

Supplementary Information

Photoactive network formation mechanism in organic solar cells

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Supplementary Note

Supplementary Note 1. Exciton Dissociation Probability

To calculate exciton dissociation probability, photocurrent density (J_{ph}) versus the effective voltage (V_{eff}) of the devices were measured, where J_{ph} is the current difference between the current densities under illumination and in the dark. V_{eff} is the voltage difference between the voltage when $J_{ph} = 0$ and the applied voltage as shown below.^[1,2]

$$J_{ph} = qG_{max}P(E, T)L$$

$$J_{sat} = qG_{max}L$$

$$V_{eff} = V_0 - V_a$$

$$J_{ph} = J_{light} - J_{dark}$$

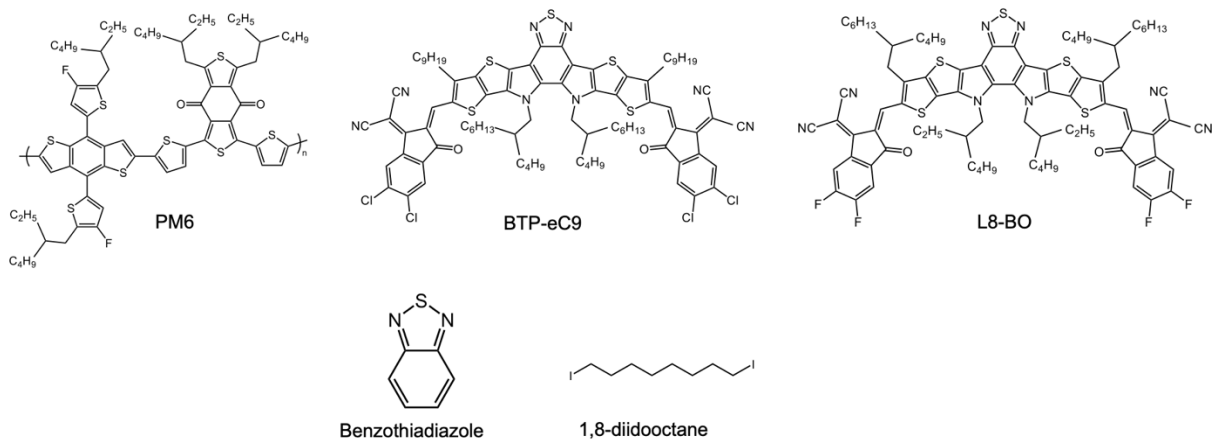
(Where, G_{max} : absorbed photons, J_{sat} : J_{ph} when V_{eff} is the highest, J_{ph} : J_{ph} under short-circuit condition, q : elementary charge, L : thickness of the film)

All excitons are dissociated into free charge carriers and collected by electrodes at high V_{eff} . The saturation photocurrent density (J_{sat}) is only limited by the number of absorbed incident photons. Higher J_{ph}/J_{sat} ($P(E, T)$) at low electric field can be obtained in the BT system. It suggests facilitating charge transfer at the interface between the photoactive layer and the electron transport layer. The values of J_{ph} of the devices increase linearly at low values of V_{eff} (< 0.2 V for both binary and ternary) and become saturated when the value of V_{eff} is greater than 0.3 V. Here, the value of J_{sat} is related to the absorbed incident photon flux. The value of G_{max} values (1.44×10^{28} , 1.47×10^{28} , $1.48 \times 10^{28} \text{ m}^{-3}\text{s}^{-1}$ for binary / 1.46×10^{28} , 1.49×10^{28} , $1.51 \times 10^{28} \text{ m}^{-3}\text{s}^{-1}$ for ternary) are proportional to the J_{sc} values of the devices. Higher values of G_{max} indicate higher light harvesting in the devices.

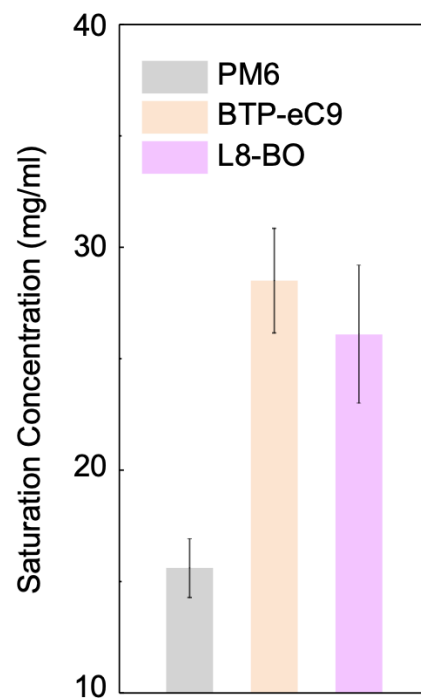
^[1] Onsager. L., et al. Initial recombination of ions. *Phys. Rev.* **54**, 554–557 (1938).

^[2] Braun. C., et al. Electric field assisted dissociation of charge transfer states as a mechanism of photocarrier production. *J. Chem. Phys.* **80**, 4157–4161 (1984).

