Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

17% Efficiency in All-Small-Molecule Organic Solar Cells Enabled by Nanoscale Phase Separation with Hierarchical Branched Structure

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Materials and Synthesis

B1 was synthesized according to the previously reported method.[1] The acceptor BO-2Cl, BO-4Cl and the interface layer PNDI-F3N-Br were commercially available from Solarmer Material Inc. PEDOT:PSS, Clevios™ P VP AI 4083, was commercially available from Heraeus. The other materials and solvent were common commercial level and used as received.

Solar cell device fabrication

The photovoltaic devices were fabricated with a conventional structure of ITO/PEDOT:PSS/BHJ/PF3N-Br/Ag. ITO-coated glass was purchased from South China Xiang's Science & Technical Company Limited. PEDOT:PSS (4083) was purchased from the Clevios™. PNDIT-F3N-Br were purchased from Solarmer Material Inc. PEDOT:PSS was diluted with the same volume of water. The fabrication process was performed under the following procedures: The ITO was ultrasonically cleaned with successive applications of detergent, deionized water, acetone and isopropanol twice. After drying, the substrates were treated with UV-ozone for 20 min, and then a 20 nm layer of PEDOT:PSS was spin-coated onto the ITO, and the ITO substrates were dried in an oven at 150°C for 15 min. The B1:BO-2Cl (D/A 1:1), B1:BO-2Cl:BO-4Cl [D/(A_1+A_2) 1:1] and B1:BO-4Cl (D/A 1:1) were dissolved in chloroform (CF) with a total concentration of 20 mg/mL and then stirred at room temperature for at least 4 hours. After spin-coating the active layer solutions at 3000 rpm for 30s to obtain a film thickness about 100 nm. Then the devices were treated with chlorobenzene (CB) Solvent vapor annealing (SVA) 50s in a 60 mm diameter dish. And then PF3N-Br methanol solution (0.5 mg/mL) was spin-coated at 2000 rpm on the active layer.

Finally, about 100-nm-thick Ag was deposited onto the active layer under vacuum at a pressure of 3×10^{-4} Pa, The areas of the mask is 0.062 cm^2 in our laboratory. The area of the mask is 0.06169 cm^2 in NIM. After the spin-coating of PEDOT:PSS, next steps were carried out in the glovebox of nitrogen atmosphere. The *J*-V tests were carried out using the solar simulator (SS-F5-3A, Enlitech) in glove box. The radiative intensity (AM 1.5 G spectrum, 100 mW cm^{-2}) was calibrated by the standard silicon solar cell.

Instruments and Measurements

Absorption spectra of the materials were measured on a Hitachi UH5300 spectrophotometer. Cyclic voltammogram (CV) measurements were conducted on a CHI650D electrochemical workstation using glassy carbon as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The AFM height and phase images were acquired on a Bruker Nanoscope V AF microscope in tapping mode in the air. The external quantum efficiency (EQE) data were obtained by using the solar-cell spectral-response measurement system (QE-R, Enlitech). TEM images were obtained on a Tecnai G2 F20 U-TWIN TEM instrument. The GIWAXS data were obtained on a XEUSS SAXS/WAXS SYSTEM (XENOCS, FRANCE) at the National Center for Nanoscience and Technology (NCNST, Beijing). Differential scanning calorimetry (DSC) measurements were tested by DSC Q100 V9.0 Build 275 analyzer under purified nitrogen gas flow with a 10 °C min^{-1} heating rate.

Transient absorption (TA) spectroscopy

Femtosecond TA measurements were performed on an Ultrafast Helios pump-probe system in collaboration with a regenerative amplified laser system from Coherent. An 800 nm pulse with a repetition rate of 1kHz, a length of 100 fs, and an energy of 7 mJ/pluse, was generated by an Ti:sapphire amplifier (Astrella, Coherent). Then the 800 nm pulse was separated into two parts by a beam splitter. One part was coupled into an optical parametric amplifier (TOPAS, Coherent) to generate the pump pulses at 850 nm or 400 nm. The other part was focused onto a sapphire plate and a YAG plate to generate white light supercontinuum as the probe beams with spectra covering 750-1600 nm. The time delay between pump and probe was controlled by a motorized optical delay line with a maximum delay time of 8 ns. The samples films were spin-coated onto the 1 mm-thick quartz plates and are encapsulated by epoxy resin in nitrogen-filled glove box to resist water and oxygen in the air. The pump pulse is chopped by a mechanical chopper with 500 Hz and then focused on to the mounted sample with probe beams. The probe beam was collimated and focused into a fiber-coupled multichannel spectrometer with CCD sensor. The energy of pump pulse was measured and calibrated by a power meter (PM400, Thorlabs).

