Supporting Information

The molecular origin of high performance in ternary organic photovoltaics identified by combinatory *in situ* structural probes

Joel Luke[1,†], Yong-Ryun Jo[3,†], Chieh-Ting Lin[2], Soonil Hong[4], Chandran Balamurugan[4,6], Jehan Kim[7], Byoungwook Park[4], Kwanghee Lee[3,4,5], James R. Durrant[2], Sooncheol Kwon[6,*], Bong-Joong Kim[3,*], Ji-Seon Kim[1,*]

[1]Department of Physics and Centre for Processable Electronics, Imperial College London, London, SW7 2AZ, UK

[2]Department of Chemistry and Centre for Processable Electronics, Imperial College London, London, SW7 2AZ, United Kingdom

[3]School of Materials Science and Engineering (SMSE), Gwangju Institute of Science and Technology (GIST), Gwangju 500–712, Republic of Korea

[4]Heeger Center for Advanced Materials (HCAM), Gwangju Institute of Science and Technology (GIST), Gwangju 500–712, Republic of Korea

[5]Research Institute for Solar and Sustainable Energies (RISE), Gwangju Institute of Science and Technology (GIST), Gwangju 500–712, Republic of Korea

[6]Department of Energy and Materials Engineering, Dongguk University-Seoul, Seoul, 04620 Republic of Korea

[7]Pohang Accelerator Laboratory (PAL), Pohang University of Science and Technology (POSTECH), Pohang 790–784, Republic of Korea

*Correspondence to: kwansc12@dongguk.edu; kimbj@gist.ac.kr; ji-seon.kim@imperial.ac.uk

† J. L. and Y. J. contributed equally to this work.

BHJ Samples	Annealing Temperature (°C)	Jsc (mA/cm²)	Voc (V)	FF	PCE (%)
Binary	50	8.29 (±0.010)	0.760 (±0.004)	0.539 (±0.032)	3.40 (±0.006)
Binary	85	8.58 (±0.030)	0.790 (±0.006)	0.636 (±0.026)	4.36 (±0.032)
Binary	125	11.6 (±0.230)	0.710 (±0.002)	0.586 (±0.028)	4.88 (±0.192)
Binary	160	10.8 (±0.200)	0.730 (±0.005)	0.548 (±0.027)	4.26 (±0.078)
Ternary	50	4.17 (±0.120)	0.770 (±0.004)	0.308 (±0.028)	0.94 (±0.011)
Ternary	85	10.2 (±0.502)	0.800 (±0.004)	0.477 (±0.016)	3.86 (±0.015)
Ternary	125	11.3 (±0.350)	0.820 (±0.007)	0.556 (±0.006)	5.37 (±0.163)
Ternary	160	10.8 (±0.540)	0.810 (±0.005)	0.600 (±0.004)	5.26 (±0.179)

Table S1. Summary average of device parameters of binary and ternary OPVs annealed at different temperatures. The corresponding average and standard deviations for each parameter were derived from more than four devices.

