

Molecular interaction induced dual fibrils towards organic solar cells with certified efficiency over 20%

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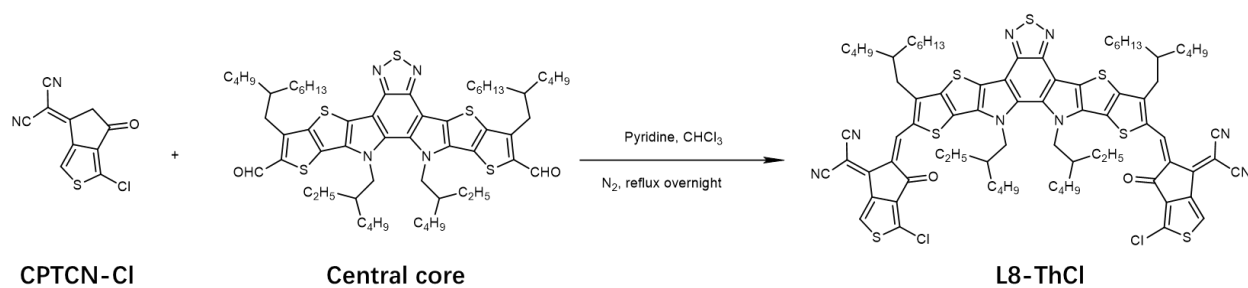
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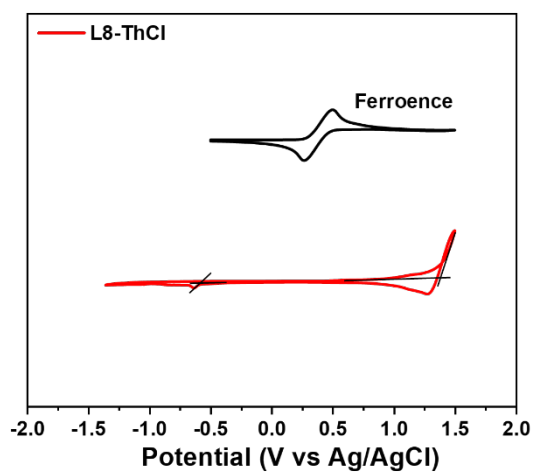
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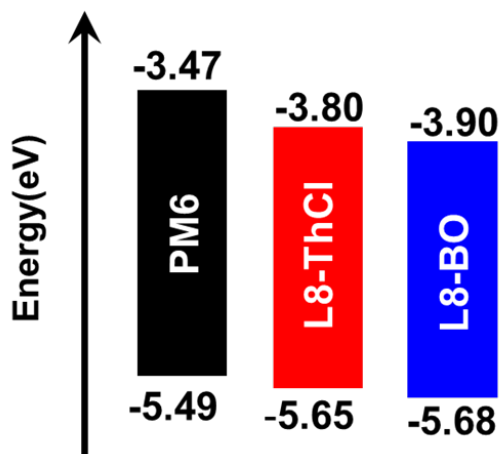
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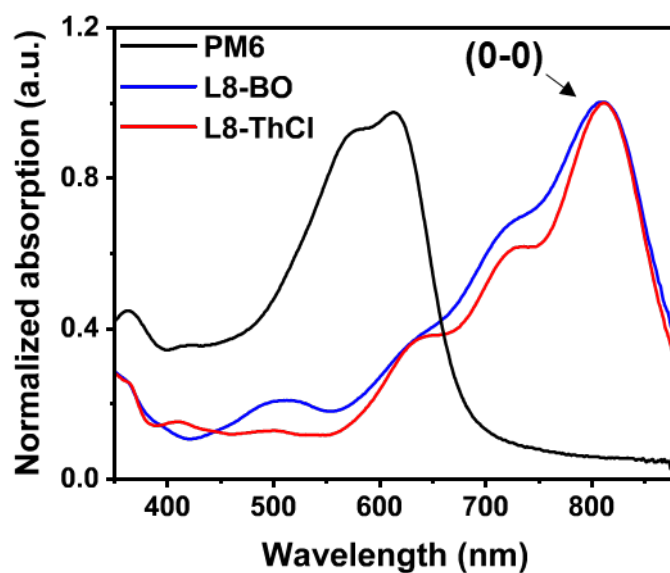
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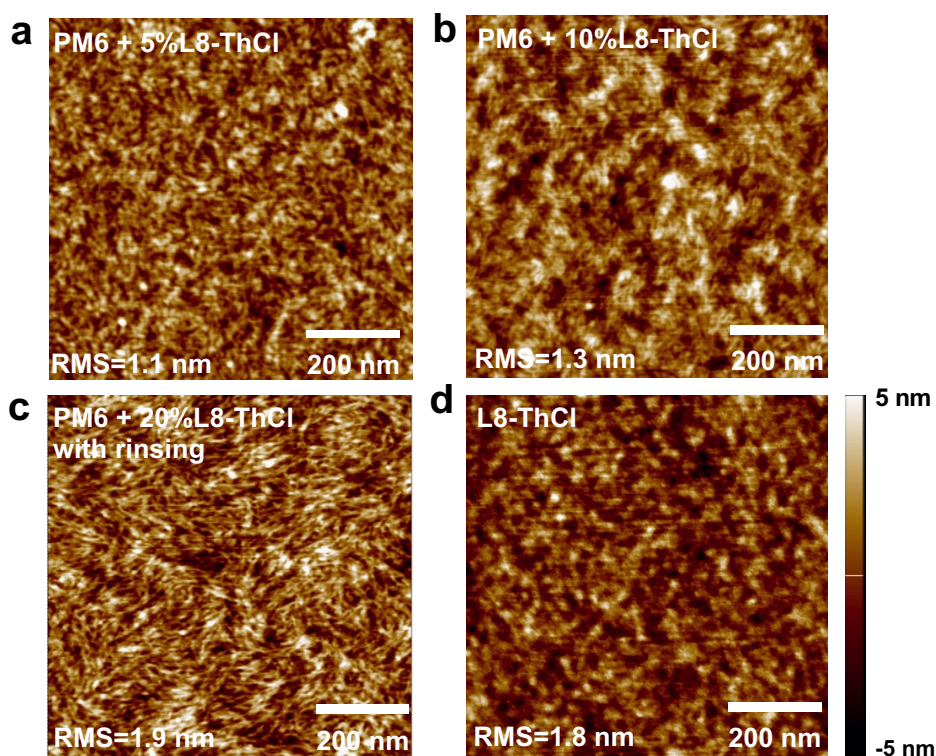
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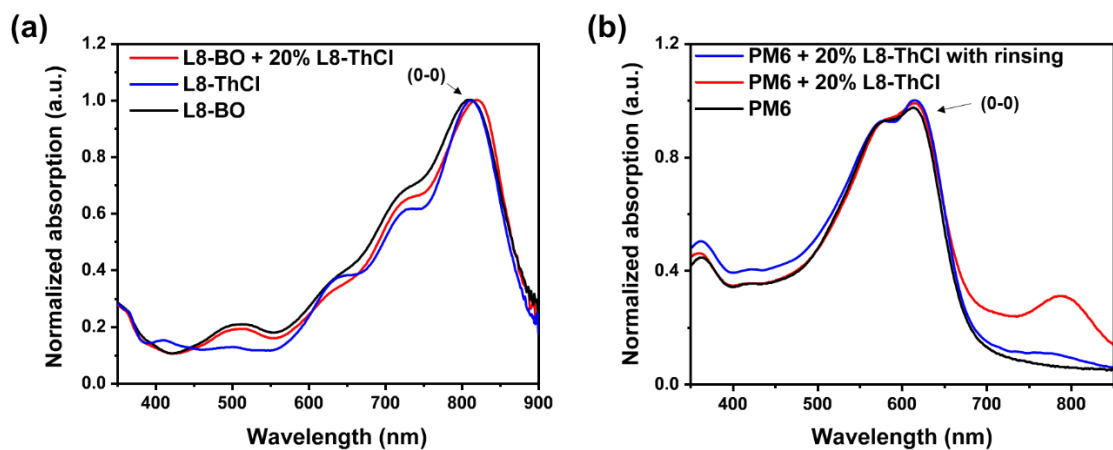
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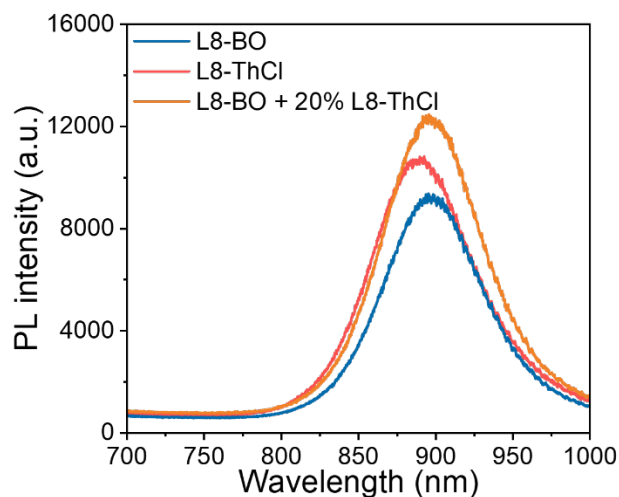