Time-resolved photoluminescence (TRPL) spectroscopy

The TRPL decay spectra were measured using a time-resolved single-photon counting (TCSPC) system. An 800 nm pluse was generated by a Ti:sapphire amplifier (Maitai HP, SpectraPhysics) with frequency of 80 MHz and length of 35 fs. Then the 800 nm pulse was guided into a frequency doubler to generate 400 nm pulse. The pulse was separated by a beam splitter that one part worked as the TCSPC gate pulse, and the other part was coupled in to a confocal microscopy system (Nanofinder FLEX2, Tokyo Instruments, Inc.) to excited the samples. The PL photons was collected by a fiber connected spectrometer (DU420A-OE, ANDOR) to record the PL spectra, and the PL decay profiles were measured by the TCSPC module (SPC-150, Becker & Hickl). The pump power density was 8 μJ cm^{-2} and the laser spot diameter was 2 μm.

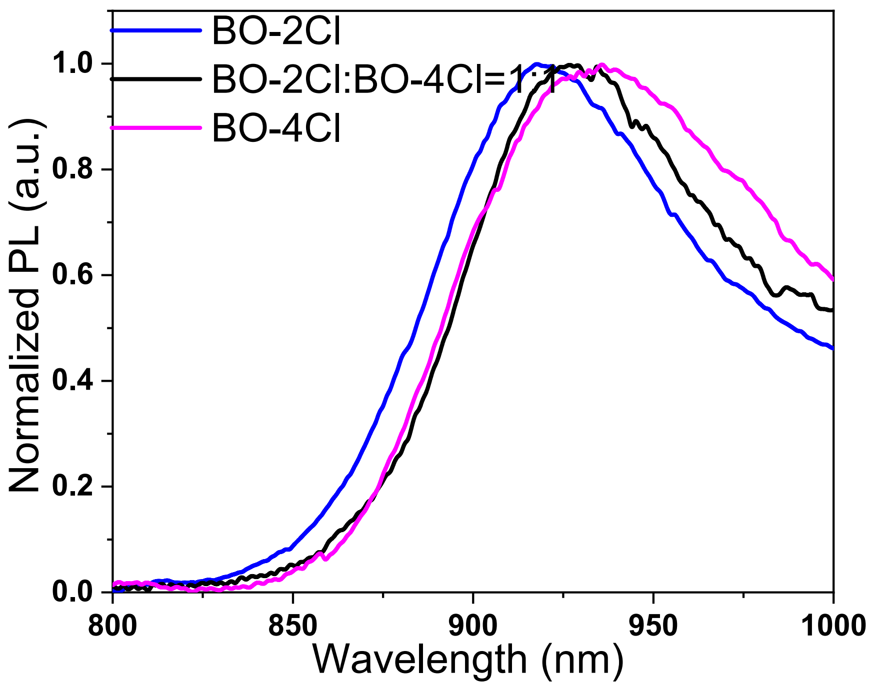

Figure S1. a) Normalized PL spectra of BO-2Cl, BO-2Cl:BO-4Cl=1:1, and BO-4Cl thin films.

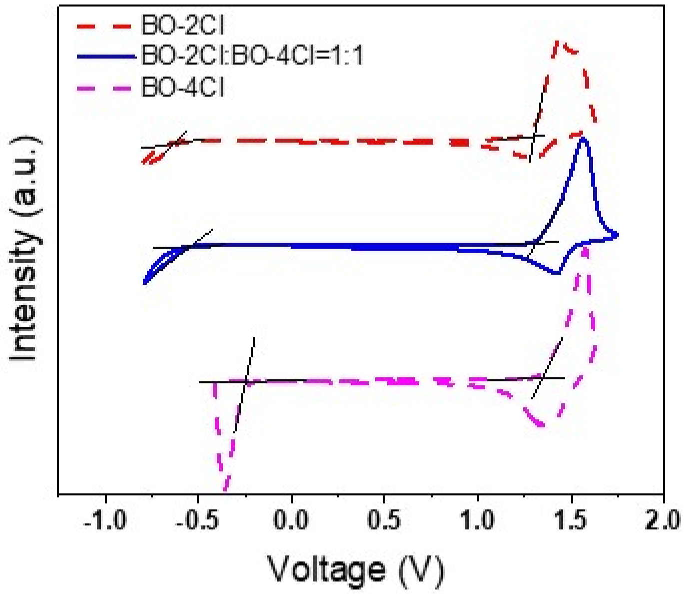

Figure S2. Electrochemical cyclic voltammetry curves of BO-2Cl, BO-2Cl:BO-4Cl=1:1, and BO-4Cl.