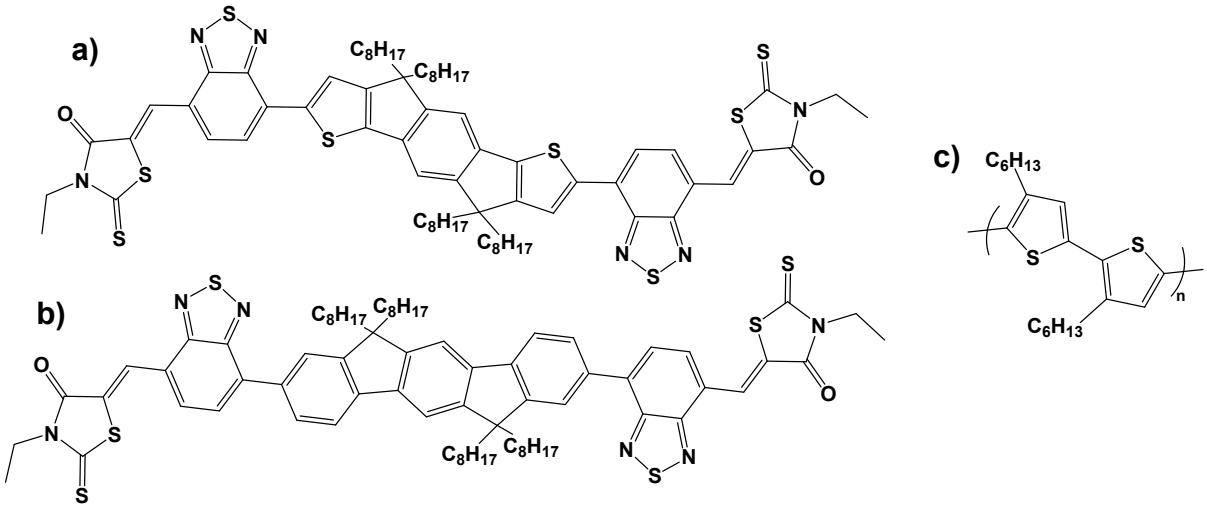

Figure S1. Chemical structures of O-IDTBR (a), O-IDFBR (b), and P3HT (c).

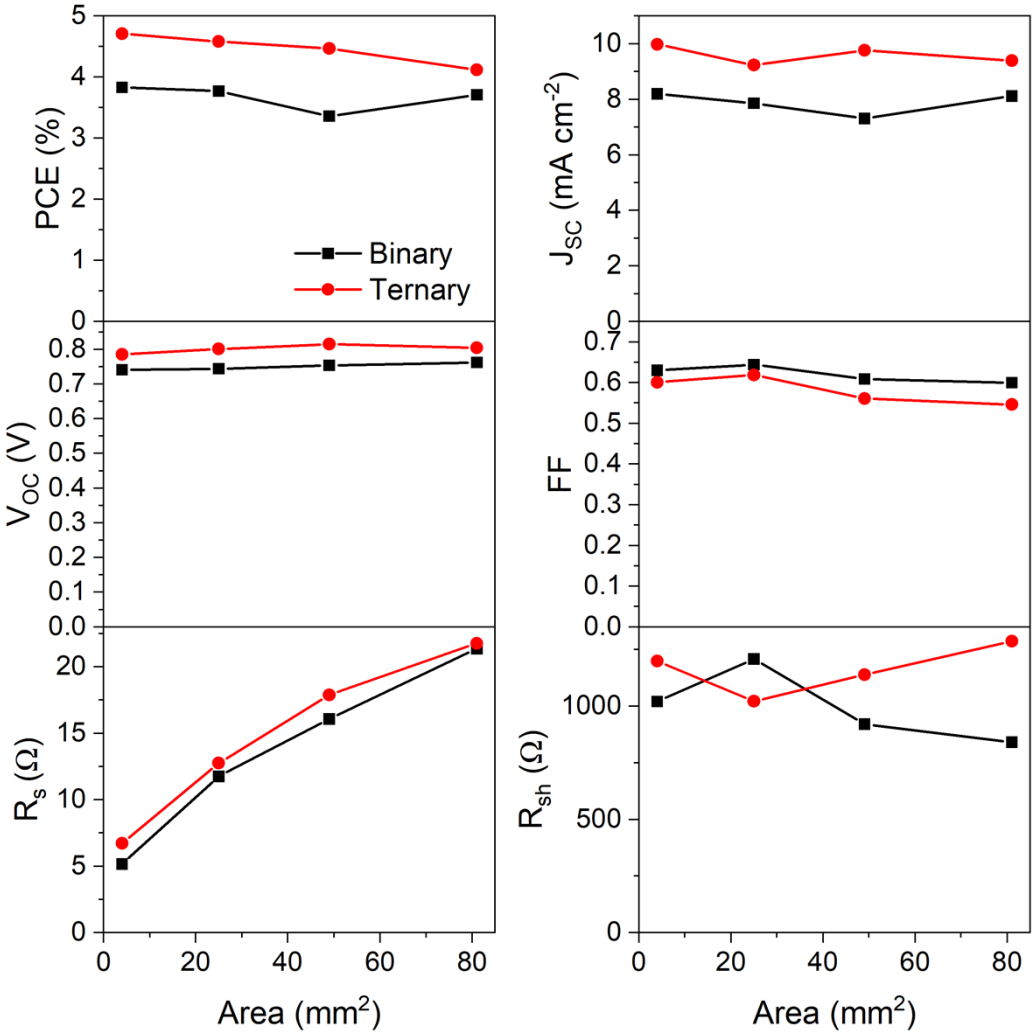

Figure S2. Area dependent device performance: Device parameters for the binary and ternary blends as a function of device area for the fresh devices used in the degradation study.