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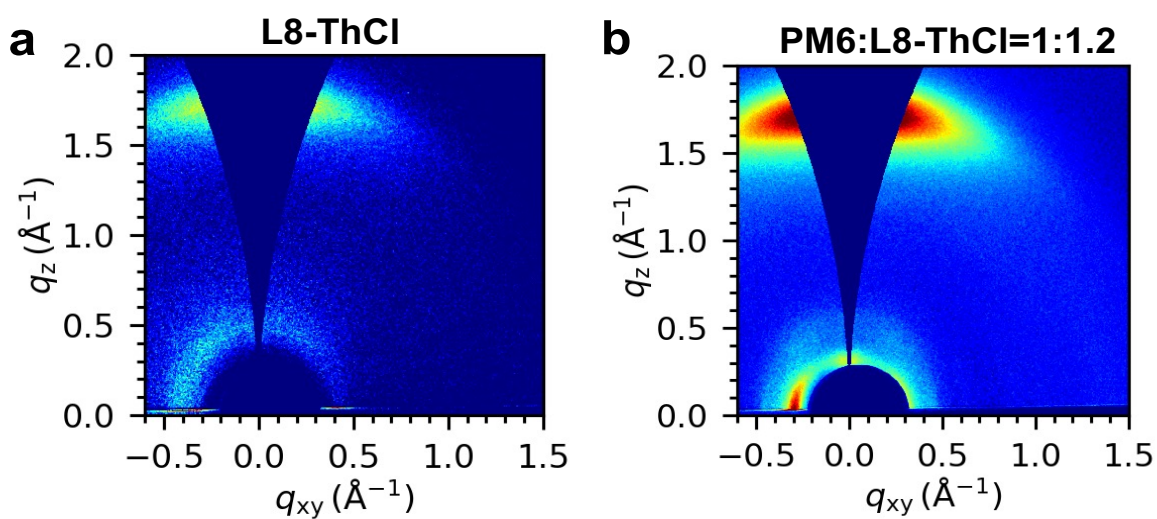
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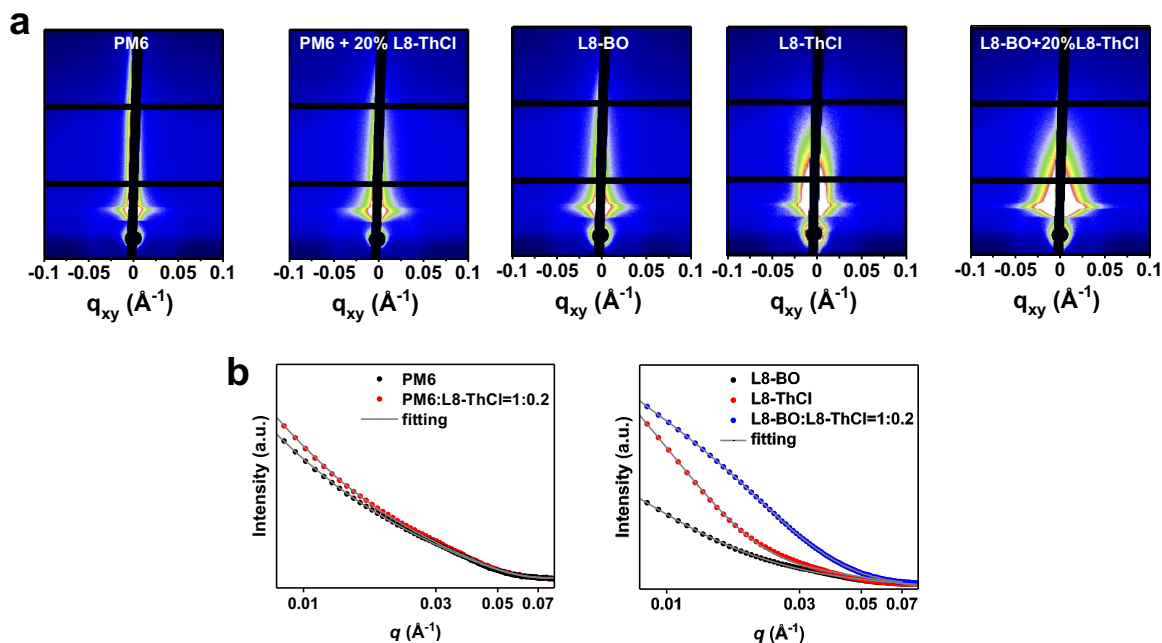
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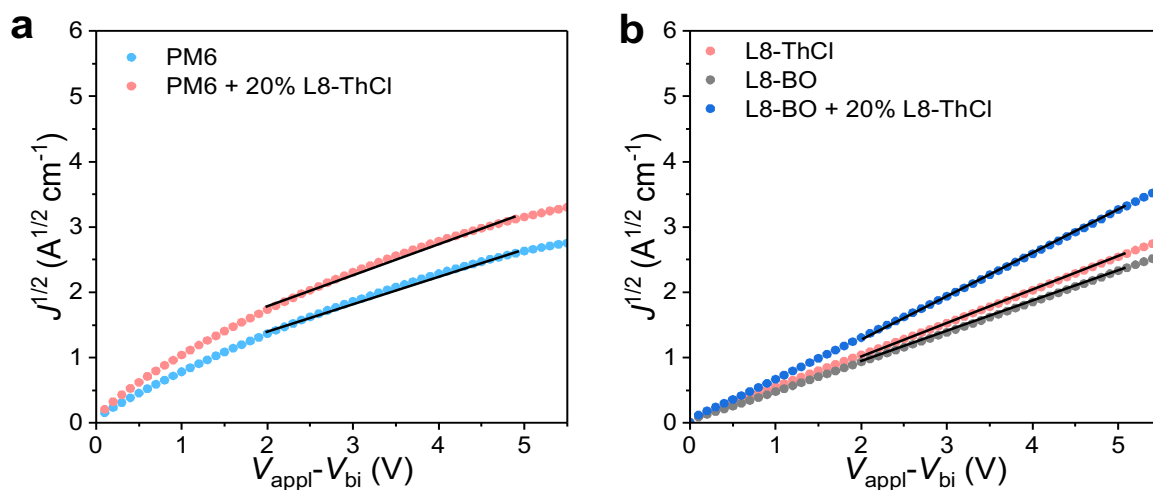
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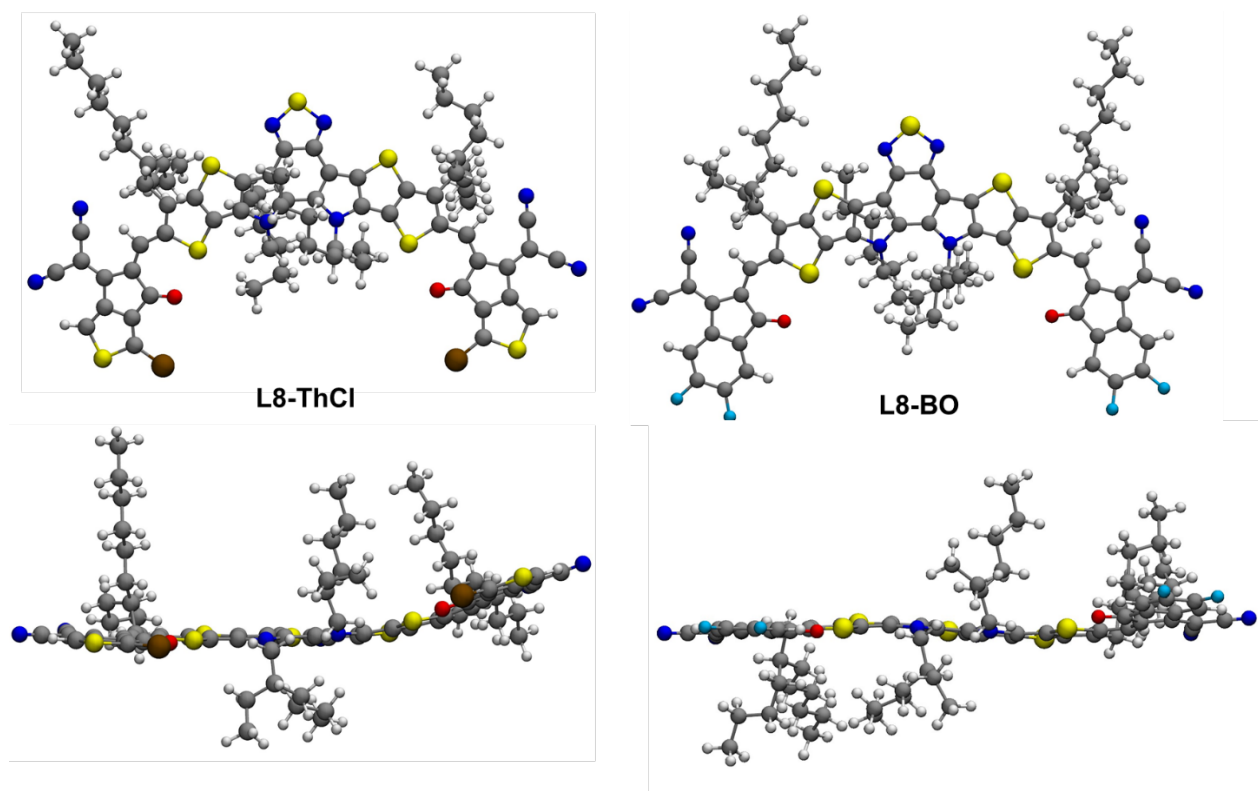
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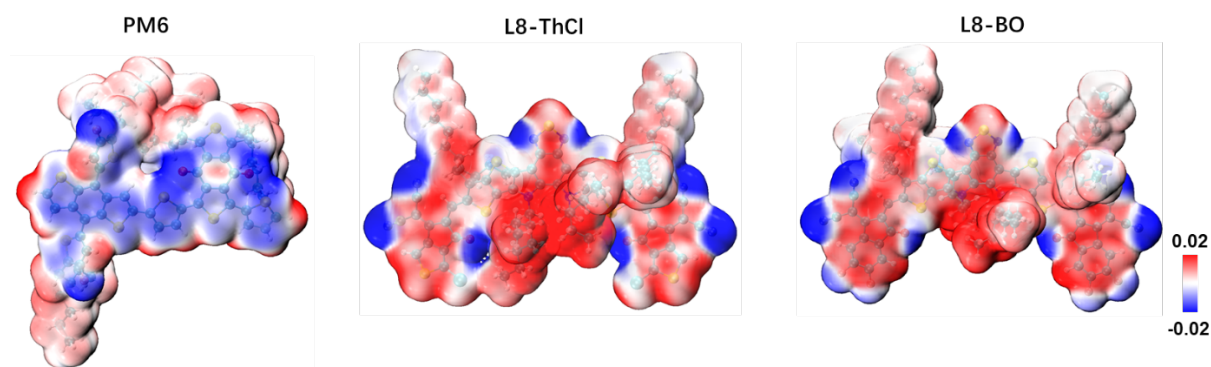
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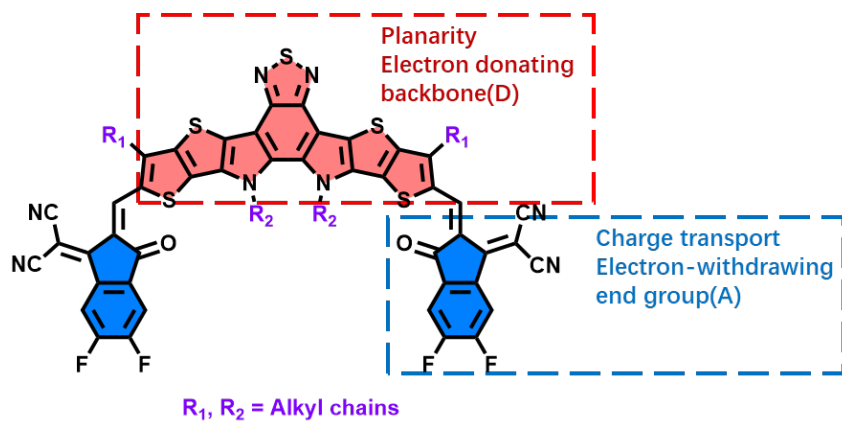
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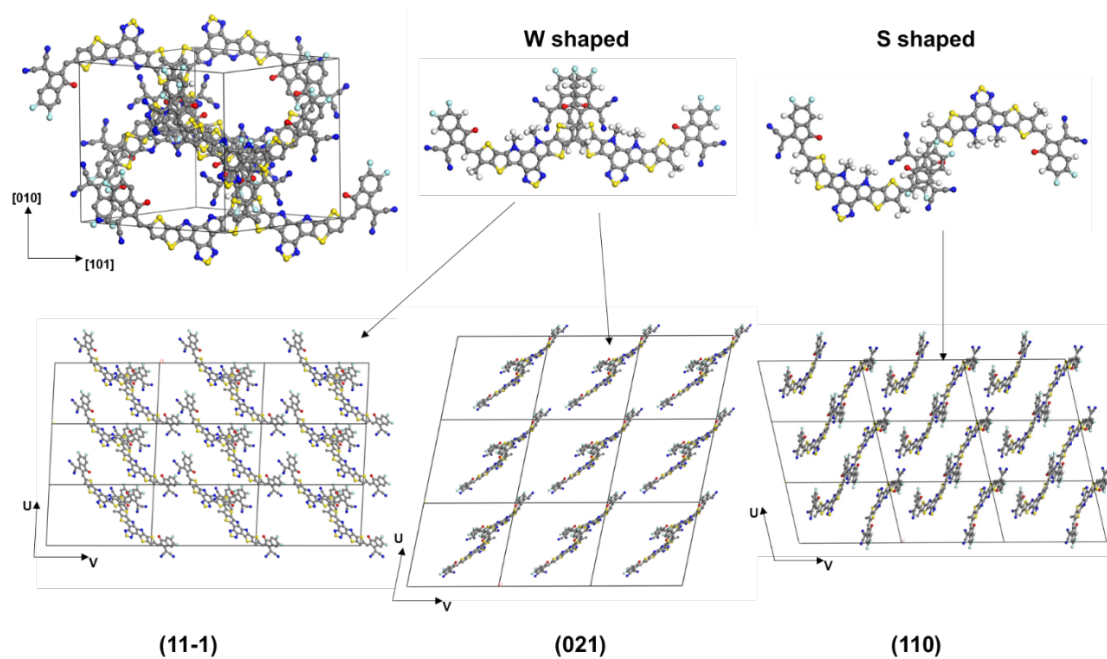
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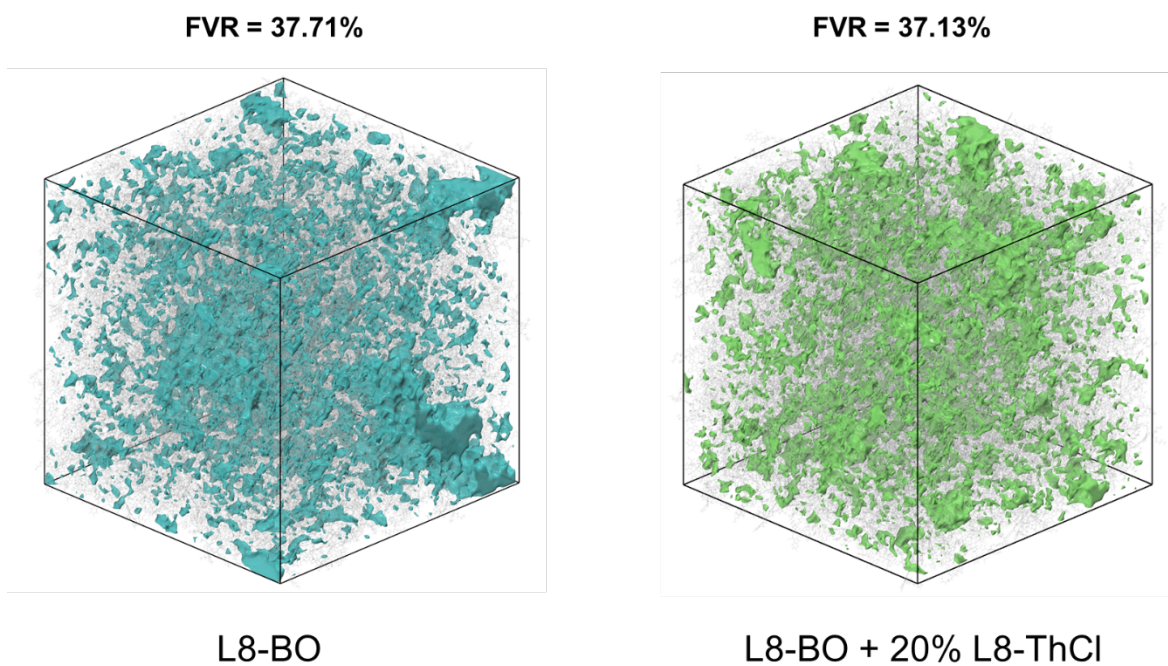