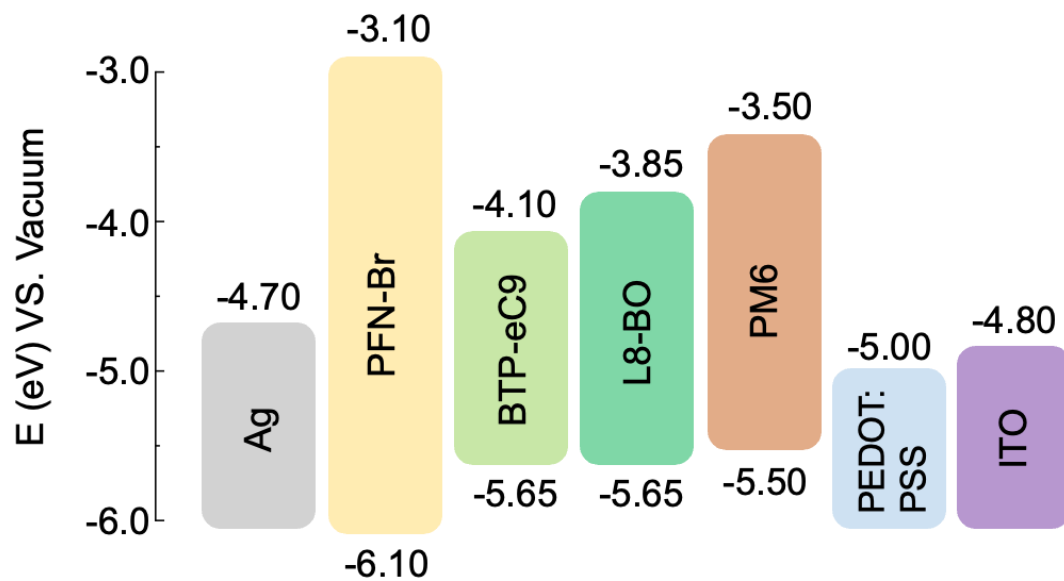
Supplementary Figures



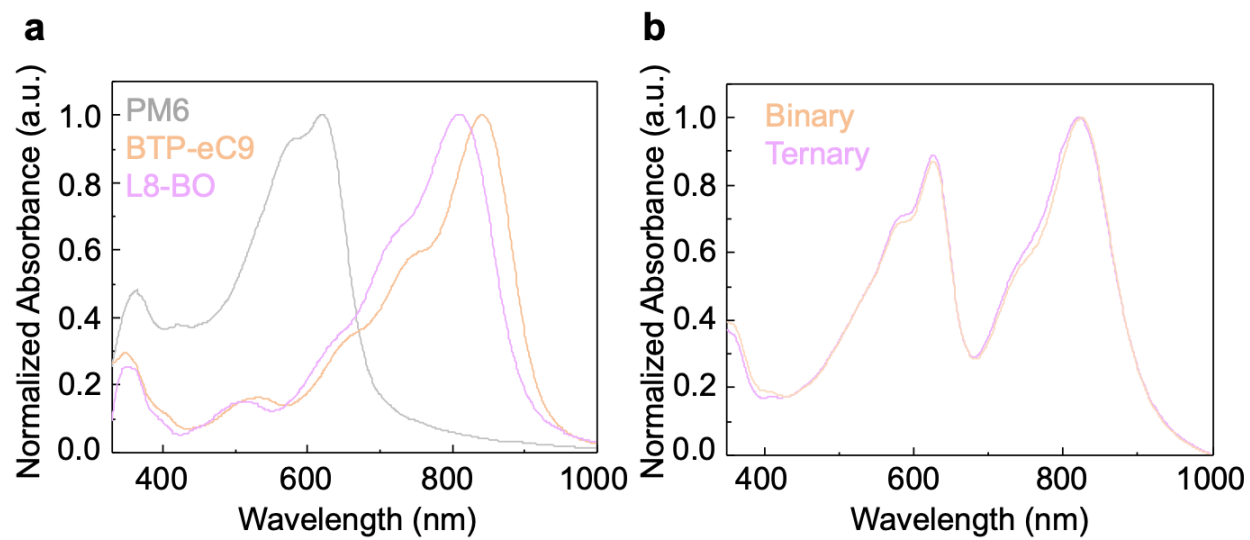
Supplementary Figure 1. Molecular structures of PM6 (donor), BTP-eC9 (acceptor 1), L8-BO (acceptor 2), benzothiadiazole, and 1,8-diiodooctane additives.