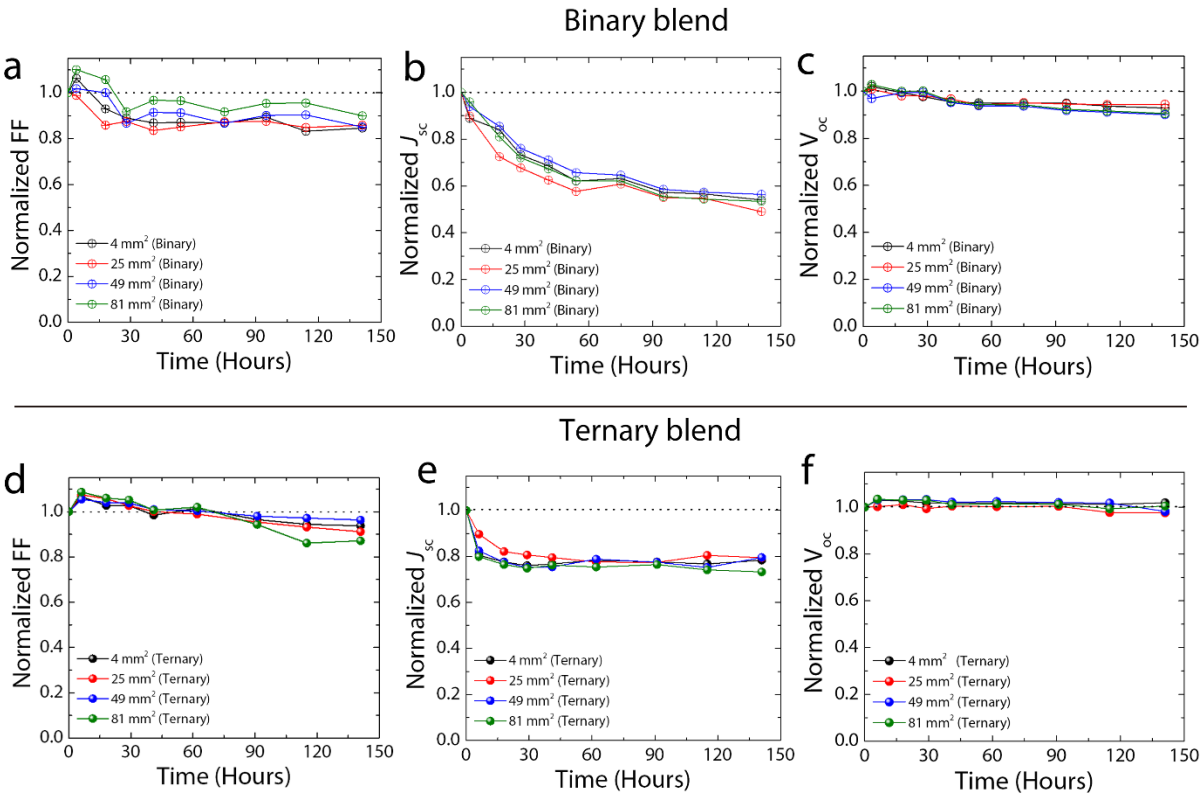

Figure S3. Device degradation: Various parameters evaluated at different areas of binary and ternary devices as a function of illumination time in air.