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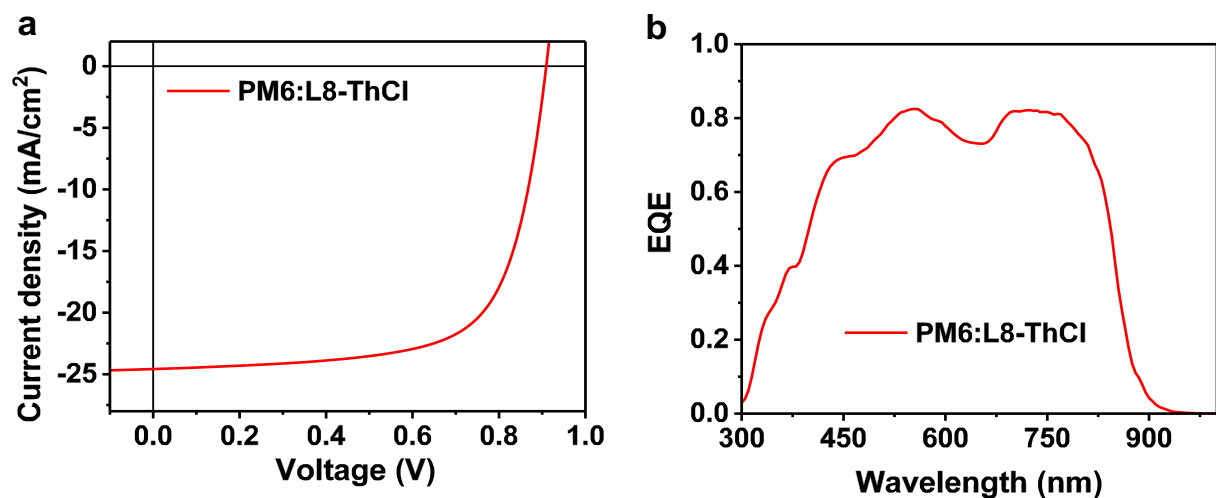
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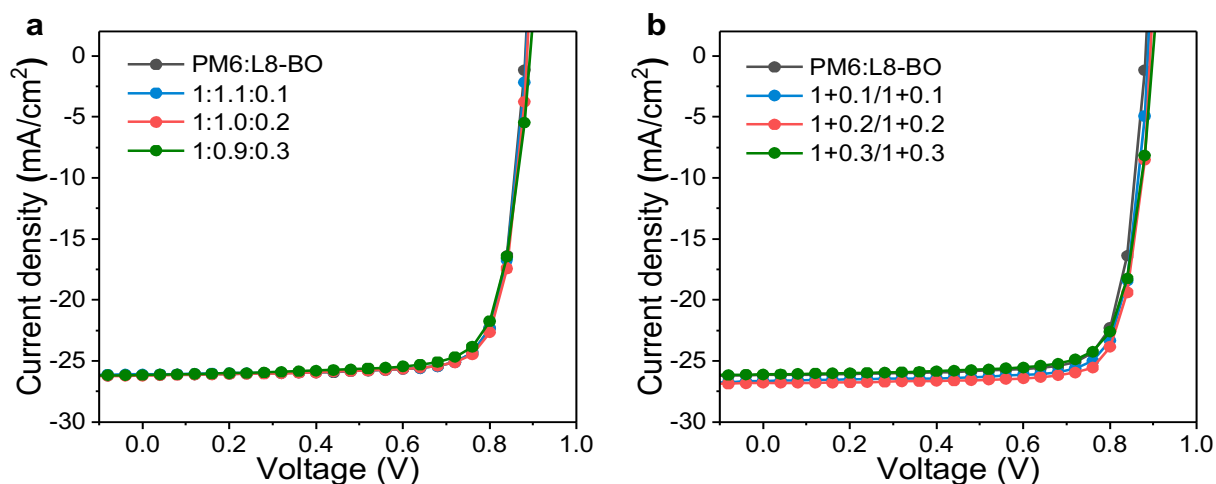
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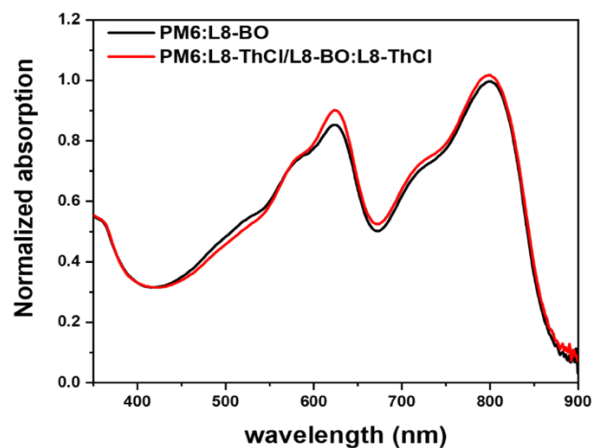
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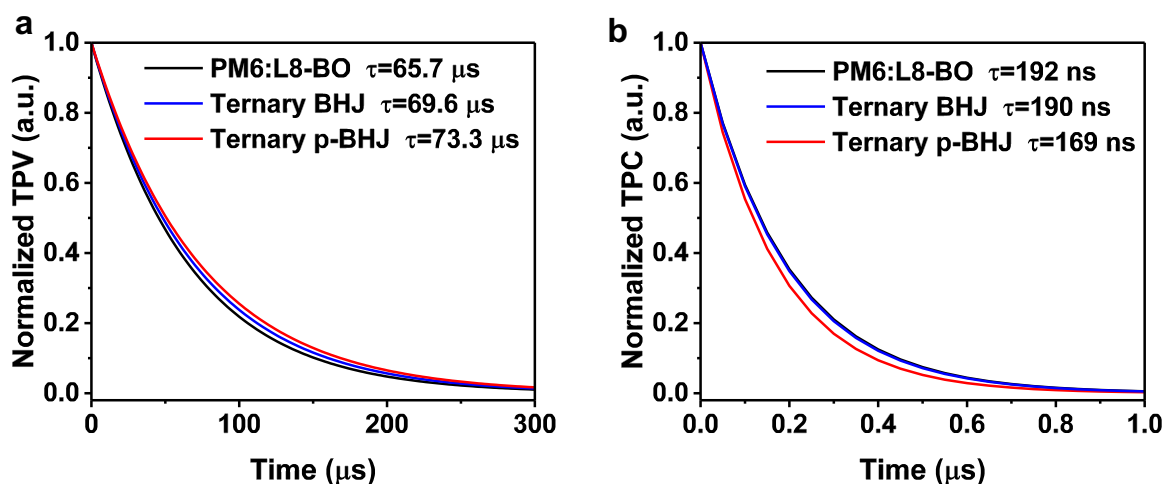
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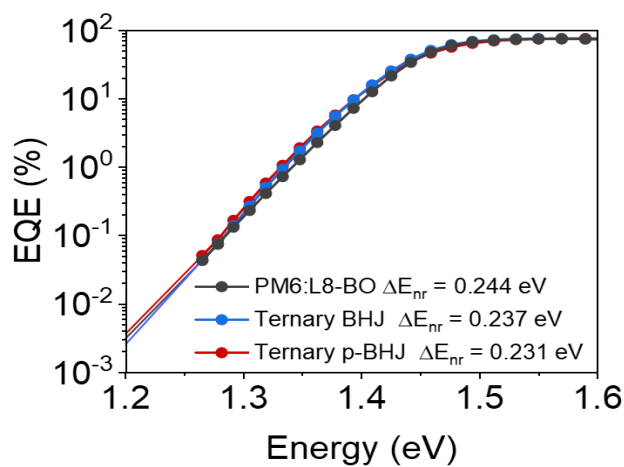
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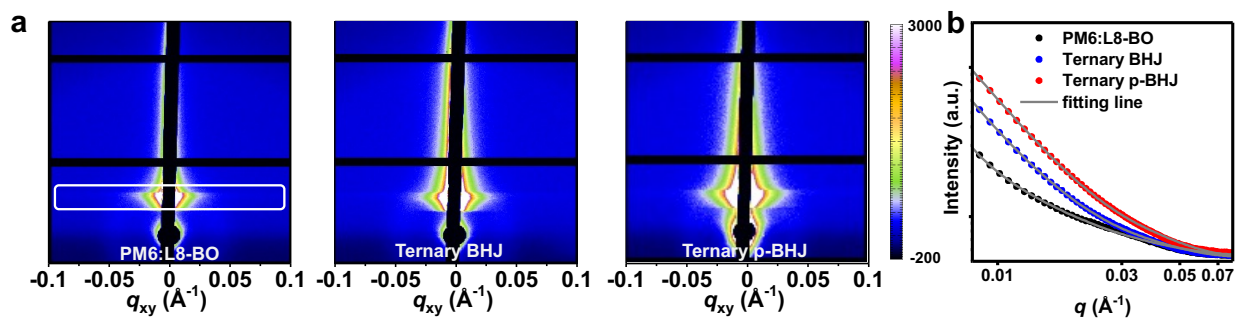
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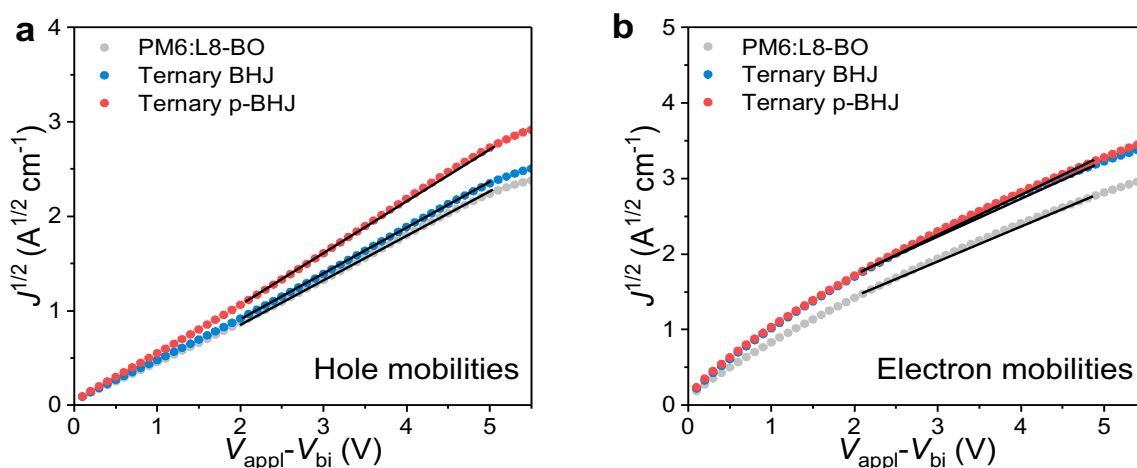
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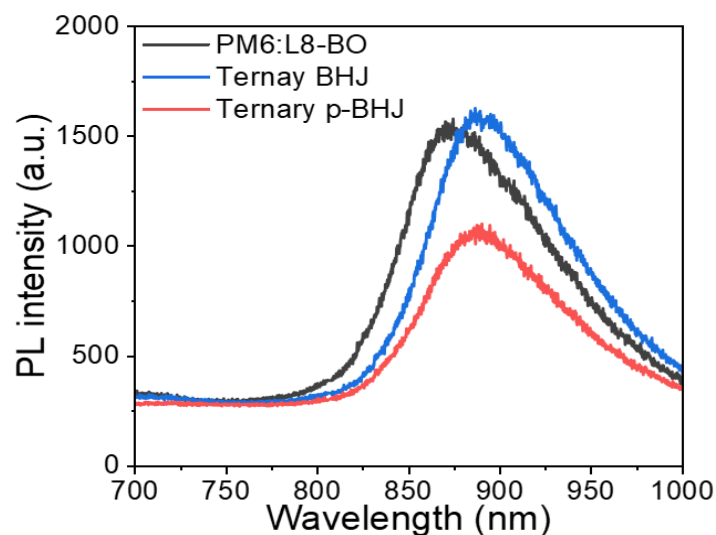