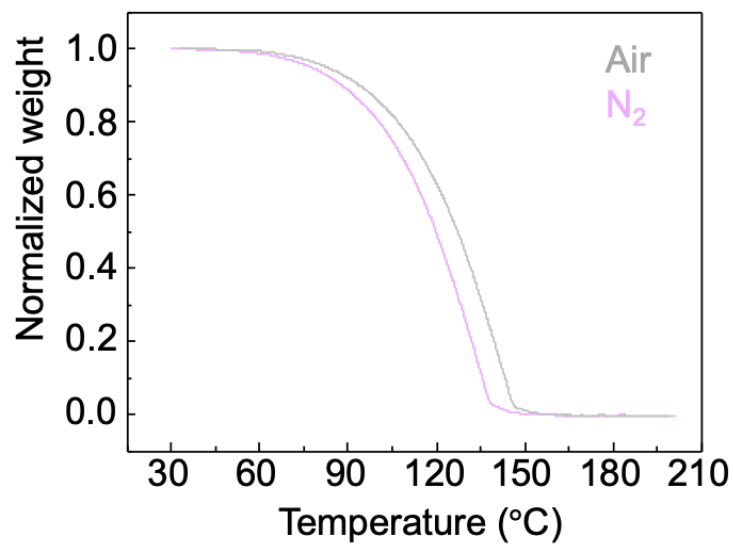
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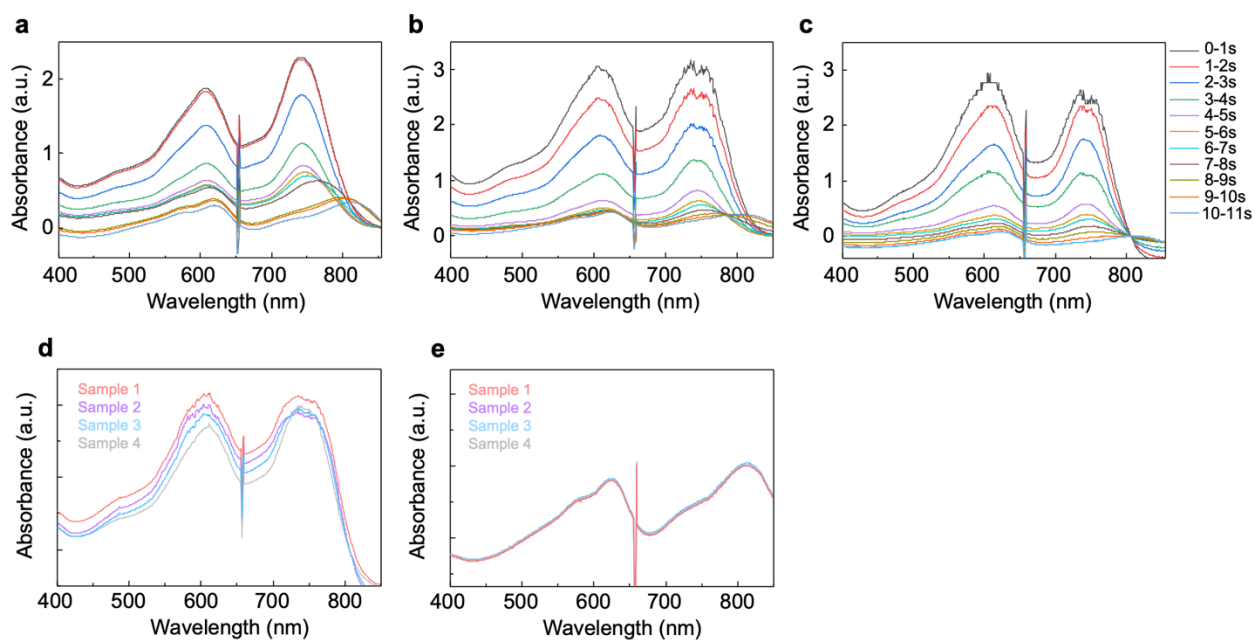
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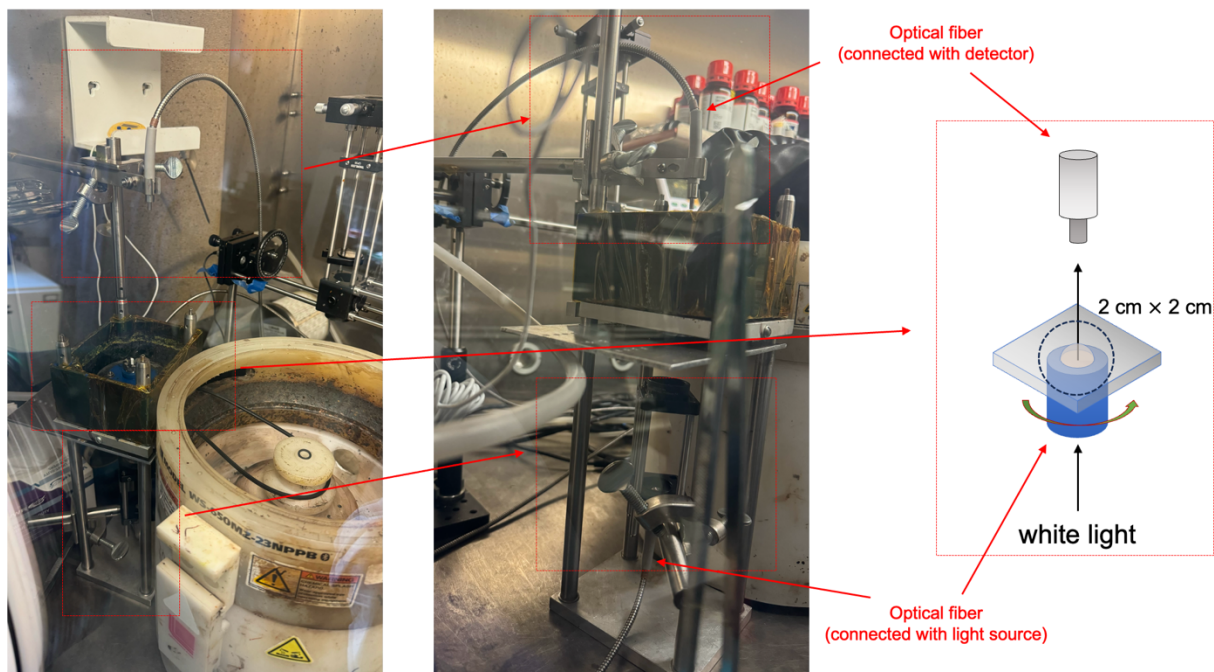
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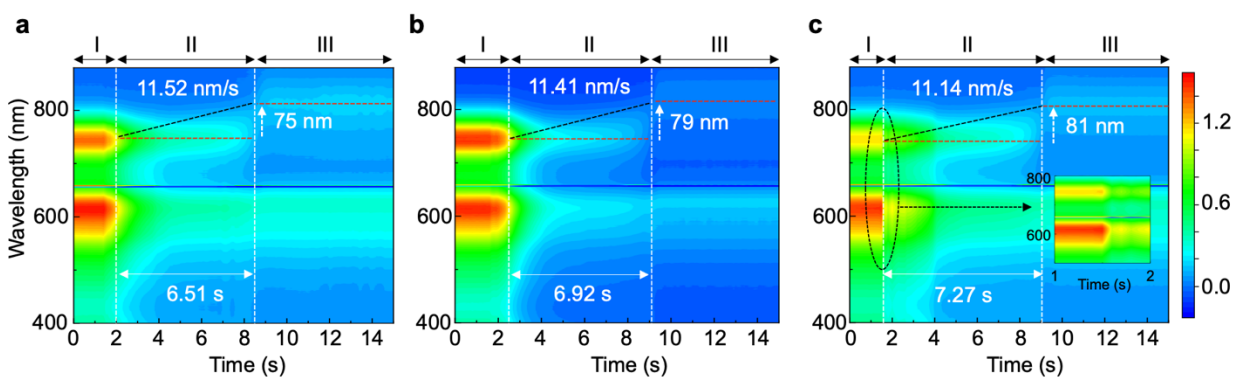