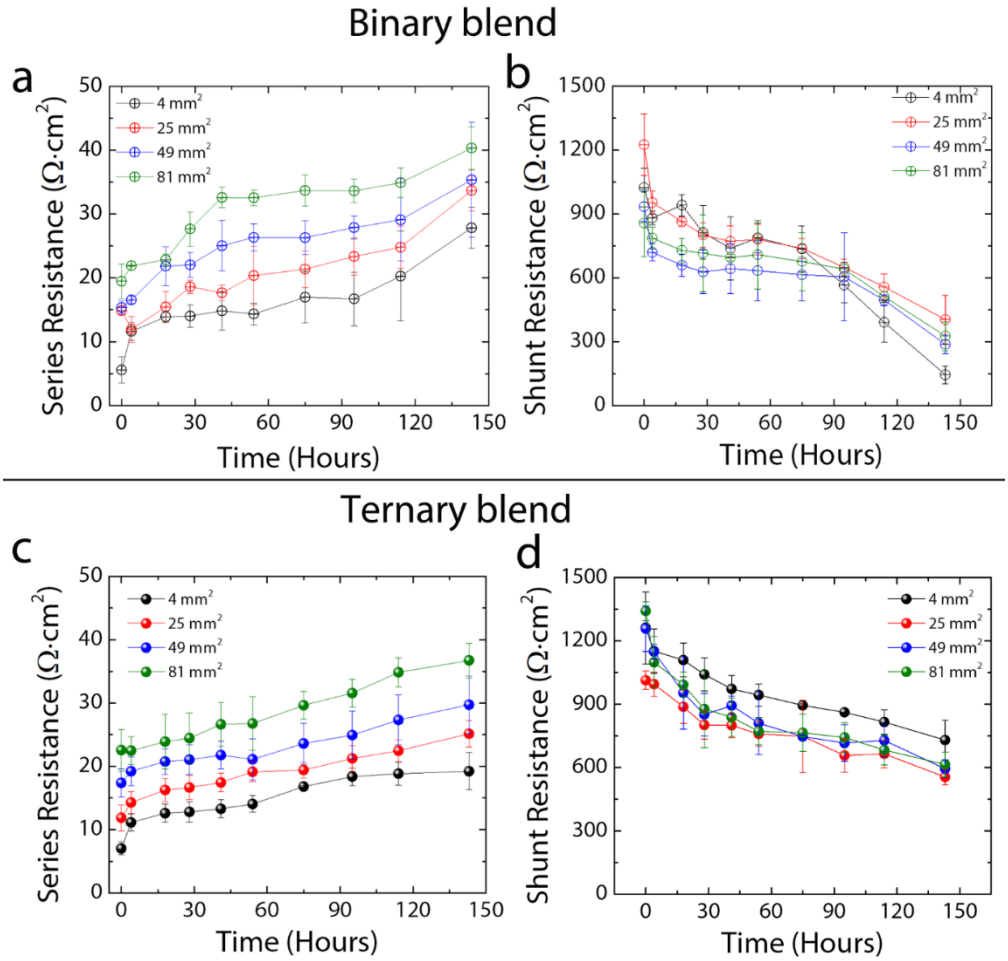

Figure S4. Series and shunt resistance ($\Omega \cdot cm^2$) evaluated at different areas of binary and ternary devices as a function of illumination time in air.