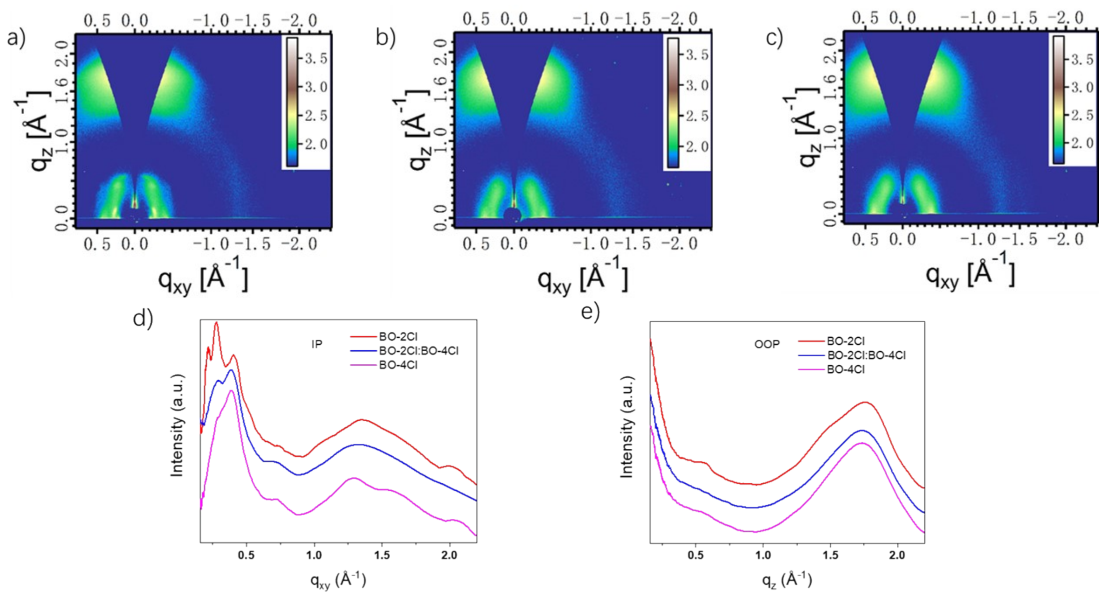

Figure S3. 2D GIWAXS patterns of a) BO-2Cl, b) BO-2Cl:BO-4Cl (1:1 by weight) and c) BO-4Cl. d) In-plane (IP) and e) out-of-plane (OOP) line-cut profiles of the GIWAXS data.

Appendix: Summary of the Report
Report No.: GXgf2021-10455
Client: INSTITUTE OF CHEMISTRY, CAS
Sample: Organic Solar Cells
Type/Model: Organic Solar Cells
DUT S/N: 43-M1-F-1
Manufacturer: INSTITUTE OF CHEMISTRY, CAS
Date of Test: 03/11/2021
Temperature Sensor/Control System: None
Environmental conditions: (23.1±1) C°, RH (41.2±2) %
Mask: An aperture area of 6.169 mm^2 (M1, Certificate No.: CDjc2019-6589)

The test has been conducted by the PV Metrology Lab of NIM (National Institute of Metrology, China). Measurement of irradiance intensity and all other measurements are traceable to the International System of Units (SI). Data in this report apply only at the time of the test for the sample. For more details, please refer to the text of the report.

Forward Scan：

Area (mm^2)	I_{sc}(mA)	V_{oc}(V)	P_{max}(mW)
6.169	1.595	0.844	1.040
I_{max}(mA)	V_{max}(V)	FF (%)	η (%)
1.445	0.720	77.3	16.9

I-V Characterization Methods:
JJF 1622-2017: Calibration Specification of Solar Cells：Photoelectric Properties
Secondary Reference Cell:
Device S/N: 81#; Device Material: Mono-Si
Solar Simulator:
Classification: AAA (Double-light source: Xeon and Halogen);
Total irradiance: 1000 W/m^2 based on I_{sc} of the above Secondary Reference Cell.

Figure S4. Summary of the certificate from NIM, China.