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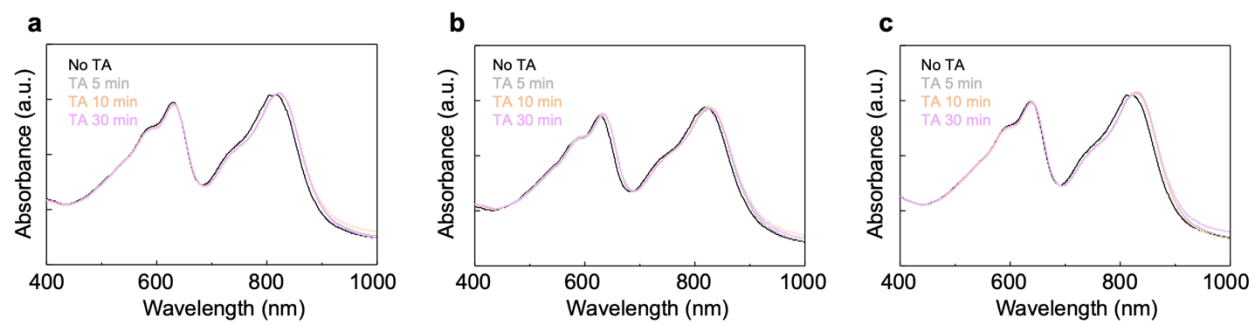
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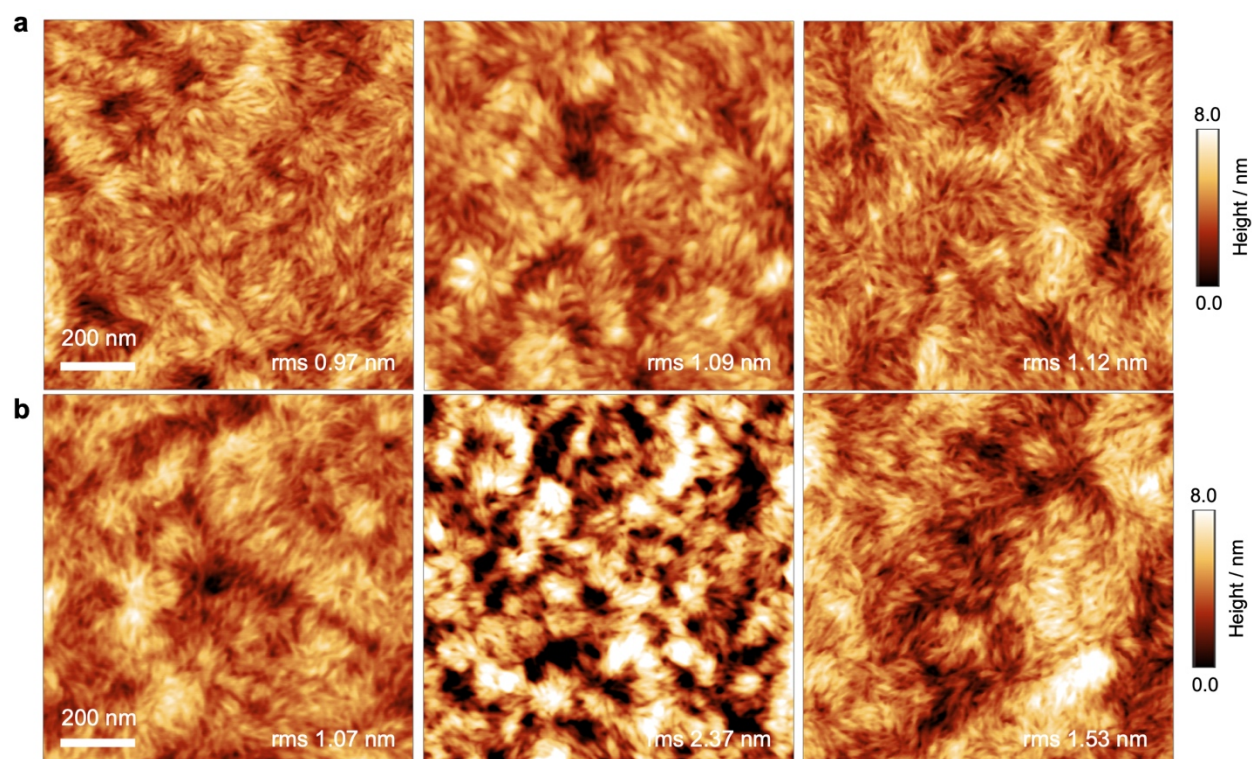
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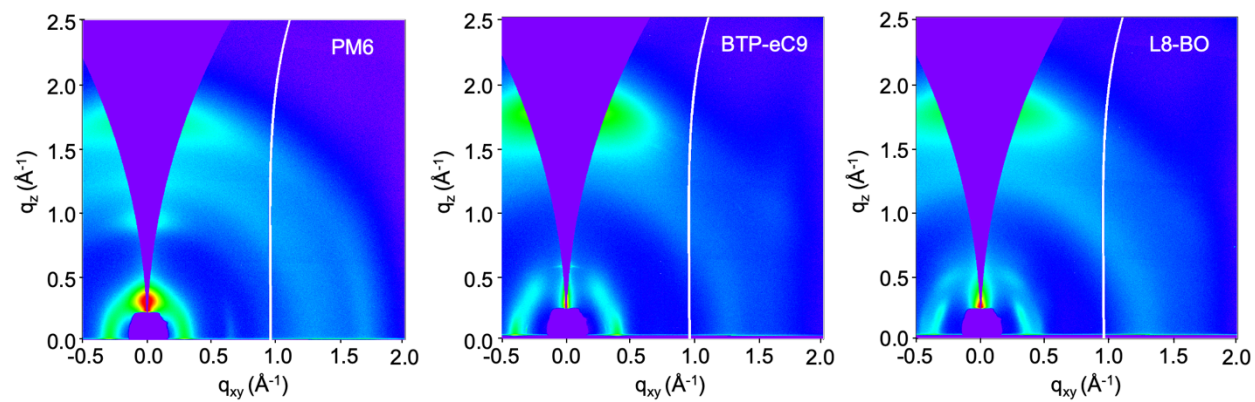
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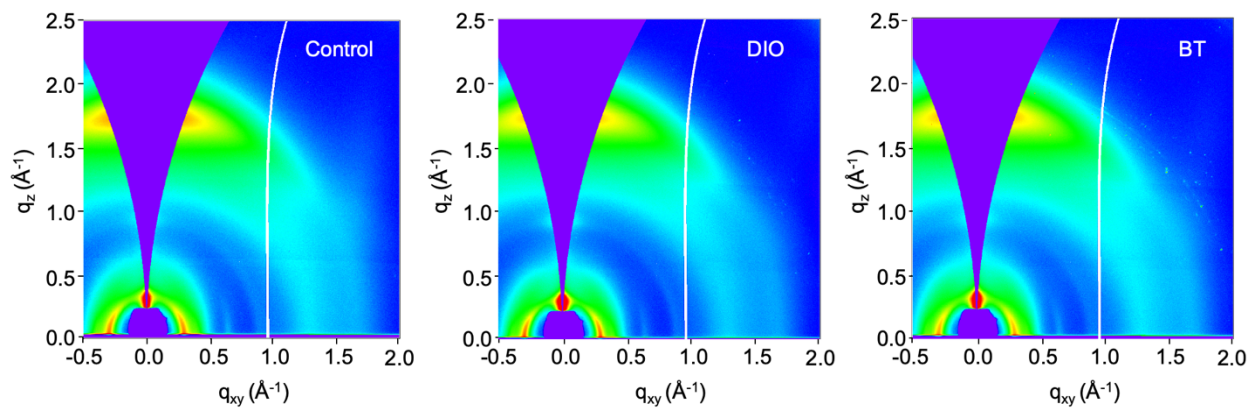