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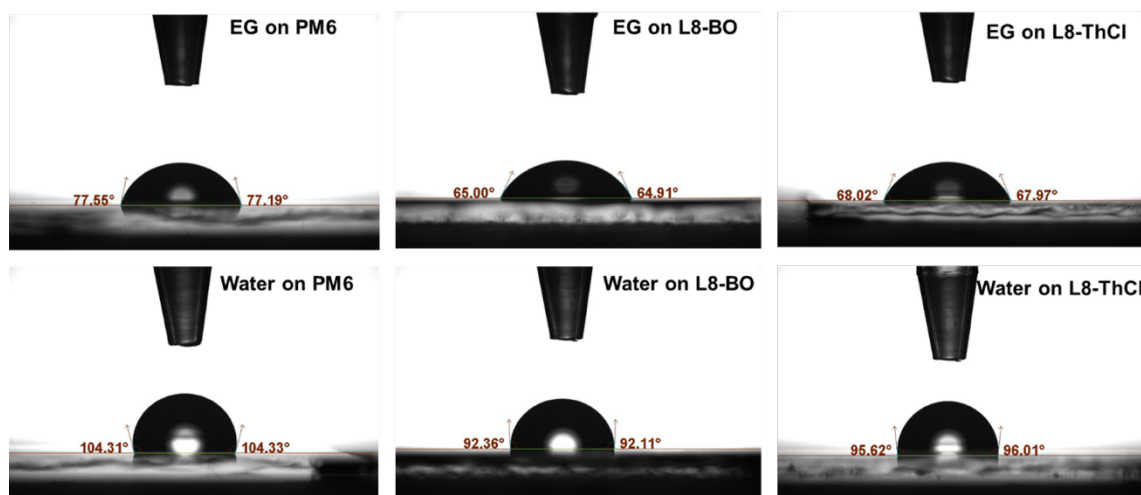
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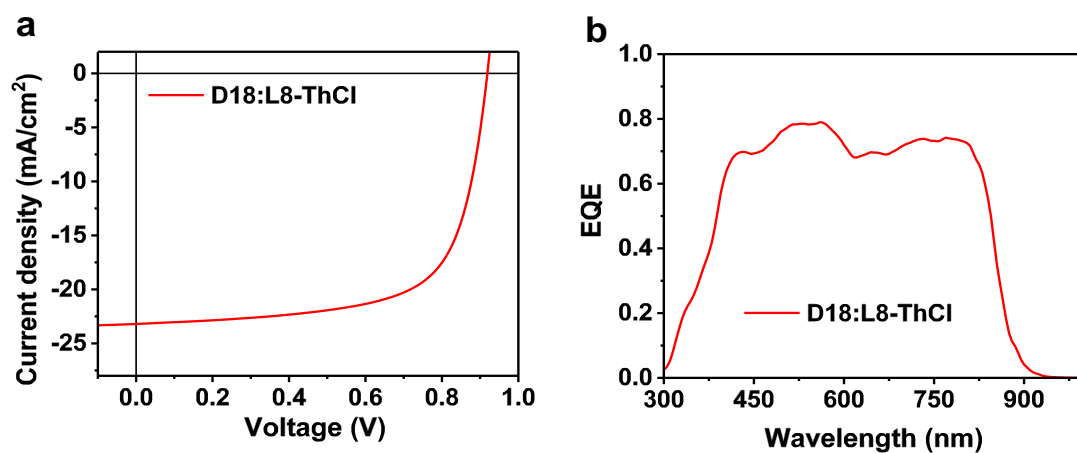
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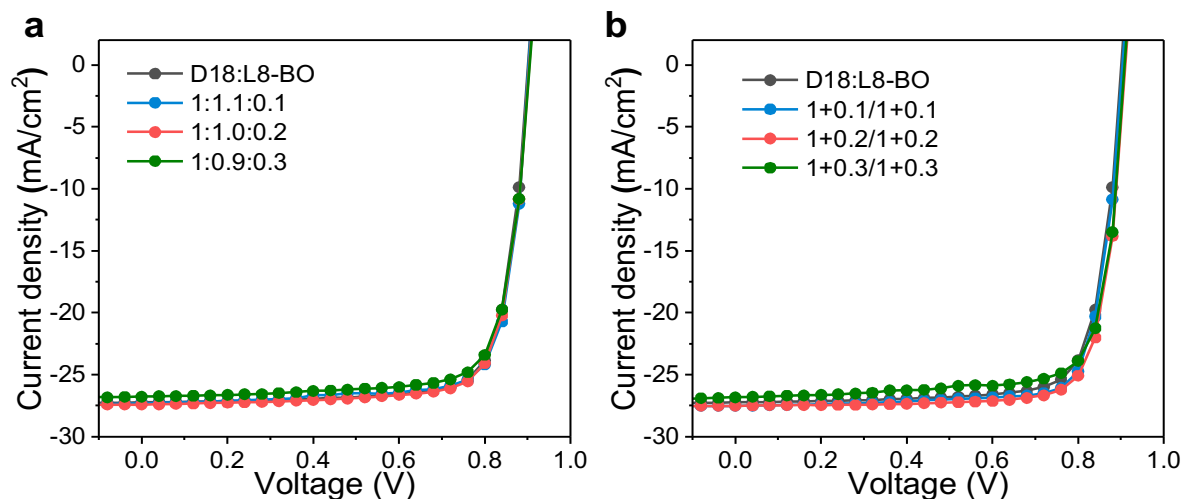
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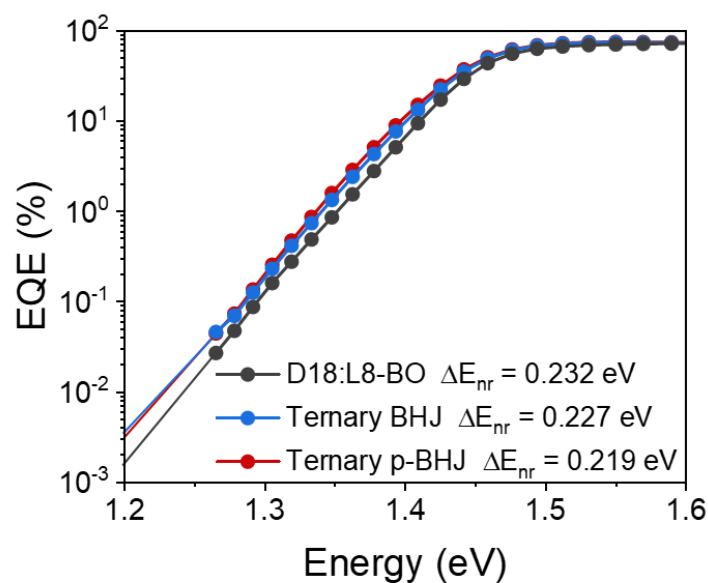
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Supplementary Fig. 26. J-V curves of D18:L8-BO OSCs. **a**, D18:L8-BO binary, and D18:L8-BO:L8-ThCl ternary (with different ratios) OSCs with D18, L8-BO and L8-ThCl directly mixed in the same solution. **b**, D18:L8-BO binary, and D18+L8-ThCl/L8-BO+L8-ThCl ternary (with different ratios) OSCs via layer-by-layer deposition.