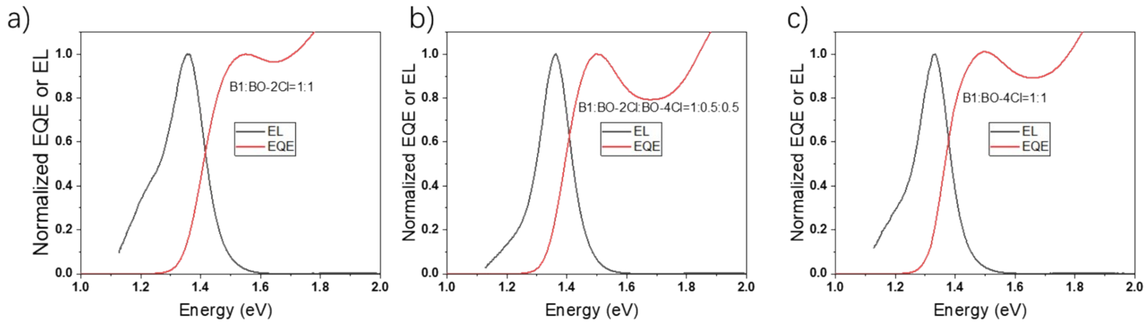

Figure S5. The bandgaps were determined from the crossing point between the EL and EQE spectra for B1:BO-2Cl, B1:BO-2Cl:BO-4Cl=1:1, and B1:BO-4Cl devices.

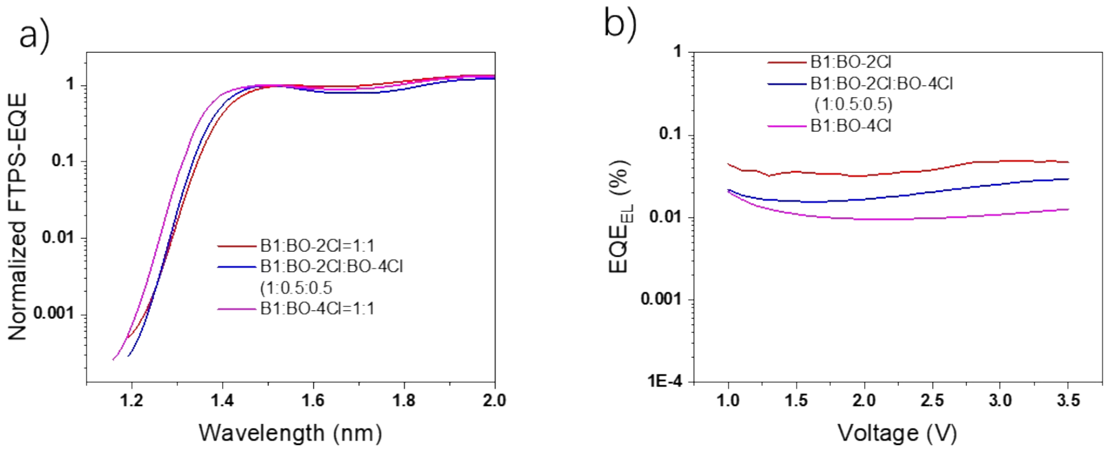

Figure S6. a) Highly sensitive EQE curves, b) EQE_{EL} curves of the B1:BO-2Cl, B1:BO-2Cl:BO-4Cl=1:1, and B1:BO-4Cl devices.

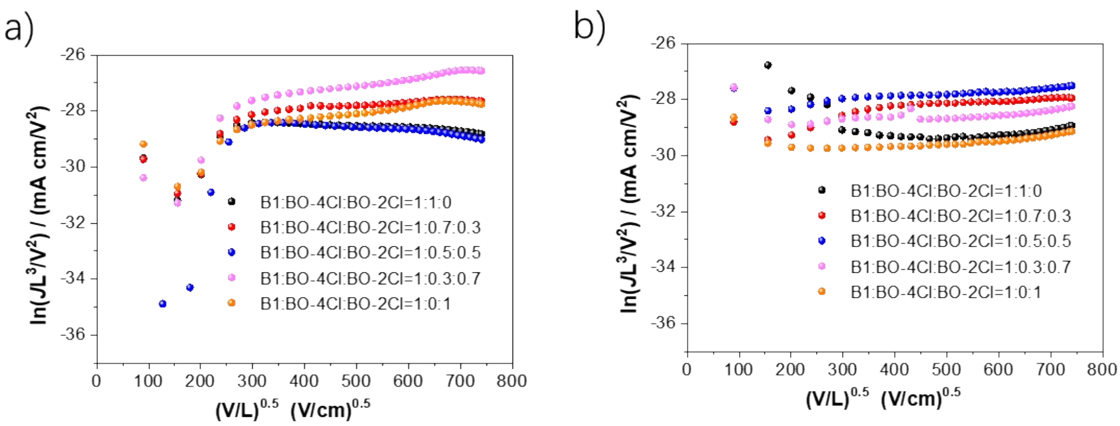

Figure S7. SCLC plots of a) hole and b) electron mobility for binary and ternary devices. The device structure for hole-only device is ITO/PEDOT:PSS/Active Layer/Au. The device structure for electron-only device is ITO/ZnO/Active Layer/Al. The film thickness of the active layer is consistent with the results of the best device.