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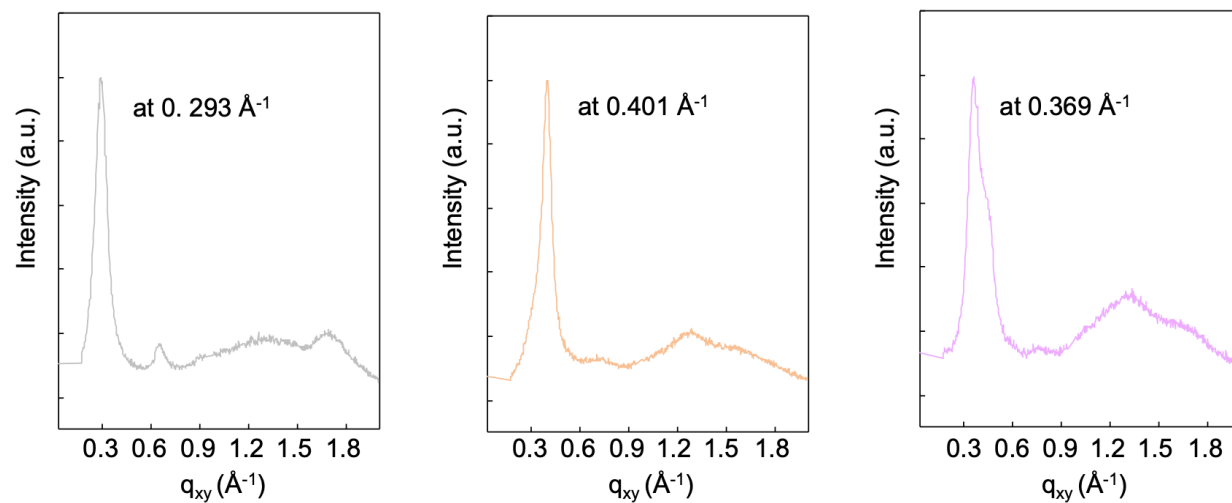
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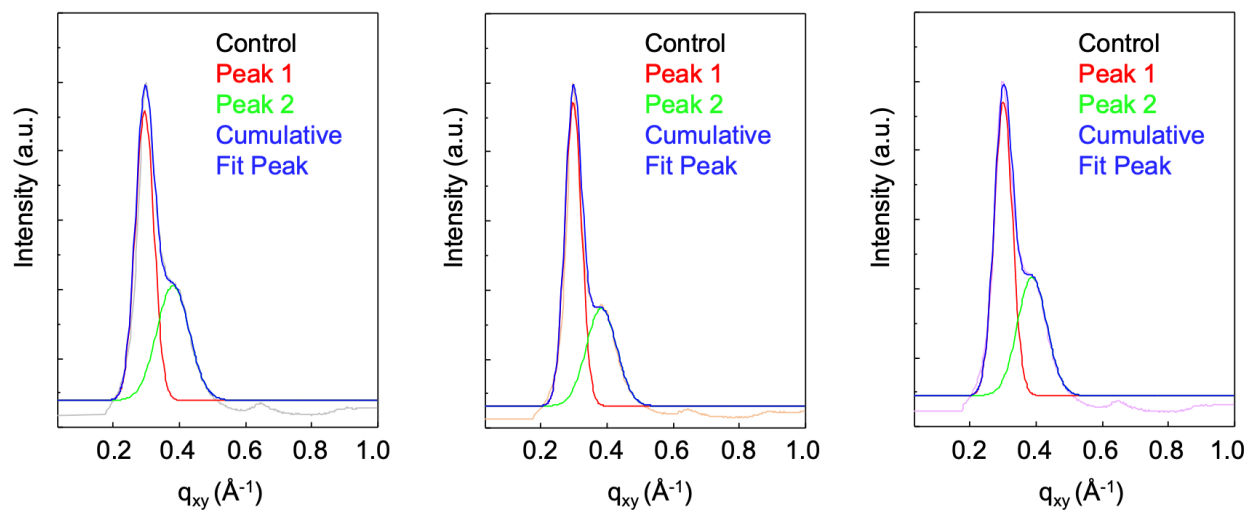
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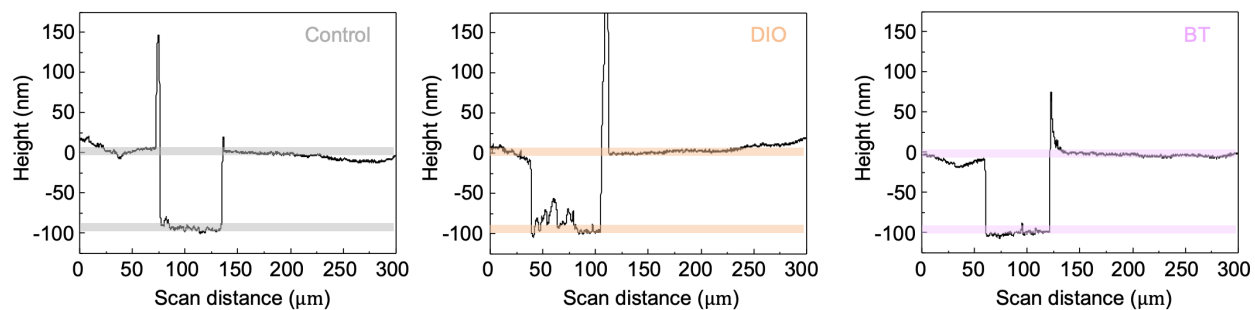