Supplementary Fig. 27. FTPS-EQE spectra of D18 based devices and the calculated non-radiative energy losses (ΔE_{nr}).


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 TESTING
 CNAS L6673



Test Report



Test Report No. AGXB124W00262

Subject unit
Organic Solar Cell

Manufacturer
Wuhan University of Technology

Commission unit
Tao Wang

Inspection category
Commissioned inspection




Chengdu Institute of Product Quality Inspection Co., Ltd.

National Photovoltaic Product Quality

Inspection & Testing Center

Supplementary Fig. 28. Certification of optimal D18:L8-ThCl/L8-BO:L8-ThCl device by the National Photovoltaic Production Quality Inspection & Testing Center of China. All elements in this figure have received written approval from the copyright holder. (Page 1 of the report)

Chengdu Institute of Product Quality Inspection Co., Ltd.
National Photovoltaic Product Quality Inspection & Testing Center
TEST REPORT

Test Report No. AGXB124W00262

Page 1 of 2

Product Name	Organic Solar Cell	Trade Mark	/
Manufacture Date	15/05/2024	Model /Type	OPV-1
Sample No.	AGXB124W00262	Sample Grade	/
Sample Quantity	One piece	Sample State	/
Delivery Date	16/05/2024	Sample Delivered personnel	Tao Wang
Commission unit	Tao Wang	Manufacturer	Wuhan University of Technology
Commission unit address	School of Materials Science and Engineering, Wuhan University of Technology, No. 122 Luoshi Road, Wuhan 430070, P. R. China	Manufacturer Address	No. 122 Luoshi Road, Wuhan 430070, P. R. China
Commission unit Zip code	430070	Manufacturer Zip code	430070
Commission unit Tel.	18507131726	Manufacturer Tel.	18507131726
Center Address	No. 355, 2 nd Tengfei Road, Southwest Airport Economic Development Zone, Chengdu, Sichuan, P. R. China.		
Measurement Date	16/05/2024		
Methods	IEC 60904-1:2020 Photovoltaic devices-Part 1: Measurement of Photovoltaic Current-Voltage Characteristics.		
Test conclusion	This column blank.		
Remarks	Cell area: 0.0408 cm ² ; Original sample No. 5A4-1 .		
Approved by	陈皓楠	Reviewed by	邓雅
Measured by	游宗英		



Supplementary Fig. 29. Certification of optimal D18:L8-ThCl/L8-BO:L8-ThCl device by the National Photovoltaic Production Quality Inspection & Testing Center of China. All elements in this figure have received written approval from the copyright holder. (Page 2 of the report)

Chengdu Institute of Product Quality Inspection Co., Ltd.
National Photovoltaic Product Quality Inspection & Testing Center
TEST REPORT

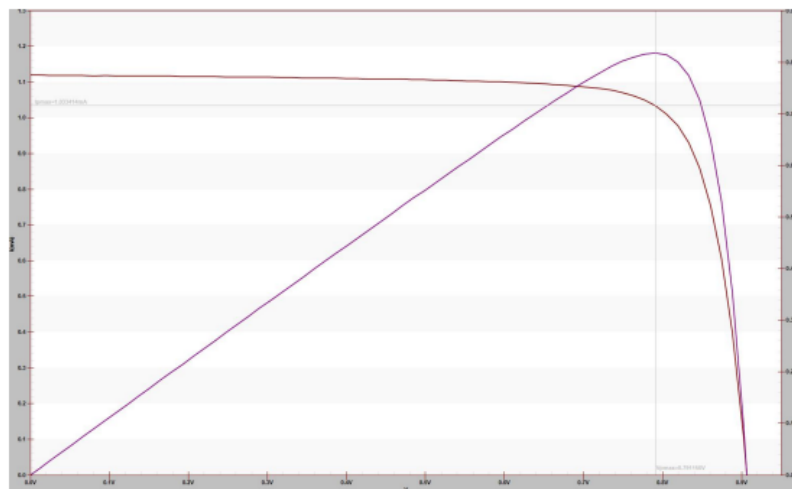
Test Report No. AGXB124W00262

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Test Results :

No.	Test item(s)	Unit	Results
1	Current-voltage characteristics measurement	---	---
1.1	Open-circuit voltage, V_{OC}	V	0.907
1.2	Short-circuit current, I_{SC}	mA	1.120
1.3	Maximum-power, P_{max}	mW	0.817
1.4	Maximum-power voltage, V_{p-max}	V	0.791
1.5	Maximum-power current, I_{p-max}	mA	1.033
1.6	Fill factor, FF	%	80.44
1.7	Conversion efficiency, η	%	20.02

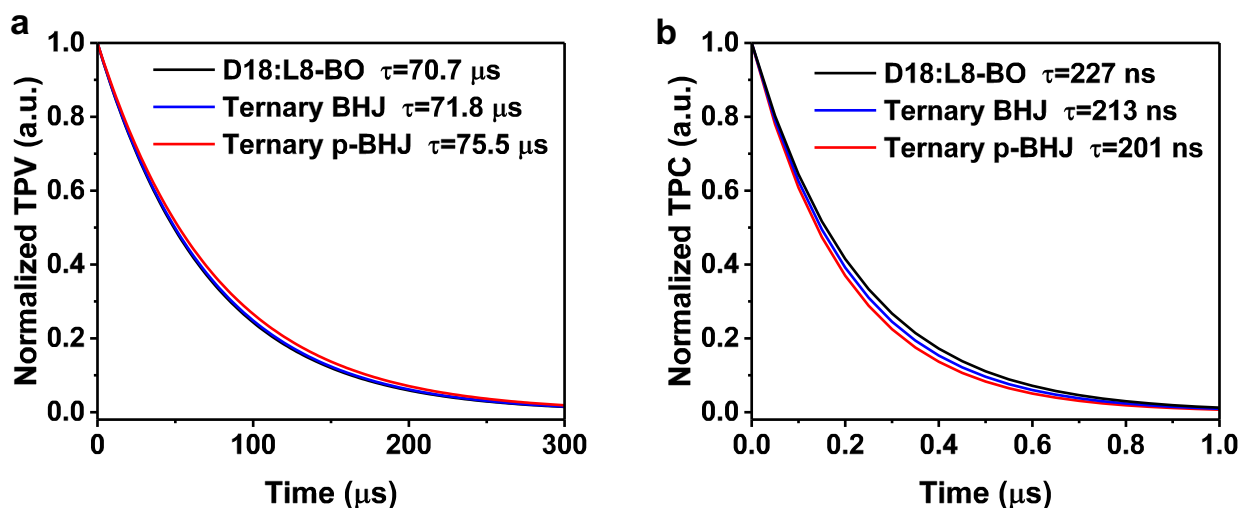
Current-voltage characteristics under STC



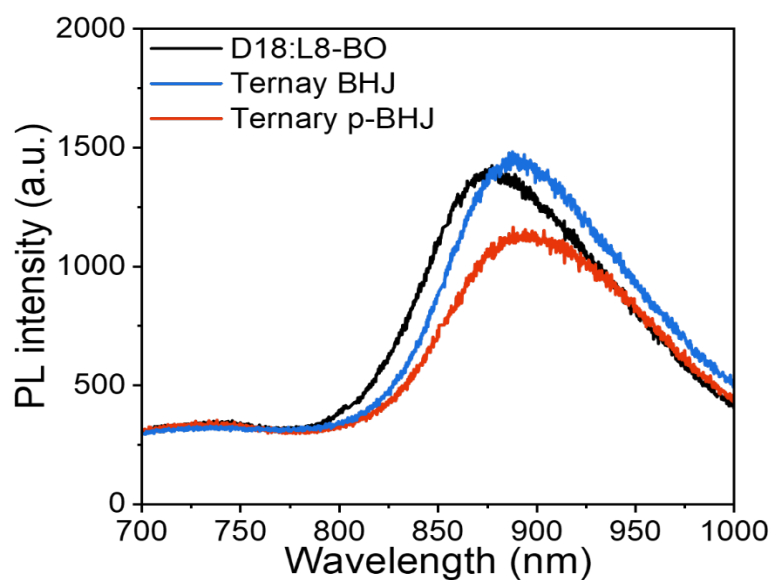
Remark: Sample was tested under the irradiation with a steady-state class calibrated AAA solar simulator (AM1.5-G 1000.0 W/m² based on mono-Si reference cell) at 25°C ± 1 °C. Designated area defined by thin metal aperture mask.