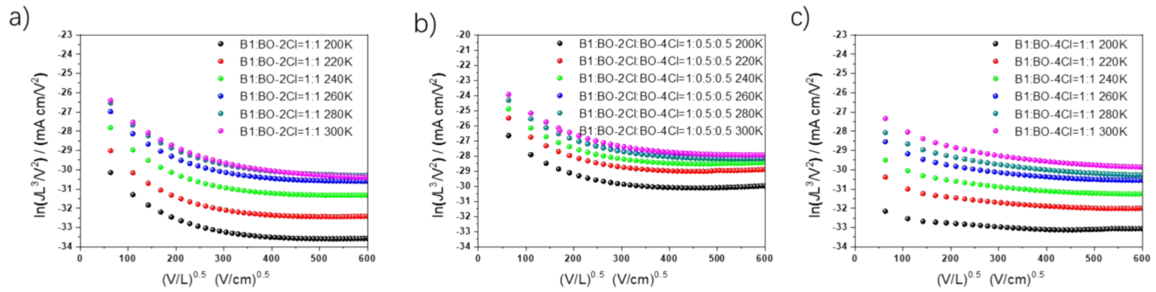

Figure S8. SCLC plots under different temperatures for a) B1:BO-2Cl, b) B1:BO-2Cl:BO-4Cl, and c) B1:BO-4Cl devices. Devices structure are ITO/ZnO/Active Layer/Al.