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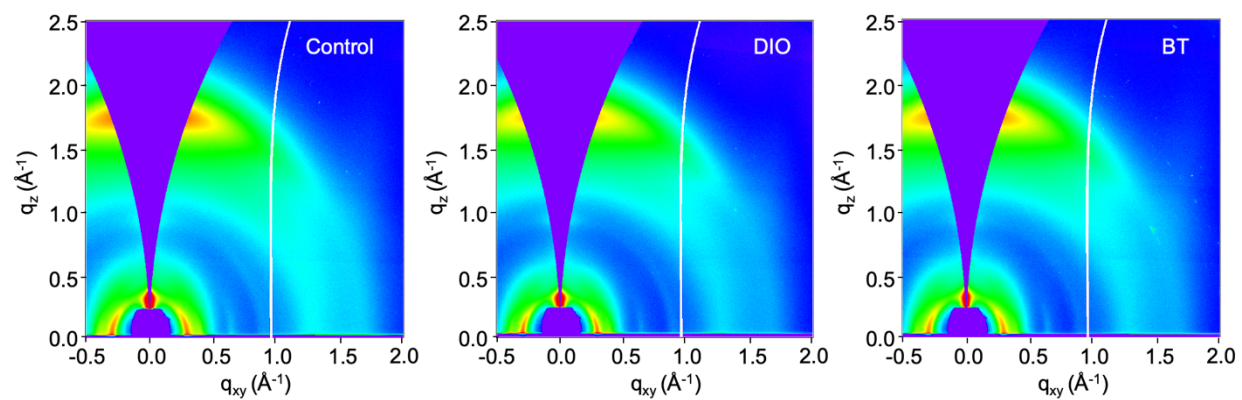
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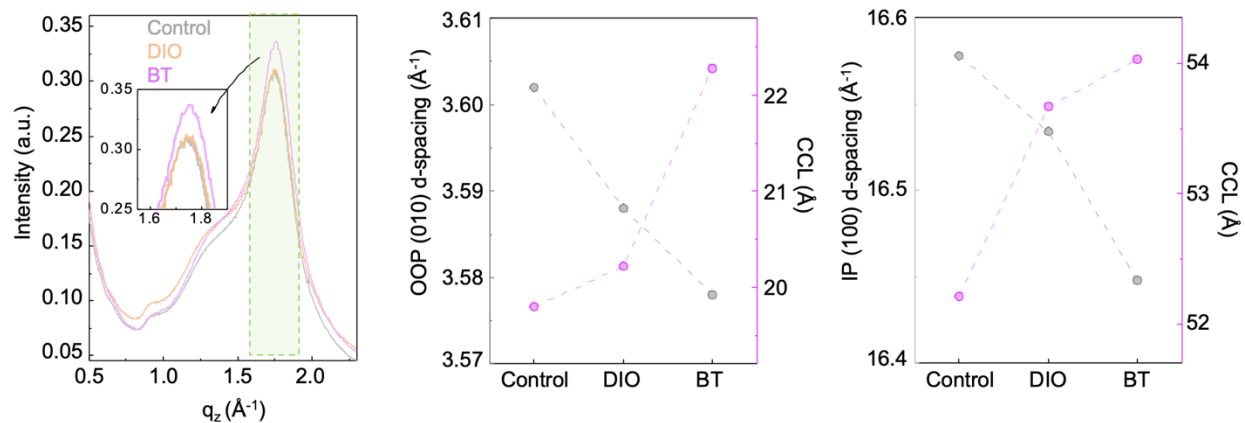
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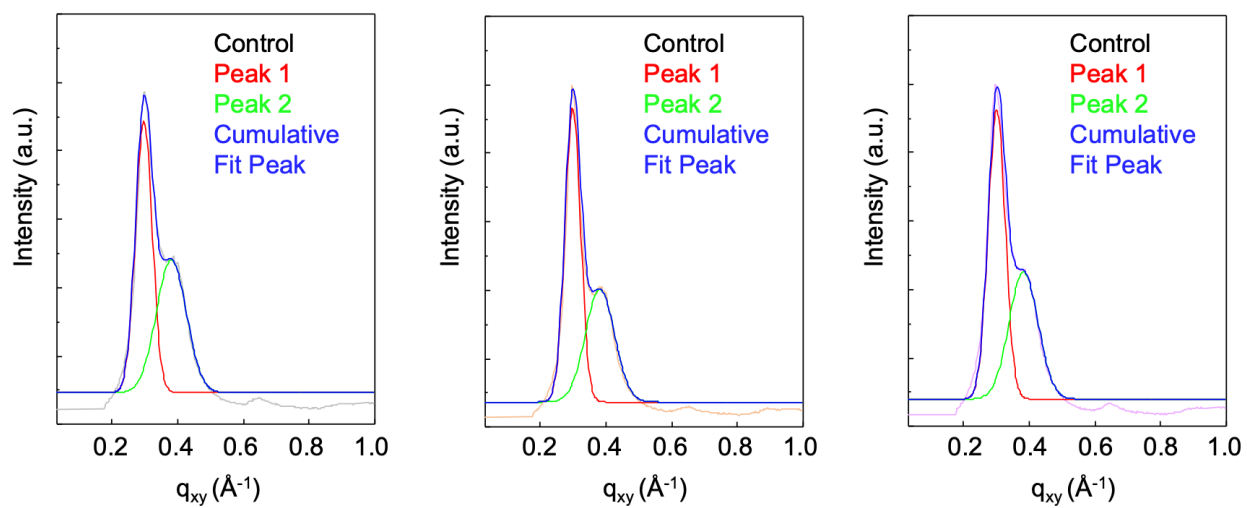
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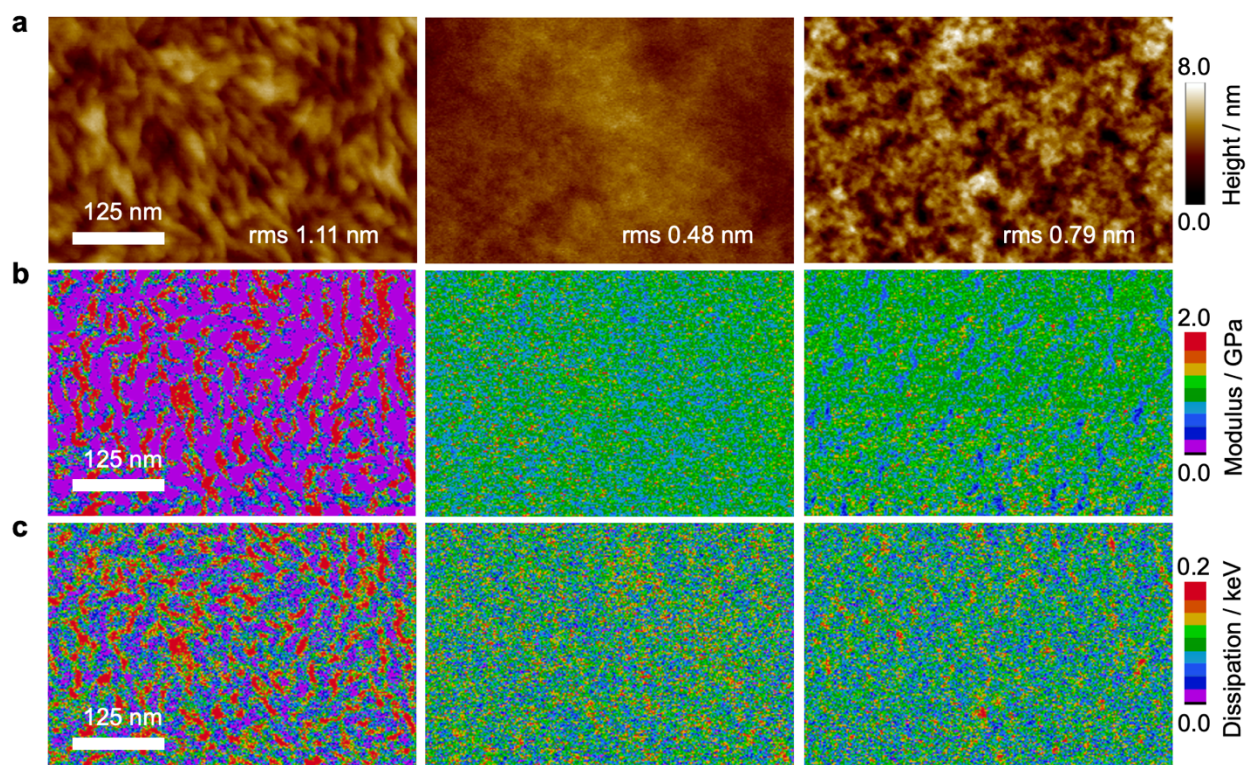