Blank

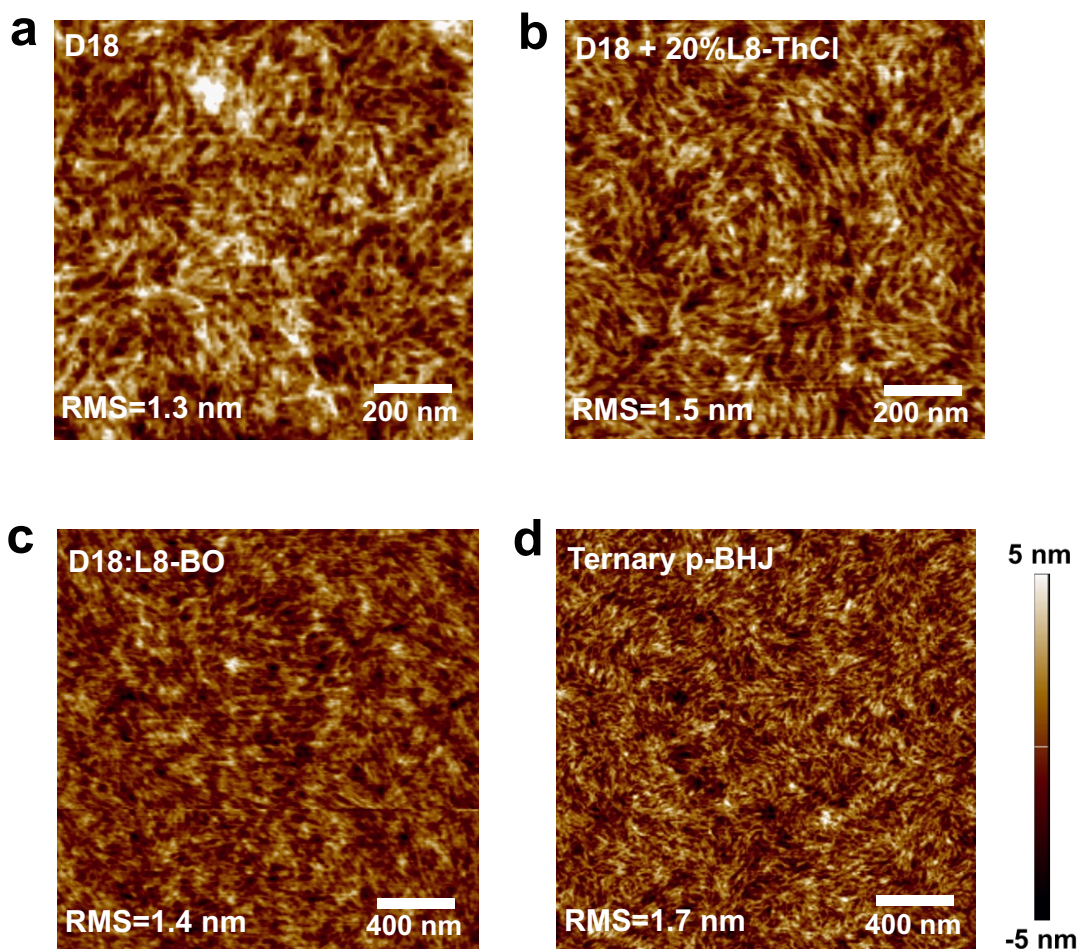
Supplementary Fig. 30. Certification of optimal D18:L8-ThCl/L8-BO:L8-ThCl device by the National Photovoltaic Production Quality Inspection & Testing Center of China. All elements in this figure have received written approval from the copyright holder. (Page 3 of the report)



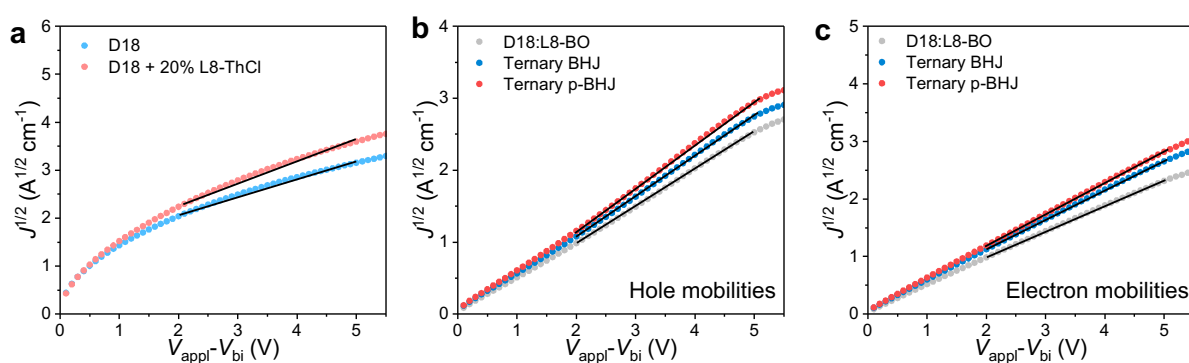
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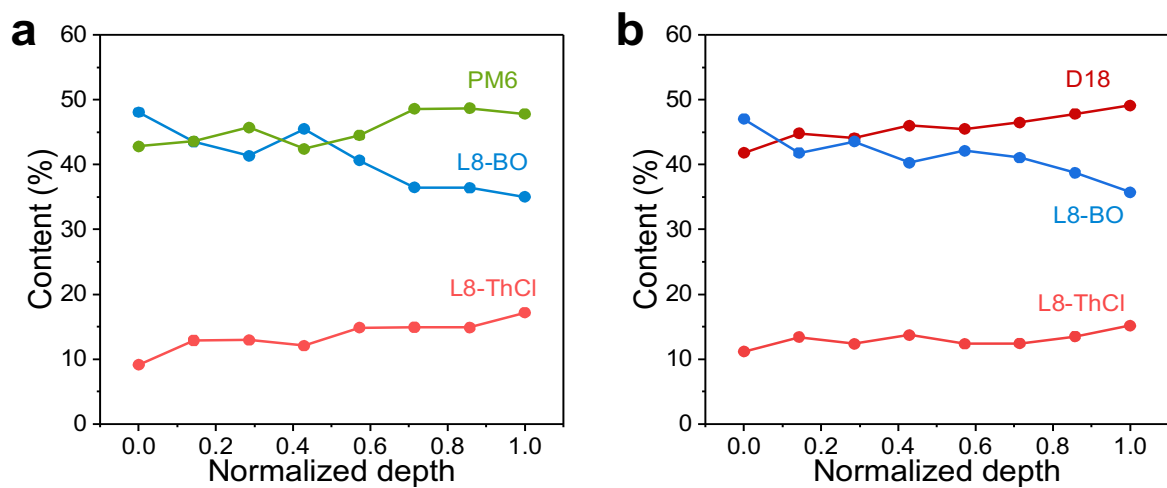
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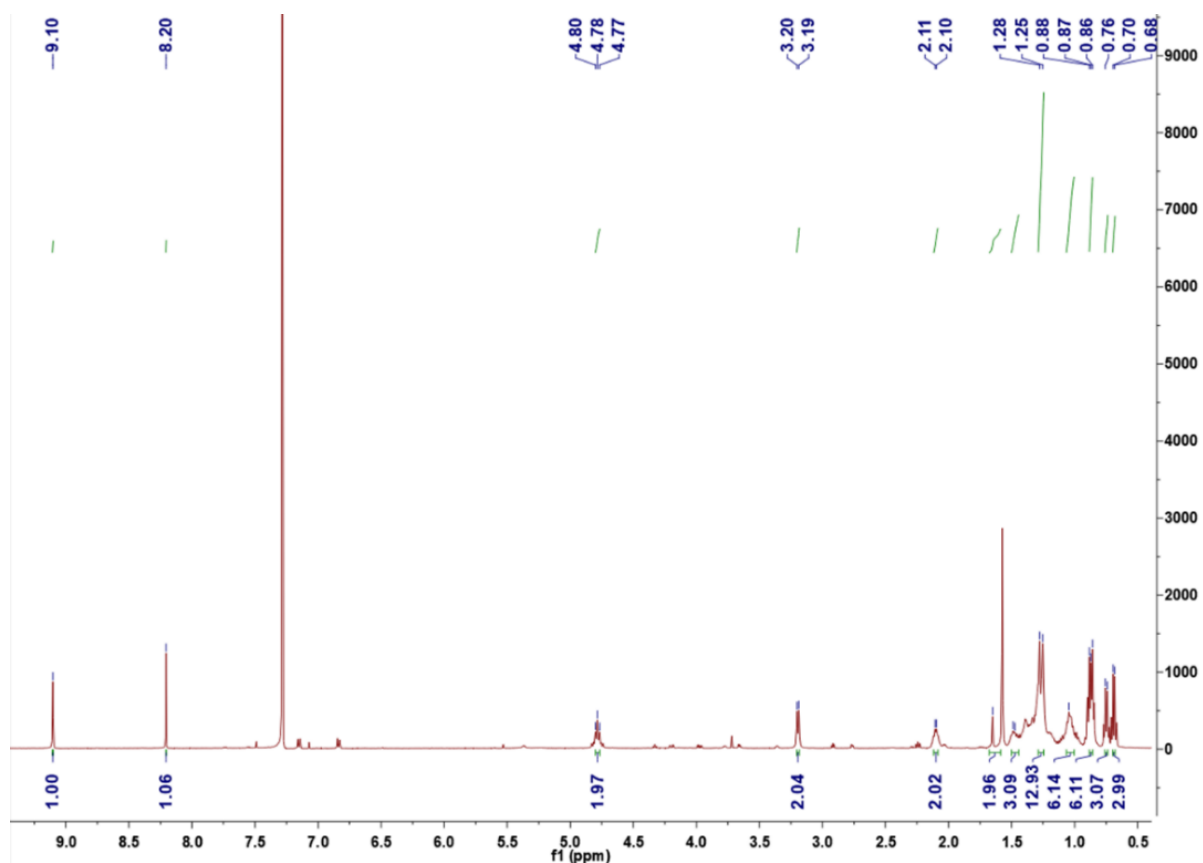
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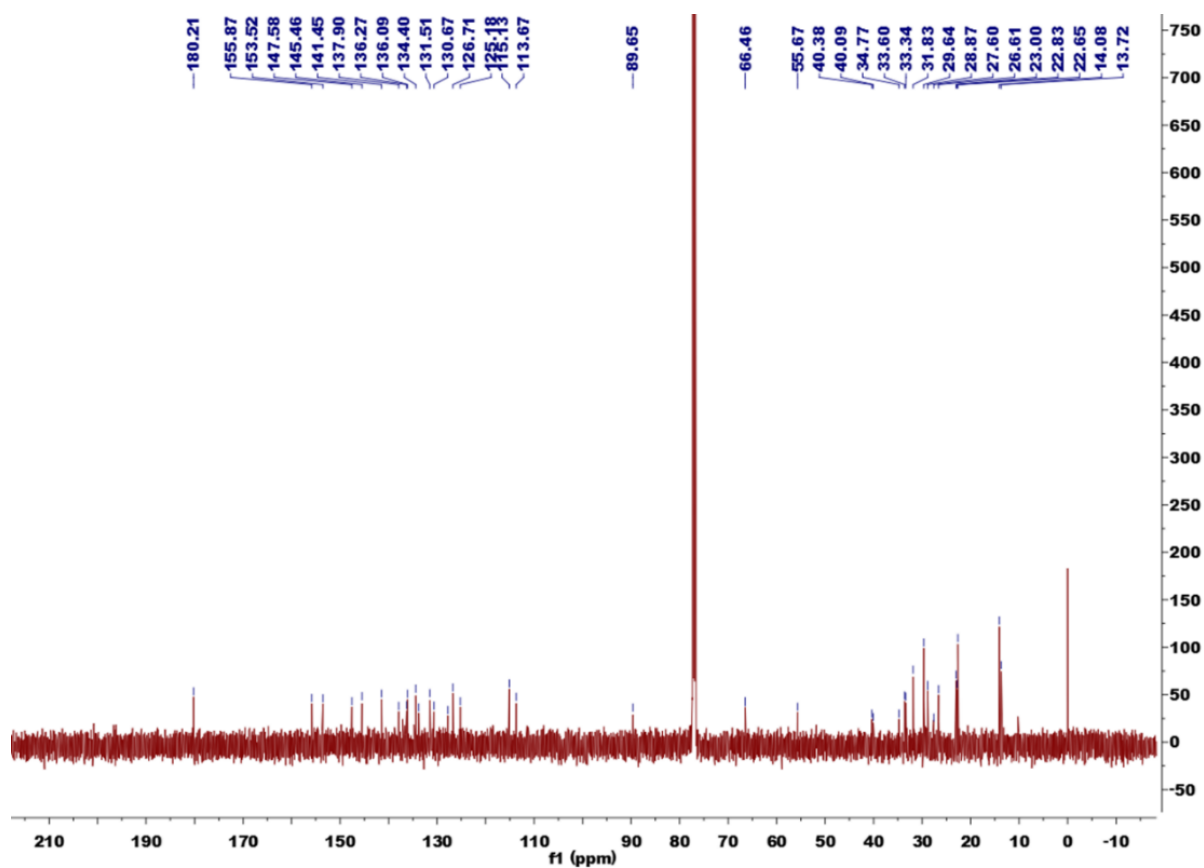
Supplementary Fig. 34. Charge transport measurements. **a**, hole mobilities of D18, D18+20%L8-ThCl. **b**, hole mobilities of D18:L8-BO, ternary BHJ and p-BHJ blend films. **c**, electron mobilities of D18:L8-BO, ternary BHJ and p-BHJ blend films.