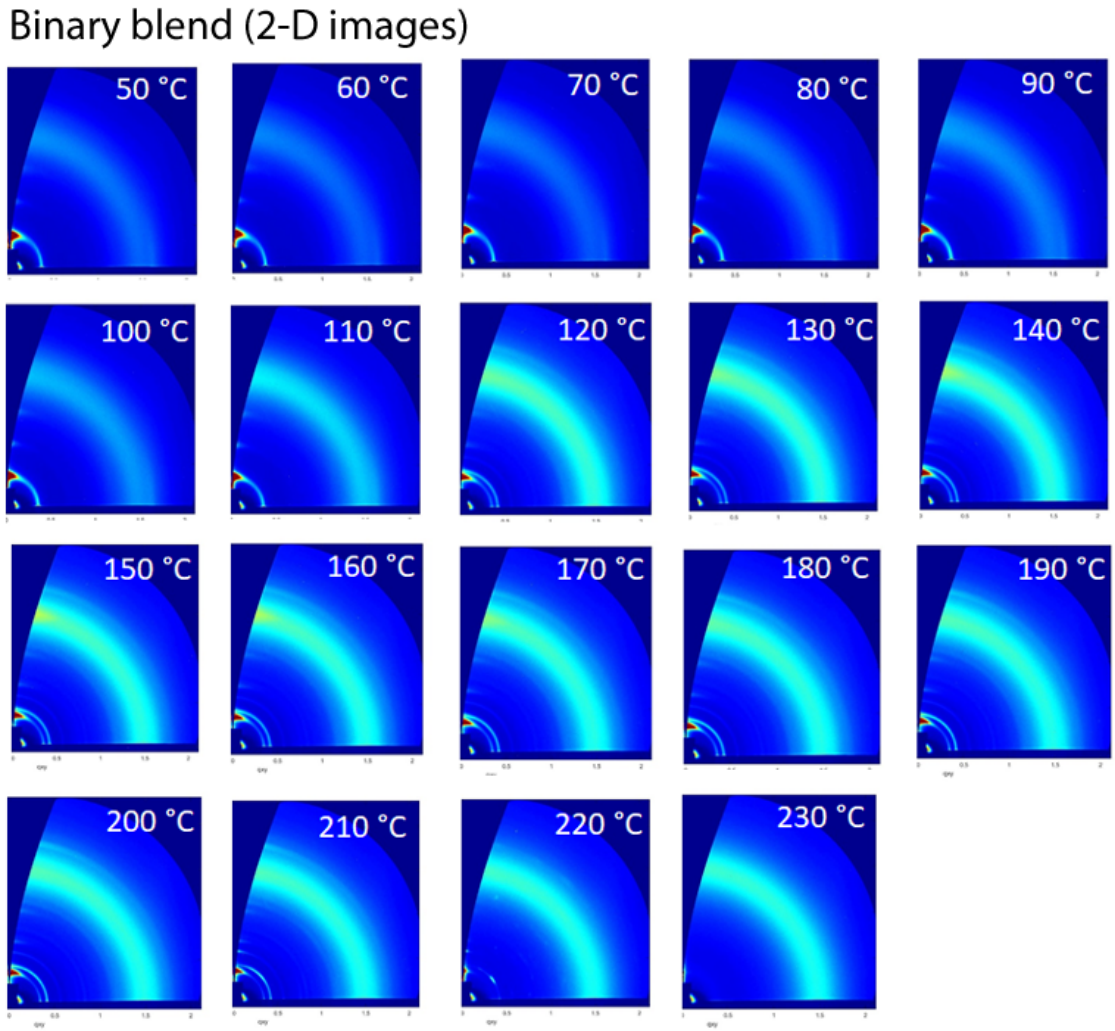

Figure S5. Temperature-dependent 2-D GIWAXS patterns of the binary blend system.