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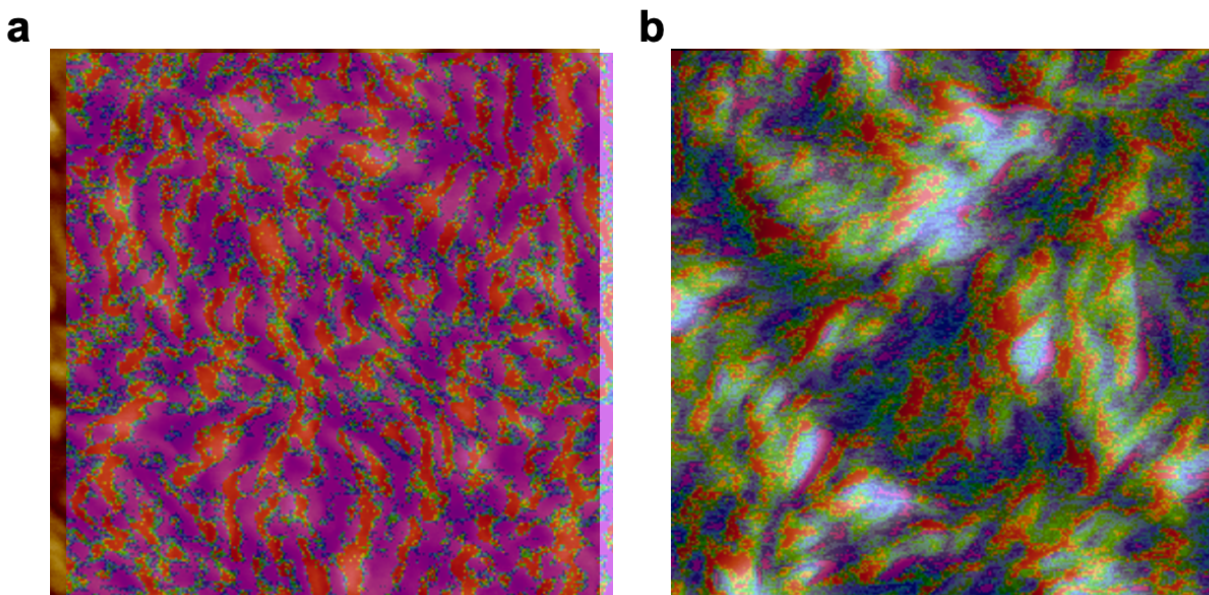
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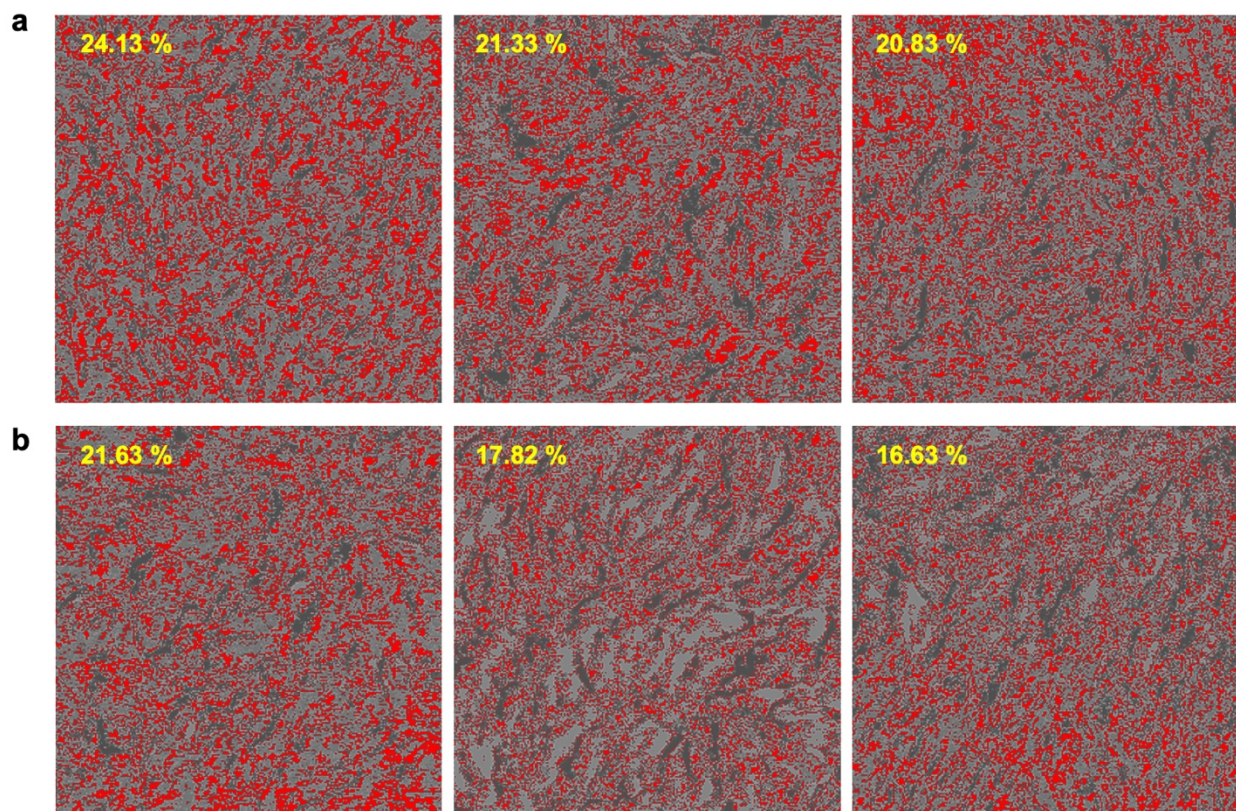
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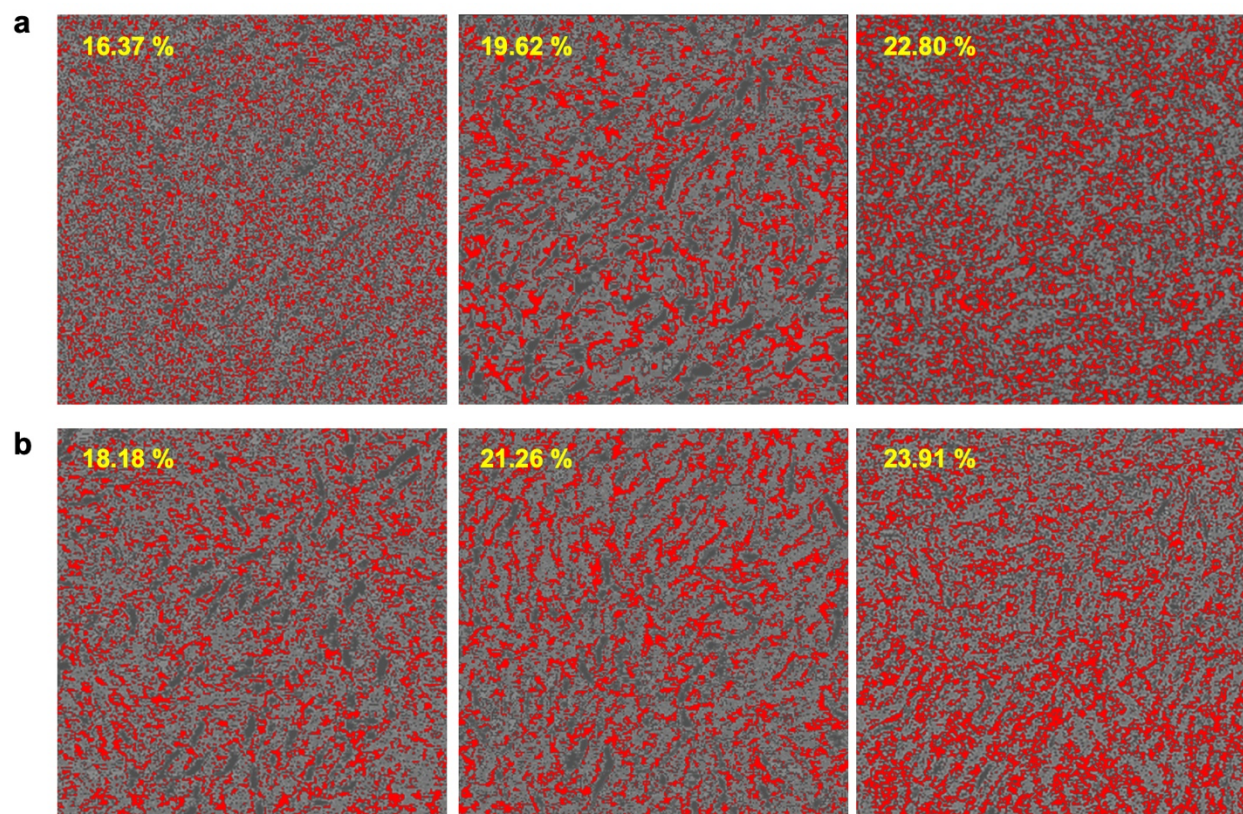