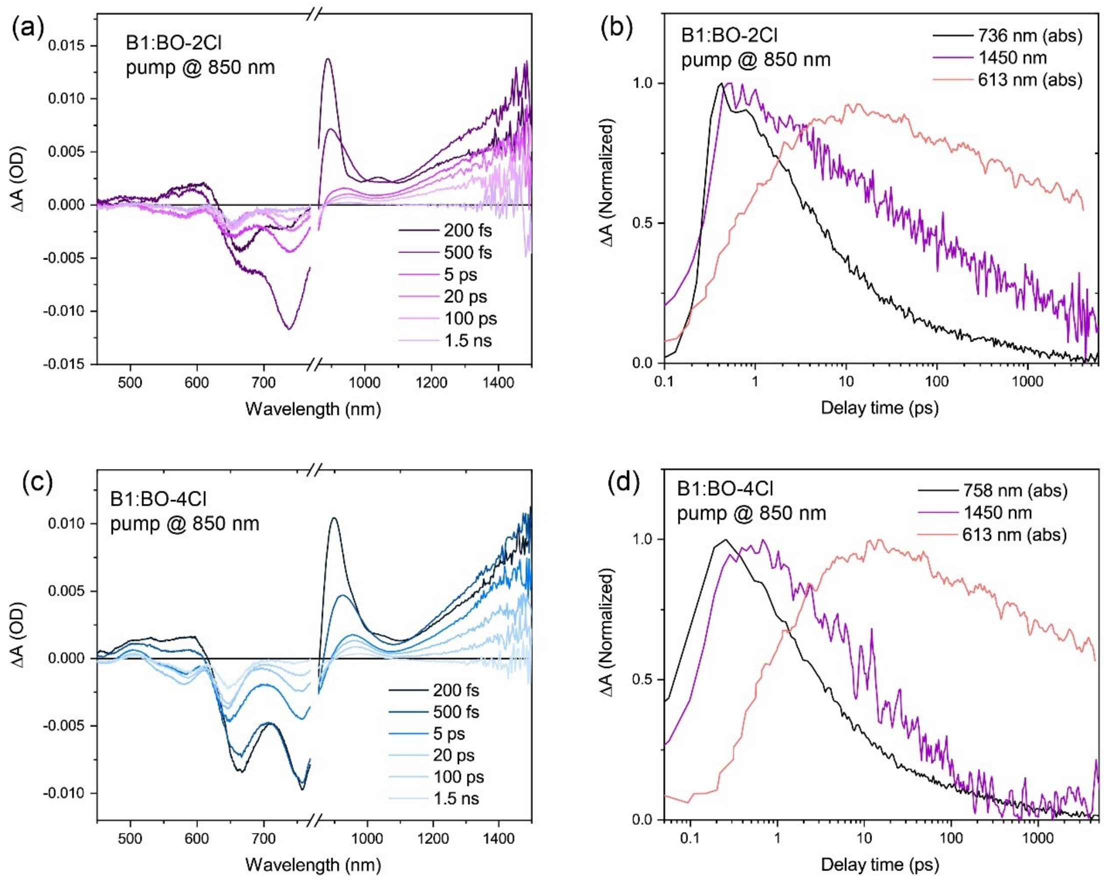

Figure S9. TA characterizations of B1:BO-2Cl and B1:BO-4Cl binary films pumped at 850 nm. (a) The TA spectra of B1:BO-2Cl film at different time delays. (b) The hole transfer dynamics in B1:BO-2Cl film. (c) The TA spectra of B1:BO-4Cl film at different time delays. (d) The hole transfer dynamics in B1:BO-4Cl film.

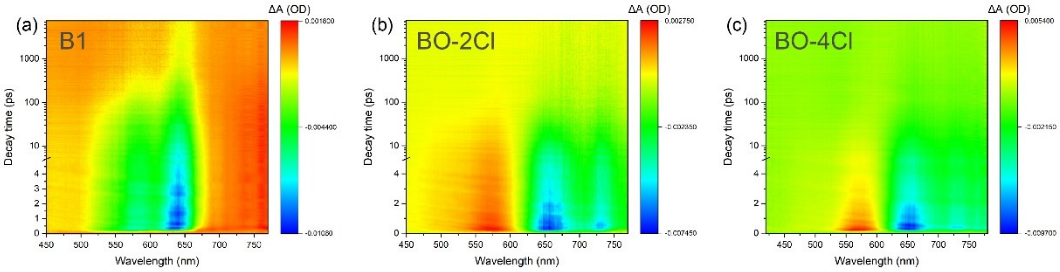

Figure S10. TA 2D plots of (a) B1, (b) BO-2Cl, and (c) BO-4Cl neat films pumped at 400 nm. It can be noticed that the donor signals are severed overlapped with the acceptor signals. In the hole transfer characterization, a relative pure B1 GSB signal at 613 nm was founded in the ternary and binary blends, and was selected for further analysis and comparison.

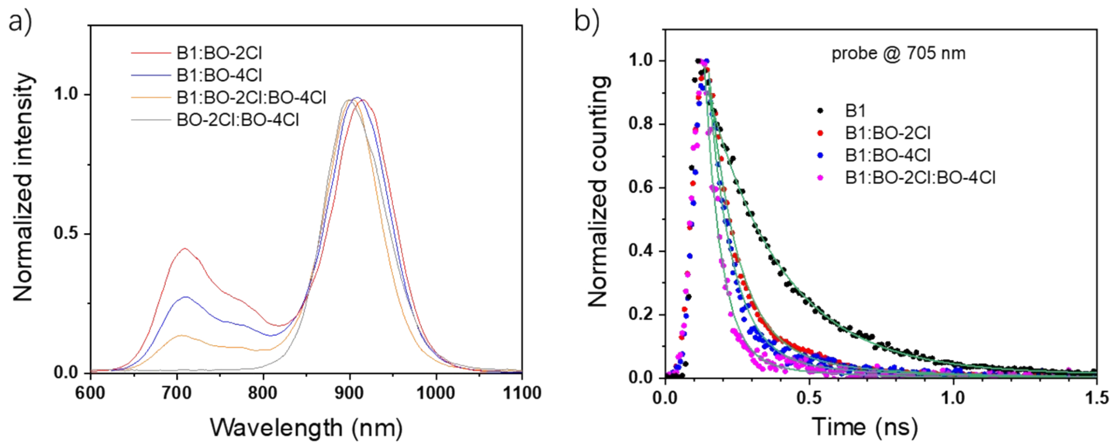

Figure S11. a) PL spectra of the B1:BO-2Cl, B1:BO-4Cl, BO-2Cl:BO-4Cl, and B1:BO-2Cl:BO-4Cl films. b) The TRPL decay kinetics of B1 neat film and binary and ternary blends probed at 705 nm. The averaged decay lifetimes are recorded inside.