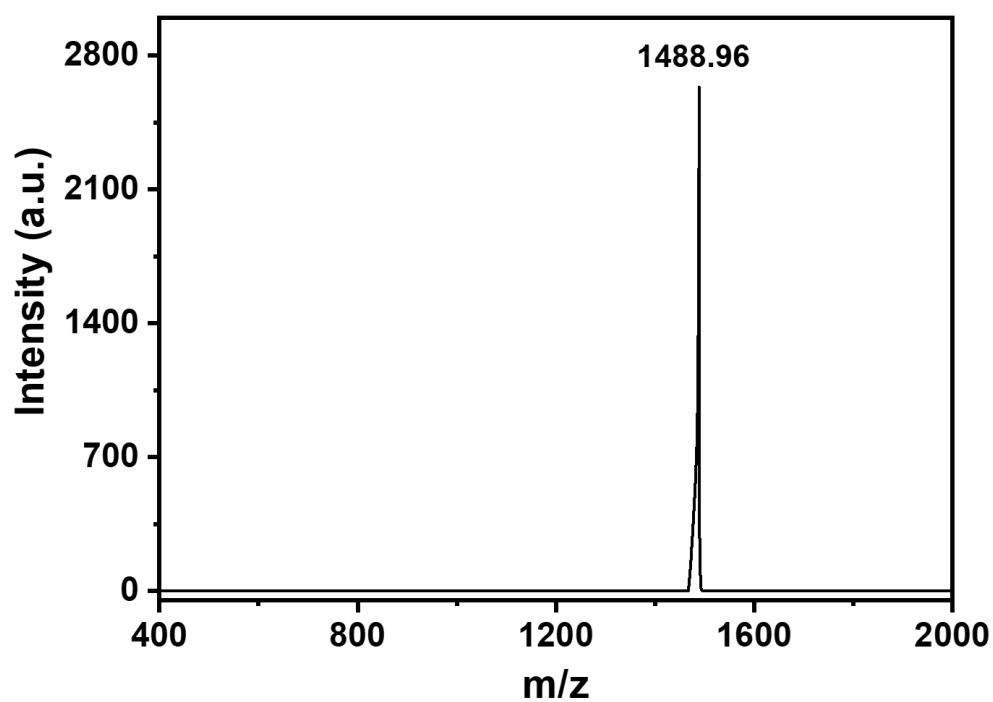
Supplementary Fig. 35. Depth profile measurements. **a**, depth-XPS of PM6+L8-ThCl/L8-BO+L8-ThCl film. **b**, depth-XPS of D18+L8-ThCl/L8-BO+L8-ThCl film.



Supplementary Fig. 36. ^1H NMR (500 MHz CDCl_3) spectrum of L8-ThCl.



Supplementary Fig. 37. ^{13}C NMR (126 MHz CDCl_3) spectrum of L8-ThCl.



Supplementary Fig. 38. MS (MALDI-TOF) spectrum of L8-ThCl.

Supplementary Tables

Supplementary Table 1. Fitting parameters of 1D GISAXS profiles of PM6, L8-BO, L8-ThCl, and blend films.

Film	2R (nm)	D	ξ (nm)	R_g (nm)
PM6	11.4	2.0	42.2	73.1
PM6:L8-ThCl=1:0.2	13.2	2.1	53.0	95.6
L8-BO	9.4	3.0	16.4	40.2
L8-ThCl	11.7	3.0	19.1	46.8
L8-BO:L8-ThCl=1:0.2	13.5	3.0	23.1	56.6

Supplementary Table 2. Charge transport properties of PM6 and L8-BO films with or without L8-ThCl.

Film	$\mu_h (10^{-4} \text{ cm}^{-1} \text{ V}^{-1} \text{ S}^{-1})$	$\mu_e (10^{-4} \text{ cm}^{-1} \text{ V}^{-1} \text{ S}^{-1})$
PM6	4.51	-
PM6:L8-ThCl=1:0.2	5.71	-
L8-BO	-	3.72
L8-ThCl	-	4.42
L8-BO:L8-ThCl=1:0.2	-	7.31

Supplementary Table 3. Photovoltaic performance of PM6:L8-BO based devices with different ratio of L8-ThCl.

Active layer	PCE (%)	FF (%)	J_{SC} (mA/cm ²)	V_{OC} (V)
PM6:L8-BO:L8-ThCl=1:1.1:0.1	18.5 (18.1±0.4)	80.3 (80.1±0.2)	-26.1 (-25.8±0.3)	0.883 (0.880±0.003)
PM6:L8-BO:L8-ThCl=1:1.0:0.2	18.7 (18.5±0.2)	80.4 (79.9±0.5)	-26.2 (-26.0±0.2)	0.889 (0.886±0.003)
PM6:L8-BO:L8-ThCl=1:0.9:0.3	18.1 (17.6±0.5)	77.7 (77.4±0.3)	-26.1 (-25.6±0.5)	0.893 (0.891±0.002)
PM6+10% L8-ThCl/ L8-BO+10%L8-ThCl	19.0 (18.6±0.4)	80.6 (80.1±0.5)	-26.6 (-26.2±0.4)	0.887 (0.884±0.003)
PM6+20% L8-ThCl/ L8-BO+20%L8-ThCl	19.4 (19.1±0.3)	81.1 (80.5±0.6)	-26.8 (-26.6±0.2)	0.895 (0.891±0.004)
PM6+30% L8-ThCl/ L8-BO+30%L8-ThCl	18.4 (18.0±0.4)	78.6 (78.1±0.5)	-26.1 (-25.7±0.4)	0.899 (0.896±0.003)

Note: the average parameters with standard deviation were calculated from 20 devices.

Supplementary Table 4. Fitting parameters of 1D GISAXS profiles of PM6:L8-BO, ternary BHJ and p-BHJ blend films.

Film	ξ_p (nm)	η (nm)	D	2R _g (nm)
PM6:L8-BO	19.3	4.7	3.0	23.1
Ternary BHJ	19.5	5.5	3.0	27.0
Ternary p-BHJ	21.2	5.6	3.0	27.4

Supplementary Table 5. Charge transport properties of PM6:L8-BO, ternary BHJ and p-BHJ blend films.

Film	$\mu_h (10^{-4} \text{ cm}^{-1} \text{ V}^{-1} \text{ S}^{-1})$	$\mu_e (10^{-4} \text{ cm}^{-1} \text{ V}^{-1} \text{ S}^{-1})$	μ_h/μ_e
PM6:L8-BO	3.82	3.47	1.10
Ternary BHJ	4.02	4.42	0.91
Ternary p-BHJ	4.65	4.60	1.01

Supplementary Table 6. Summary of contact angles (θ), surface tensions (γ) and compatibility (χ) of PM6, L8-BO and L8-ThCl.

Materials	Contact Angle (water) ($^{\circ}$)	Contact Angle (EG) ($^{\circ}$)	γ (mN/m)	χ
PM6	104.32	77.37	24.776	
L8-BO	92.24	64.95	28.442	
L8-ThCl	95.82	68.00	27.895	
PM6/L8-BO				0.126
PM6/L8-ThCl				0.092
L8-BO/L8-ThCl				0.003

Supplementary Table 7. Photovoltaic performance of D18:L8-BO based devices with different ratio of L8-ThCl.

