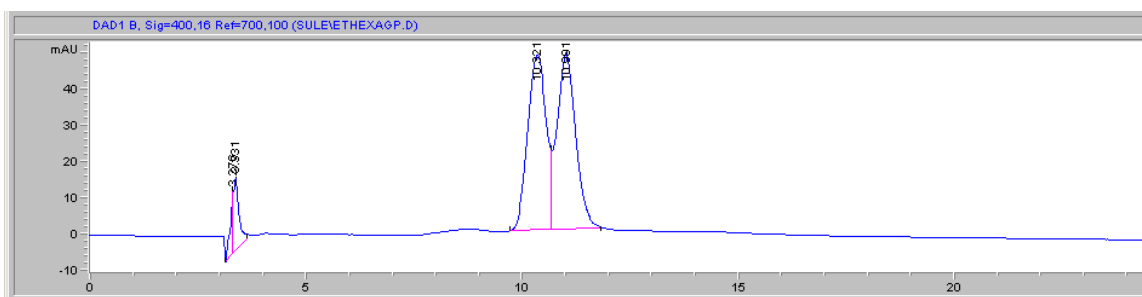


Figure S9: HPLC of compound **4c**, peaks at 10.32-10.98 min; toluene, 1 ml/min (top). UV-Vis of the peak at 10.32 min (bottom).

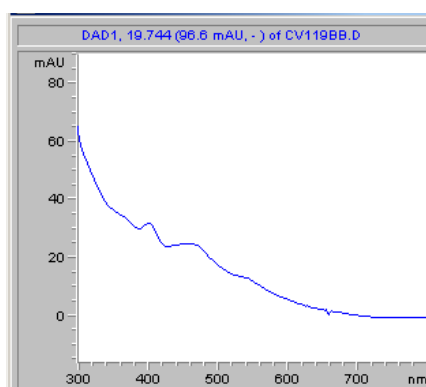
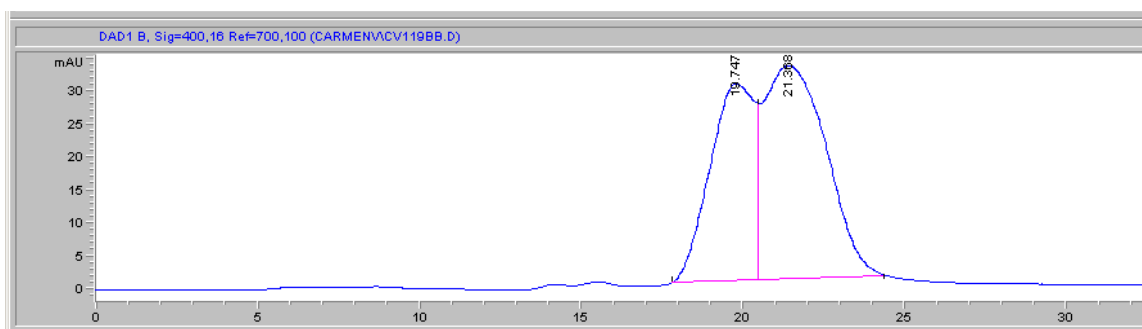


Figure S10: HPLC of compound **5c**, peaks at 19.74-21.36 min; toluene, 1 ml/min (top). UV-Vis of the peak at 19.74 min (bottom).

UV-Vis

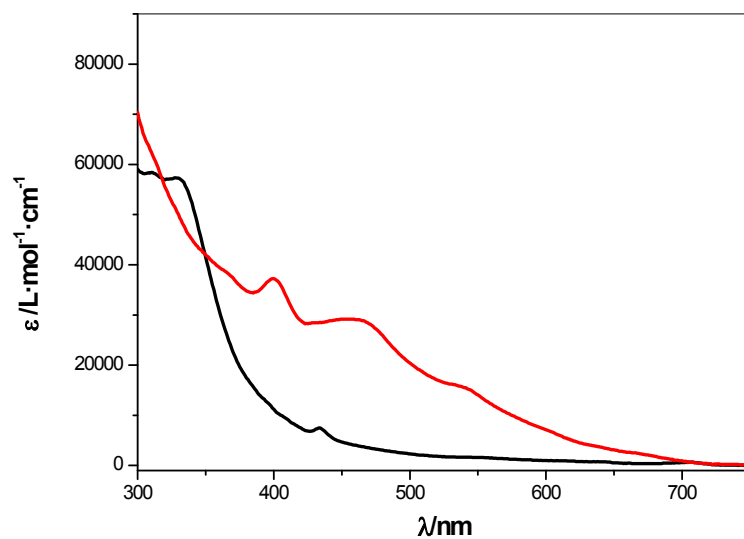


Figure S11: UV-vis spectra of compounds **4b** (black) and **5b** (red) recorded in toluene at 25 °C.