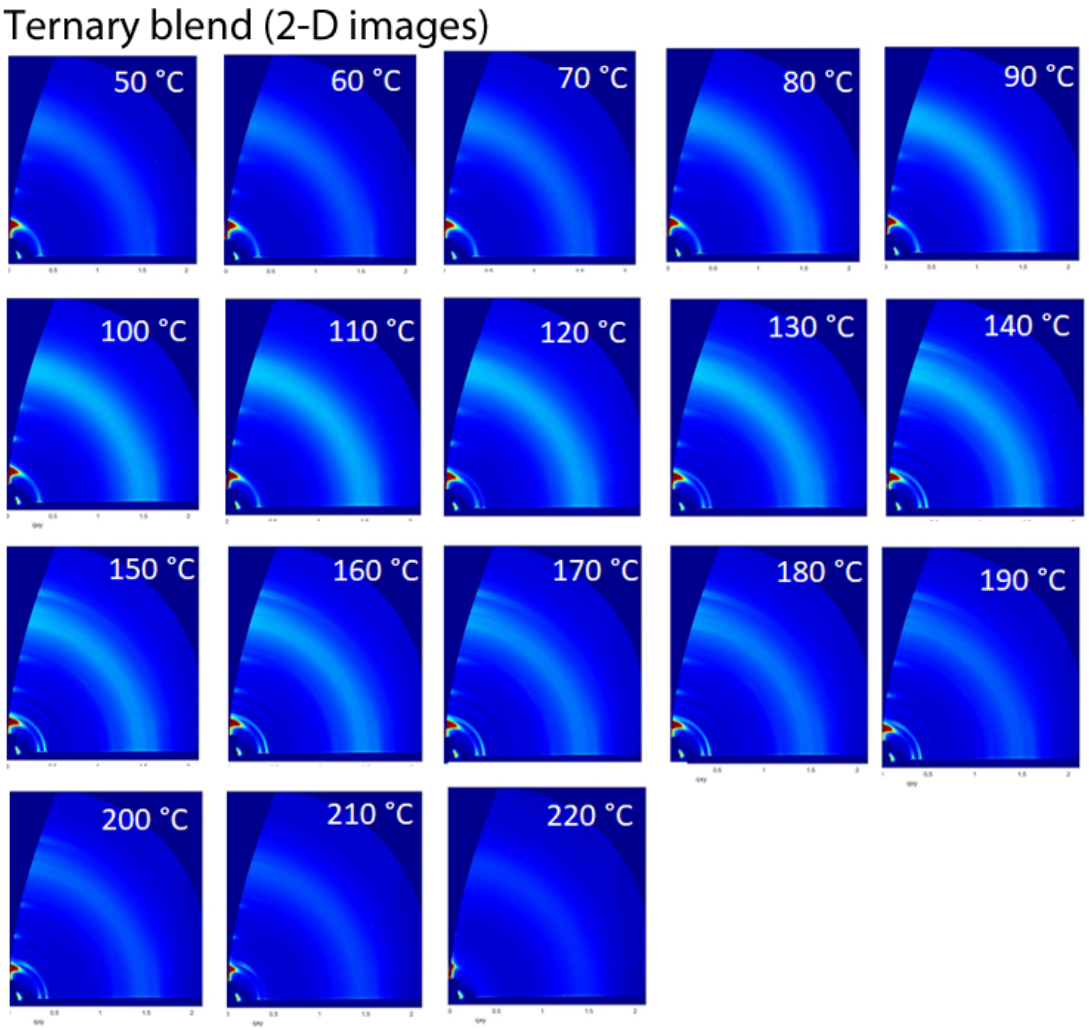

Figure S6. Temperature-dependent 2-D GIWAXS patterns of the ternary blend system.