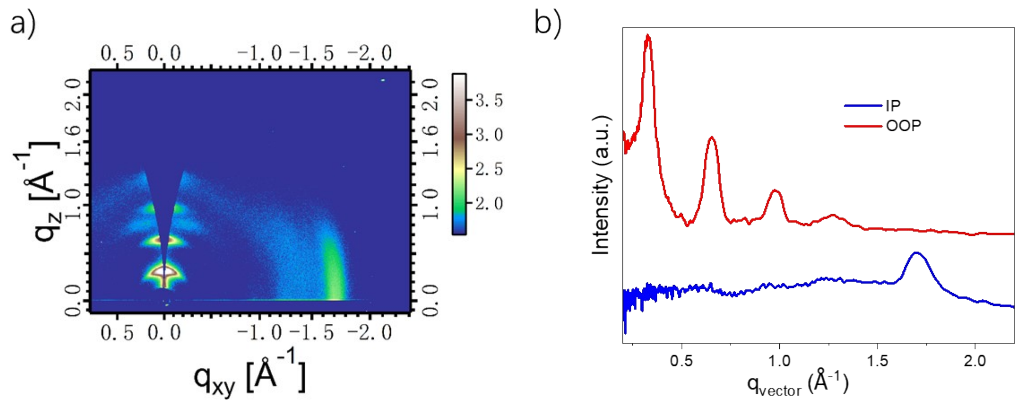

Figure 12. a) 2D GIWAXS pattern of pure B1. b) In-plane (IP) and out-of-plane (OOP) line-cut profiles of the GIWAXS data.

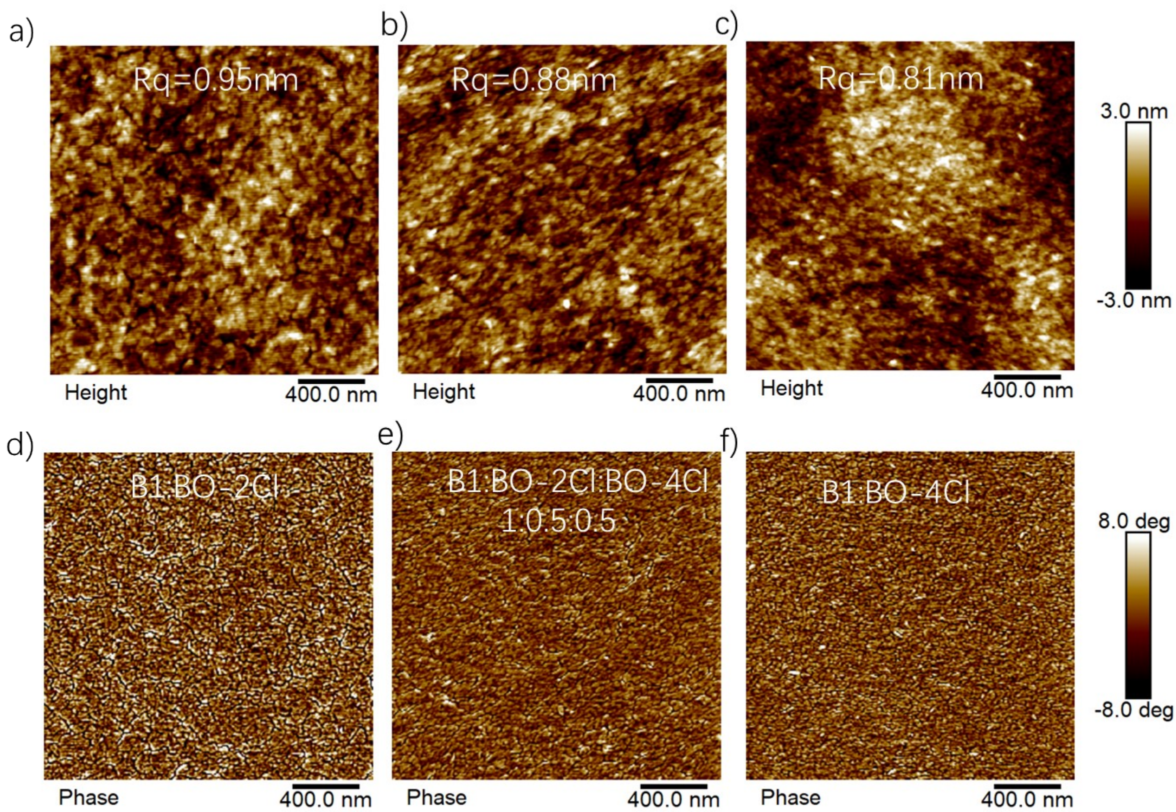

Figure S13. AFM height images of a) B1:BO-2Cl, b) B1:BO-2Cl:BO-4Cl=1:1, and c) B1:BO-4Cl blend films. AFM phase images of d) B1:BO-2Cl, e) B1:BO-2Cl:BO-4Cl=1:1, and f) B1:BO-4Cl blend films.