Active layer	PCE (%)	FF (%)	J_{sc} (mA/cm ²)	V_{oc} (V)
D18:L8-BO:L8-ThCl=1:1.1:0.1	19.3 (19.0±0.3)	78.5 (78.1±0.4)	-27.3 (-27.0±0.3)	0.902 (0.899±0.003)
D18:L8-BO:L8-ThCl=1:1.0:0.2	19.5 (19.3±0.2)	78.4 (77.9±0.5)	-27.4 (-27.1±0.3)	0.904 (0.902±0.002)
D18:L8-BO:L8-ThCl=1:0.9:0.3	18.8 (18.3±0.5)	77.8 (77.2±0.6)	-26.7 (-26.1±0.6)	0.905 (0.904±0.001)
D18+10% L8-ThCl/ L8-BO+10%L8-ThCl	19.8 (19.4±0.4)	79.6 (79.1±0.5)	-27.5 (-27.1±0.4)	0.904 (0.903±0.001)
D18+20% L8-ThCl/ L8-BO+20%L8-ThCl	20.1 (19.8±0.3)	80.3 (79.9±0.4)	-27.5 (-27.3±0.2)	0.910 (0.906±0.004)
PM6+30% L8-ThCl/ L8-BO+30%L8-ThCl	19.1 (18.7±0.4)	78.5 (77.9±0.6)	-26.8 (-26.5±0.3)	0.909 (0.907±0.002)

Note: the average parameters with standard deviation were calculated from 20 devices.

Supplementary Table 8. Summary of photovoltaic performance of D18+20%L8-ThCl/L8-BO+20%L8-ThCl devices.

No.	PCE (%)	FF (%)	J_{SC} (mA/cm ²)	V_{OC} (V)
1	19.78	80.05	27.20	0.908
2	19.58	79.80	27.20	0.902
3	20.05	80.29	27.48	0.909
4	20.01	80.01	27.49	0.910
5	19.86	80.18	27.40	0.904
6	19.89	79.93	27.46	0.906
7	19.70	79.55	27.43	0.903
8	19.89	80.32	27.22	0.910
9	20.01	80.22	27.44	0.909
10	19.74	79.63	27.39	0.905
11	20.02	80.24	27.43	0.909
12	19.67	79.83	27.28	0.904
13	19.78	80.02	27.30	0.905
14	19.68	79.60	27.34	0.904
15	19.80	79.91	27.24	0.910
16	19.53	79.68	27.13	0.903
17	19.87	80.08	27.48	0.903
18	19.74	79.97	27.14	0.909
19	19.75	80.18	27.28	0.903
20	20.10	80.32	27.50	0.910

Supplementary Table 9. Charge transport properties of D18 based films.

Film	μ_h (10^{-4} cm ² V ⁻¹ S ⁻¹)	μ_e (10^{-4} cm ² V ⁻¹ S ⁻¹)	μ_h/μ_e
D18	5.81	-	-
D18 + 20% L8-ThCl	6.78	-	-
D18:L8-BO	4.95	3.97	1.24
Ternary BHJ	5.19	4.82	1.08
Ternary p-BHJ	5.97	5.54	1.08

Supplementary Methods

GISAXS modelling

The crystallized aggregates of organic semiconductors in thin films were quantified by fitting the 1D GISAXS profiles *via* a versatile Fractal model according to previous work.^[1] The scattering intensity of thin films can be expressed as **equation 1**, where $P(q)$ and $S(q)$ are the form factor and fractal structure factor, respectively, constant B is the incoherent scattering background. $P(q)$ includes the product of particle volume fraction ϕ , the square of scattering length density difference between crystalline and amorphous polymers $\Delta\rho^2$ and the crystalline particle volume V_p . $S(q)$ is given by **equation 2**, where $2R$ refers to the size of the primary crystalline particle, ξ and D represent the correlation length and fractal dimension of the crystalline domain, and R_g is regarded as the size of the crystalline domain (**equation 3**).

$$I(q) = P(q)S(q) + B \quad (1)$$

$$S(q) = 1 + \frac{\sin[(D-1)\tan^{-1}(q\xi)]}{(qR)^D} \frac{D\Gamma(D-1)}{\left[1 + \frac{1}{(q\xi)^2}\right]^{\frac{D-1}{2}}} \quad (2)$$

$$R_g = \sqrt{\frac{D(D+1)}{2}} \eta \quad (3)$$

SCLC measurements

The electron-only device with the structure of ITO/ZnO/Active layer/PDINN/Ag and the hole-only device with the structure of ITO/PEDOT:PSS/Active layer/MoO₃/Ag were fabricated. The SCLC measurements employ the Mott-Gurney equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$ to estimate the electron and hole mobilities from dark J - V curves obtained from these devices. Here, J is the current density, ε_r is the relative dielectric constant of the active layer, ε_0 is the permittivity of free space, μ is the charge mobility, and L is the thickness of the active layer. $V = V_{app} - V_{bi}$, where V_{app} is the voltage applied to the OSC device, and V_{bi} is the built-in potential voltage.

Non-radiative energy loss calculation^[2]

The $E_{loss}^{non-rad}$ is calculated through the following equation $E_{loss}^{non-rad} = V_{OC}^{rad} - V_{OC}$, in which V_{OC}^{rad} was carried out by $V_{OC}^{rad} = \frac{kT}{q} \ln\left(\frac{J_{SC}}{J_0^{rad}} + 1\right) \cong \frac{kT}{q} \ln\left(\frac{q \int_0^{+\infty} EQE(E) \cdot \Phi_{AM1.5G}(E) \cdot dE}{q \int_0^{+\infty} EQE(E) \cdot \Phi_{BB}(E) \cdot dE}\right)$, where k is Boltzmann's constant, T is the temperature of the solar cell ($T = 300$ K is used in this paper), q is elementary charge, $\Phi_{AM1.5G}(E)$ and $\Phi_{BB}(E)$ are the standard solar spectrum under AM1.5G (100 mW/cm²) and black body spectrum at the temperature T , respectively.

XPS and depth profile measurements

Based on the Cl/N and N/O atom ratio, the component weight content ($x_{wt\%}$) at different depths in PM6:L8-ThCl/L8-BO:L8-ThCl can be calculated by the formulas:

$$x_{wt\%} = \frac{x_{wt}}{D_{wt} + A_{wt}} = \frac{n_x M_x}{n_{L8-ThCl} M_{L8-ThCl} + n_{L8-BO} M_{L8-BO} + n_{PM6} M_{PM6}}$$

$$\frac{N}{O} = \frac{8 \times (n_{L8-BO} + n_{L8-ThCl})}{2 \times (n_{L8-BO} + n_{L8-ThCl}) + 2 \times n_{D18}} \Rightarrow \frac{n_{PM6}}{n_{L8-BO} + n_{L8-ThCl}} = \frac{1}{\frac{N}{O} - 4} - 1$$

$$\frac{Cl}{N} = \frac{2 \times n_{L8-ThCl}}{8 \times n_{L8-ThCl} + 8 \times n_{L8-BO}} \Rightarrow \frac{n_{L8-ThCl}}{n_{L8-BO} + n_{L8-ThCl}} = 4 \frac{Cl}{N}$$

Based on the O/N and Cl/O atom ratio, the component weight content ($x_{wt\%}$) at different depths in D18:L8-ThCl/L8-BO:L8-ThCl can be calculated by the formulas:

$$x_{wt\%} = \frac{x_{wt}}{D_{wt} + A_{wt}} = \frac{n_x M_x}{n_{L8-ThCl} M_{L8-ThCl} + n_{L8-BO} M_{L8-BO} + n_{D18} M_{D18}}$$

$$\frac{O}{N} = \frac{2 \times (n_{L8-BO} + n_{L8-ThCl})}{8 \times (n_{L8-BO} + n_{L8-ThCl}) + 2 \times n_{D18}} \Rightarrow \frac{n_{D18}}{n_{L8-BO} + n_{L8-ThCl}} = \frac{N}{O} - 4$$

$$\frac{Cl}{O} = \frac{2 \times n_{L8-ThCl}}{2 \times n_{L8-ThCl} + 2 \times n_{L8-BO}} \Rightarrow \frac{n_{L8-ThCl}}{n_A} = \frac{Cl}{O}$$

M_{L8-BO} is the molecular weight of L8-BO (1480), $M_{L8-ThCl}$ is the molecular weight of L8-ThCl (1489), M_{PM6} is the molecular weight of the repeat unit of PM6 (1220), M_{D18} is the molecular weight of the repeat unit of D18 (1390), n_{L8-BO} is the mole number of L8-BO, $n_{L8-ThCl}$ is the mole number of L8-ThCl, n_{PM6} is the mole number of the repeat units of PM6, n_{D18} is the mole number of the repeat units of D18, x is one of these components. The atom ratios were calculated by the integration of areas of corresponding XPS peaks and the atomic sensitivity factors. Empirically derived set of atomic sensitivity factors for XPS can be acquired at <http://202.38.64.11/~mams/escalab/sfactors.html>.

Synthesis of L8-ThCl

CPTCN-Cl (100mg, 0.4 mmol) and the central core of L8-BO (100mg, 0.1 mmol) were dissolved in 30 mL chloroform, in which 0.5 mL of pyridine was added. Then, the solution was reacted at 80 °C overnight. After cooling to room temperature, the solvent was removed under reduced pressure and the resident solid product was washed with absolute methanol, then further purified by column chromatography on silica gel using dichloromethane as the eluent to afford L8-ThCl (90mg, 57%).

^1H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.20 (s, 1H), 4.78 (t, J = 7.9 Hz, 2H), 3.19 (d, J = 7.6 Hz, 2H), 2.10 (d, J = 6.0 Hz, 2H), 1.65 (s, 2H), 1.48 (d, J = 7.5 Hz, 3H), 1.26 (d, J = 13.4 Hz, 13H), 1.05 (s, 6H), 0.88 – 0.86 (m, 6H), 0.75 (d, J = 6.7 Hz, 3H), 0.69 (d, J = 6.7 Hz, 3H). MS(MALDI-TOF): Calcd for $C_{80}H_{88}Cl_2N_8O_2S_7$ (M^+): 1489.45, Found: 1488.96.

Supplementary References

1. Guo, C. et al. Cold-Aging and Solvent Vapor Mediated Aggregation Control toward 18% Efficiency Binary Organic Solar Cells. *Adv. Energy Mater.* **11**, 2102000 (2021).
2. Chen, X. et al. A unified description of non-radiative voltage losses in organic solar cells. *Nat. Energy*, **6**, 799 (2021).