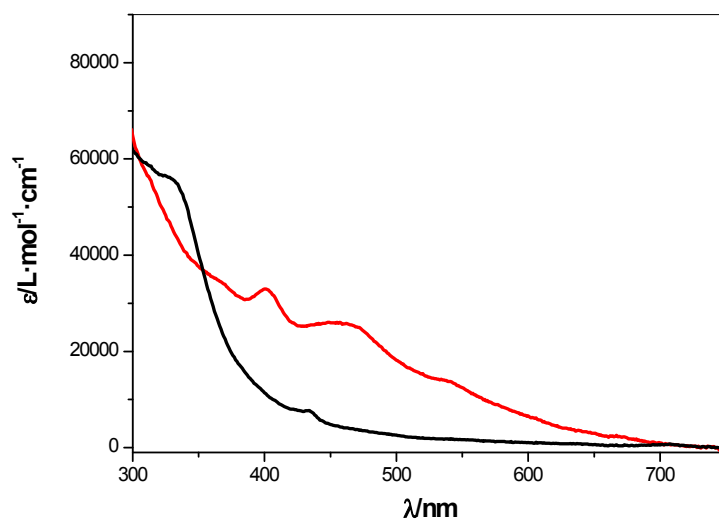


Figure S12. UV-vis spectra of compounds **4c** (black) and **5c** (red) recorded in toluene at 25 °C.

PHOTOVOLTAIC STUDIES

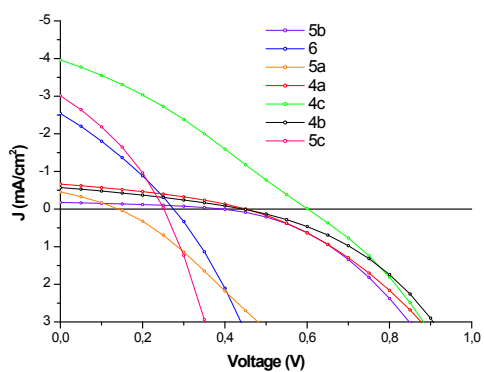


Figure S13: J-V Curves of Organic Bulk Heterojunction Photovoltaic Devices, under illumination.

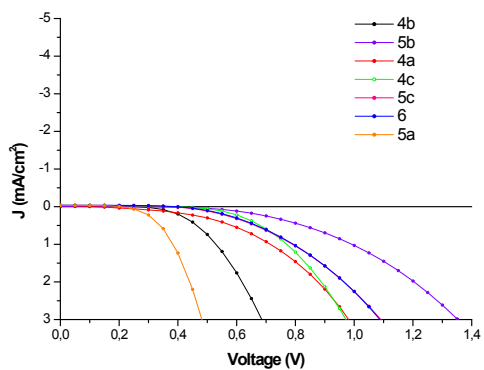


Figure S14: J-V Curves of Organic Bulk Heterojunction Photovoltaic Devices in dark.

ATOMIC FORCE MICROSCOPY

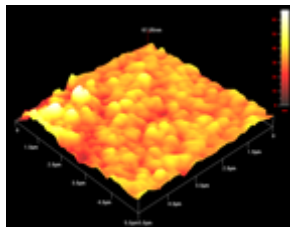


Figure S15: Atomic Force Microscopy Images of blends of **4a:P3HT**.

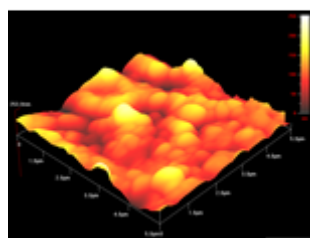


Figure S16: Atomic Force Microscopy Images of blends of **5a:P3HT**.

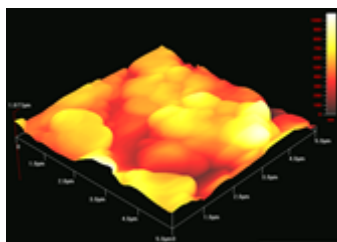


Figure S17: Atomic Force Microscopy Images of blends of **5b:P3HT**.

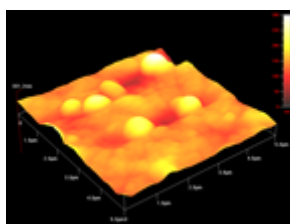


Figure S18: Atomic Force Microscopy Images of blends of **5c:P3HT**.

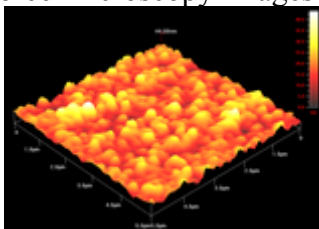
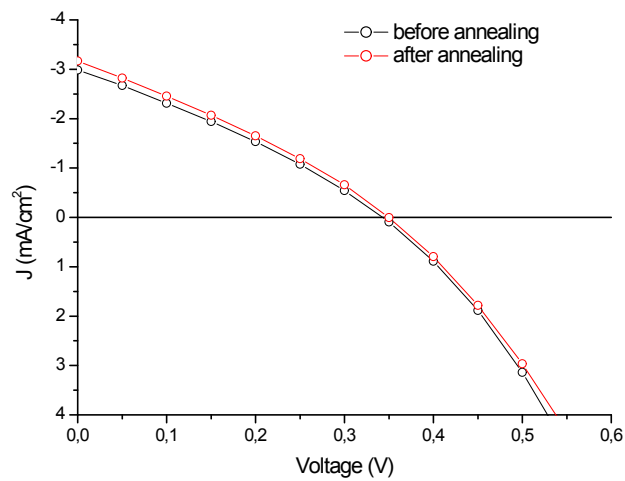


Figure S19: Atomic Force Microscopy Images of blends of **6:P3HT**.



5c (after annealing, 80 °C for 5 minutes)	3.16	350	0.29	0.33
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Figure S20: Effect of thermal annealing over the PCE of compound **5c**.