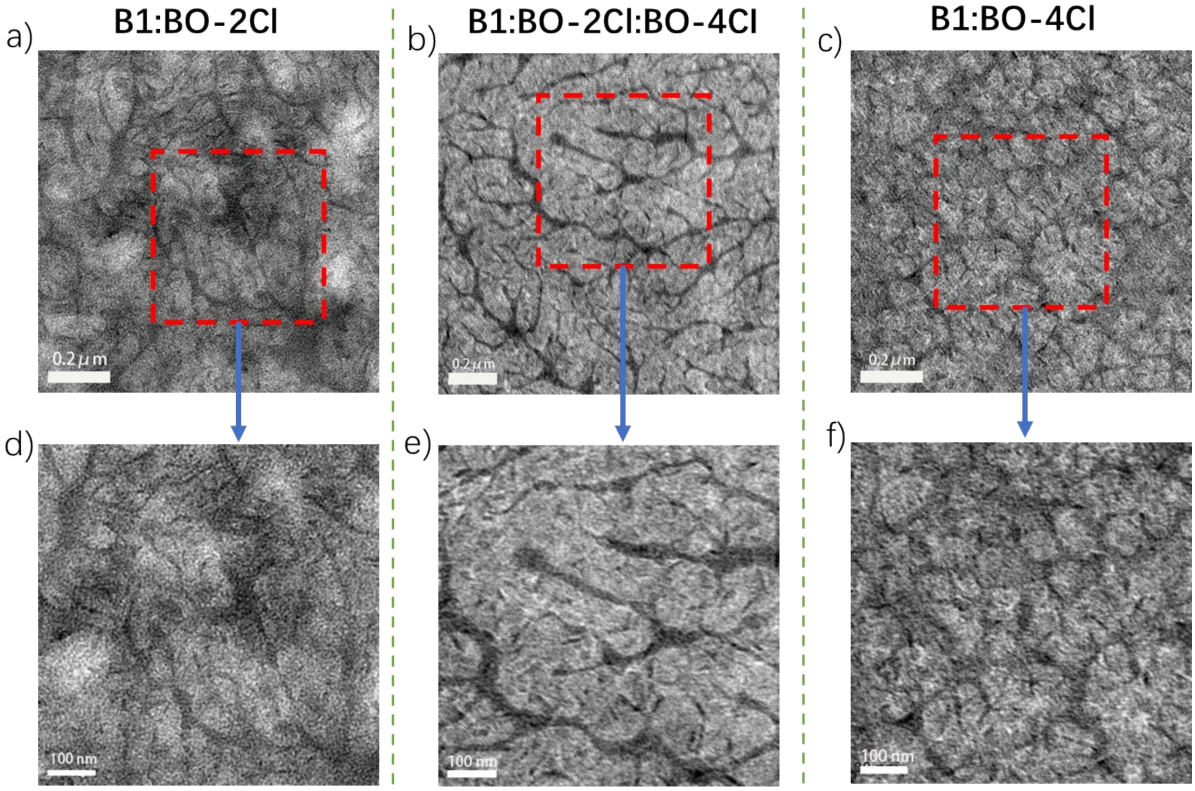

Figure S14. Different scale TEM images of a, d)B1:BO-2Cl, b, e) B1:BO-2Cl:BO-4Cl and c, f) B1:BO-4Cl blends.

Table S1. Detailed energy losses of the three OPV cells.

Active layer	E_g (eV)	qV_{OC} (eV)	E_{loss} (eV)	ΔE_1 (eV)	ΔE_2 (eV)	ΔE_3 (eV)
B1:BO-2Cl	1.42	0.86	0.56	0.26	0.10	0.20
B1:BO-2Cl:BO-4Cl 1:0.5:0.5	1.41	0.84	0.57	0.26	0.09	0.22
B1:BO-4Cl	1.38	0.82	0.56	0.26	0.06	0.24

Table S2. Fitting parameters for the TRPL decay curves.

Active layer	τ_1 (ps)	A_1 (%)	τ_2 (ps)	A_2 (%)	τ_m (ps)
B1	259.83	100	\	\	259.83
B1:BO-2Cl	99.97	91.33	480.14	8.67	132.93
B1:BO-4Cl	84.28	98.48	72.99	1.51	84.11
B1:BO-2Cl:BO-4Cl	57.81	99.19	412.44	0.81	60.70

Reference

1. J. Qin, C. An, J. Zhang, K. Ma, Y. Yang, T. Zhang, S. Li, K. Xian, Y. Cui, Y. Tang, W. Ma, H. Yao, S. Zhang, B. Xu, C. He and J. Hou, Sci. China Mater., 2020, 63, 1142-1150.