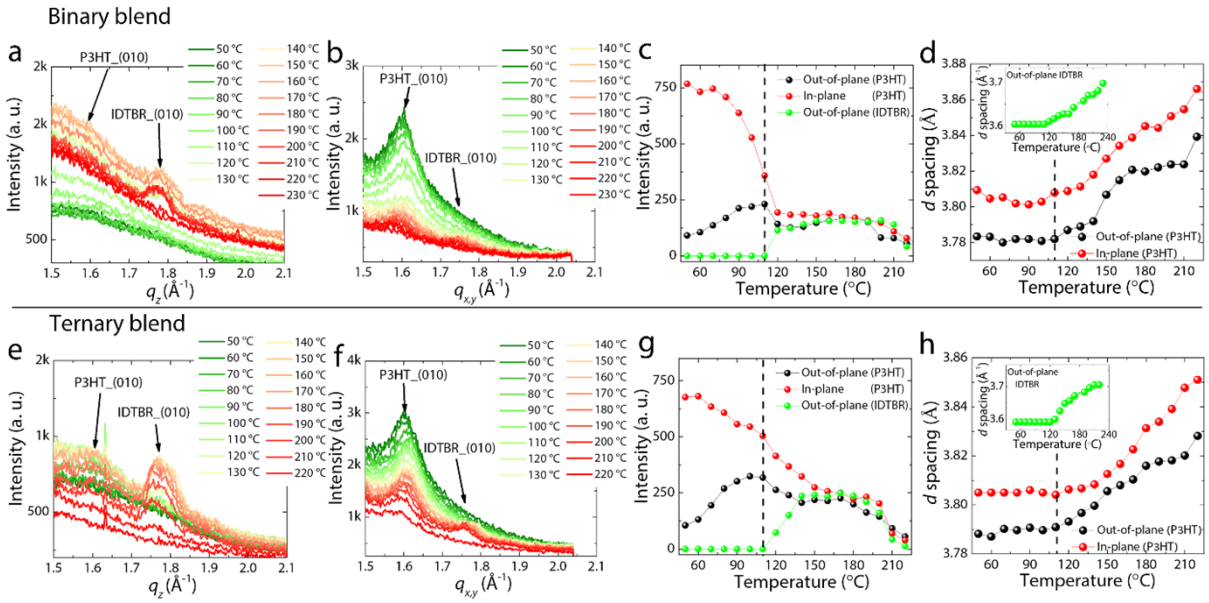

Figure S7. a and **b,** Temperature-dependent one-dimensional (1-D) GIWAXS profiles of the binary blend along the OOP and IP directions, respectively. **c** and **d,** Intensities and *d* spacings of the diffraction peaks for P3HT and O-IDTBR in the binary film along the OOP and IP directions **e** and **f,** Temperature-dependent one-dimensional (1-D) GIWAXS profiles of the ternary blend along the OOP and IP directions, respectively. **g** and **h,** Intensities and *d* spacings of the diffraction peaks for P3HT and O-IDTBR in the binary film along the OOP and IP directions.

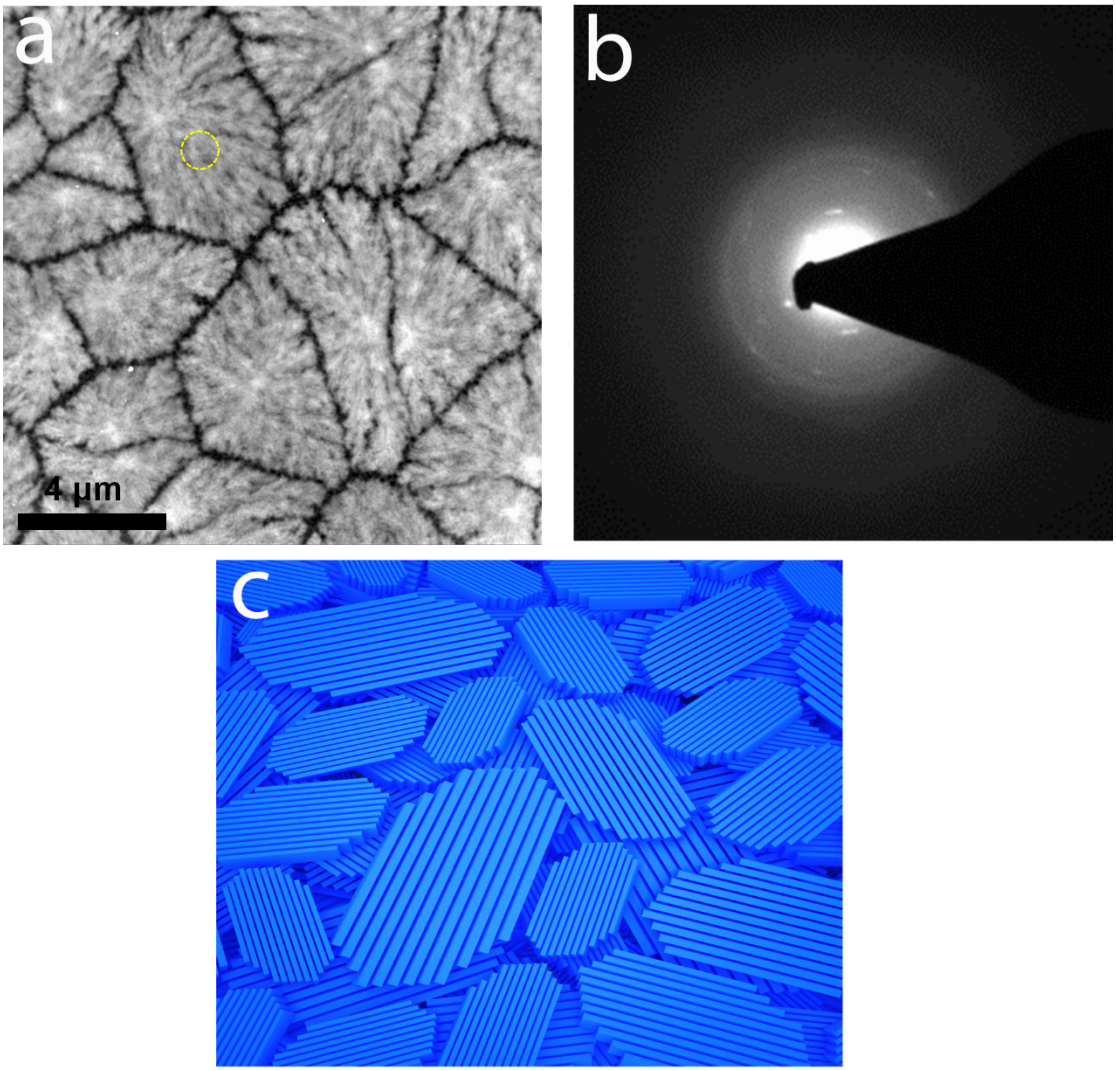

Figure S8. (a) A high-angle annular dark field scanning TEM (HAADF-STEM) image of the binary (P3HT:O-IDTBR) blend annealed at 160 °C with **(b)** a SAED pattern obtained from the area marked by a yellow circle in figure S6 (a). **(c)** A schematic image of the many randomly orientated domains of different phases of O-IDTBR molecules within a grain.

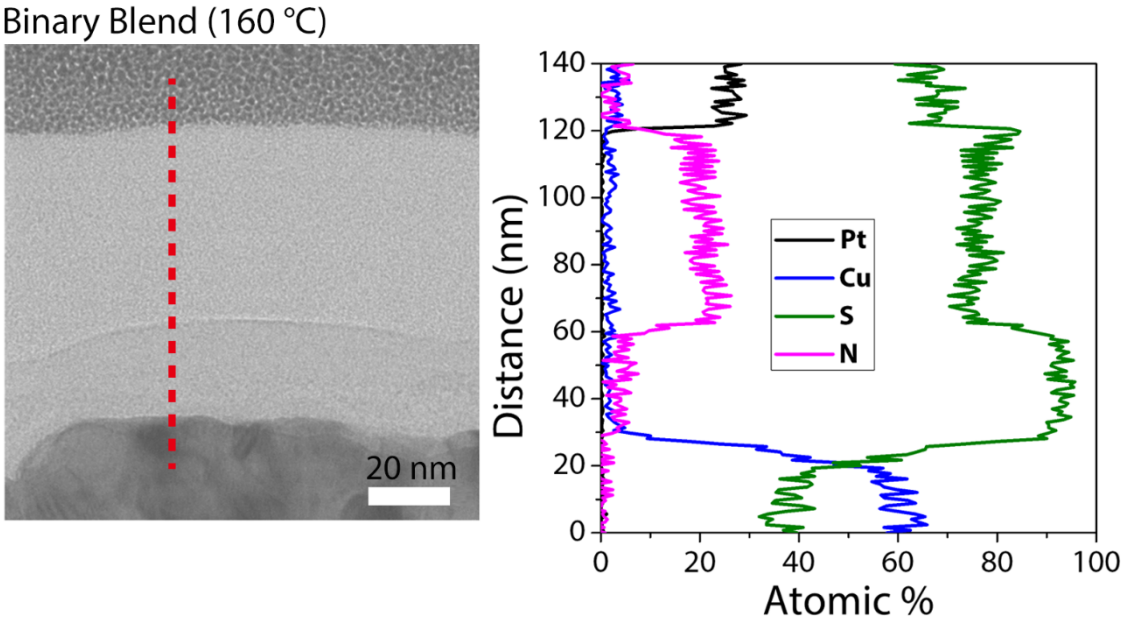

Figure S9. A cross-sectional STEM image and its corresponding electron dispersive spectroscopy (EDS) line profiles of the binary blend film annealed at 160 °C, respectively. Each red dotted line indicates the position of the EDX line scan.