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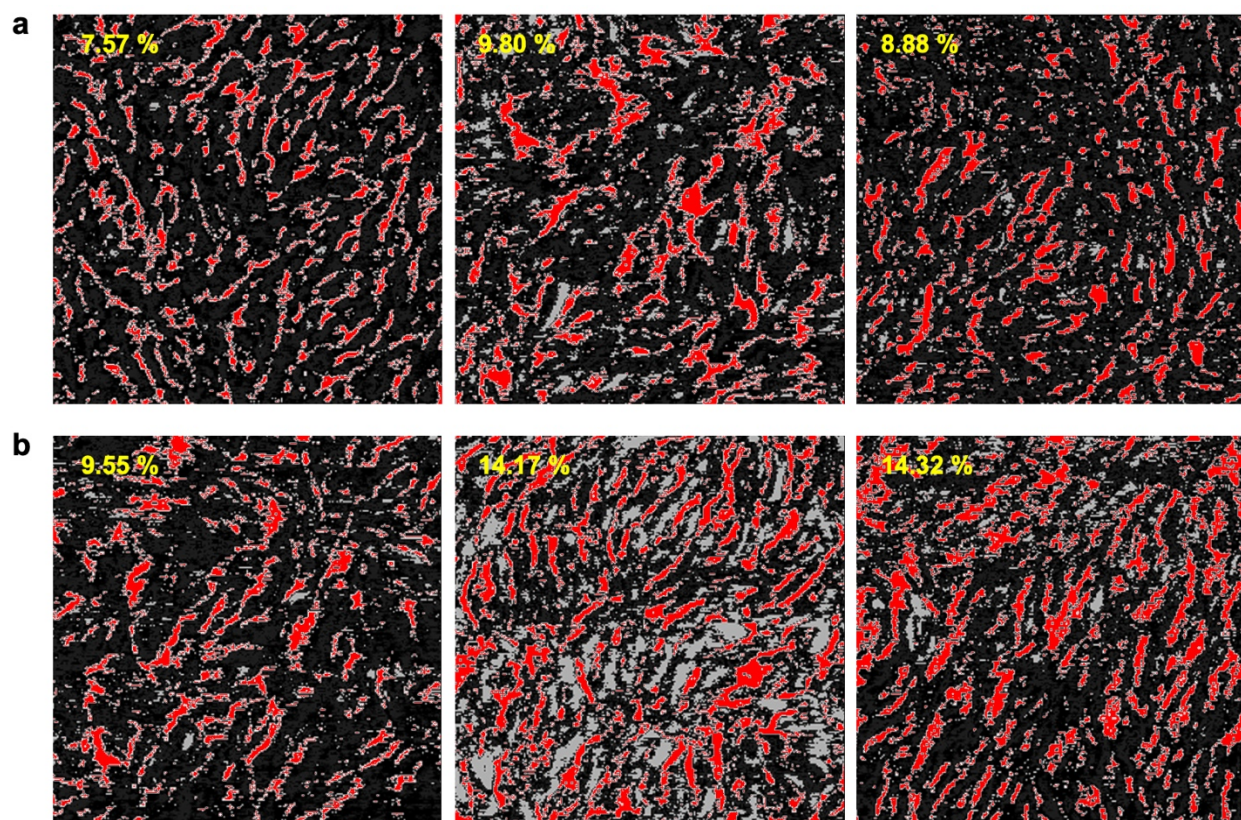
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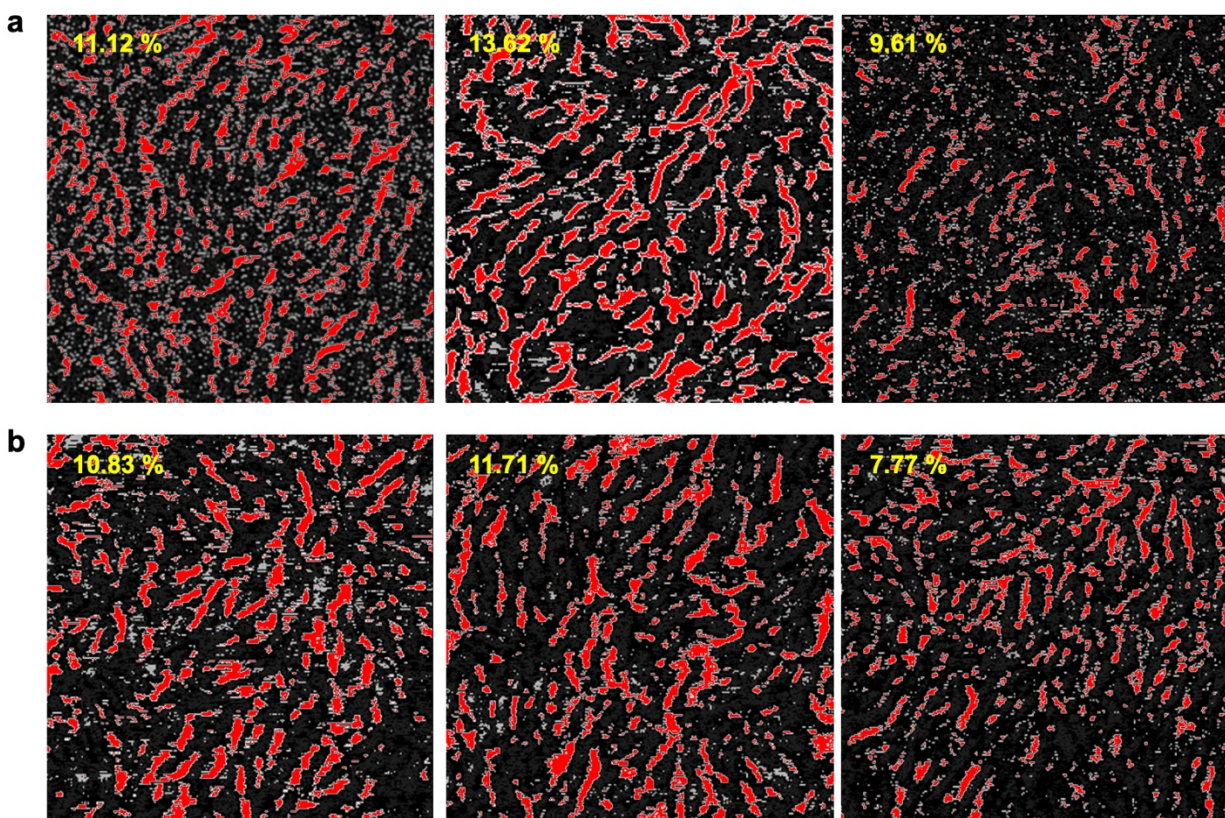
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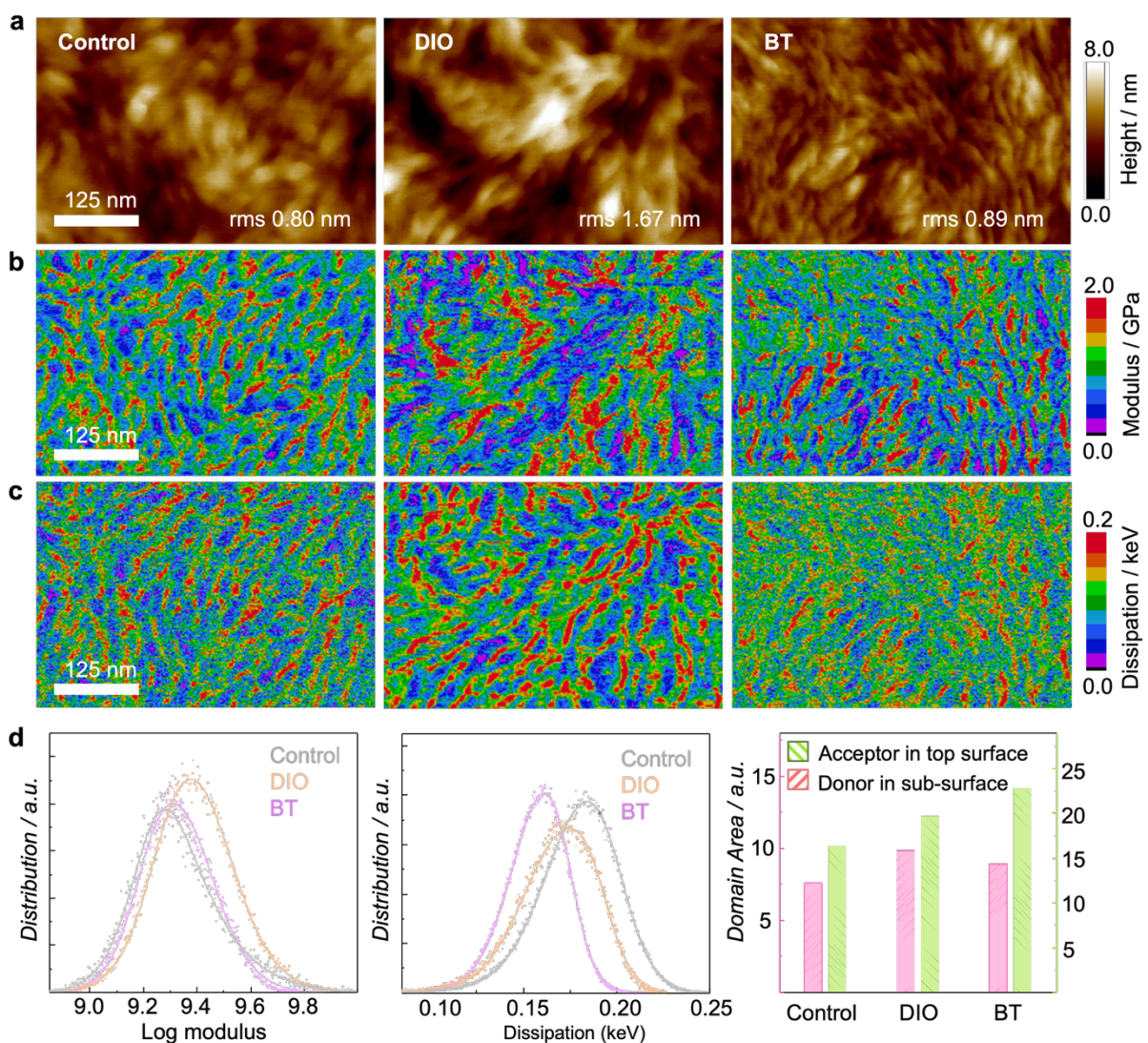
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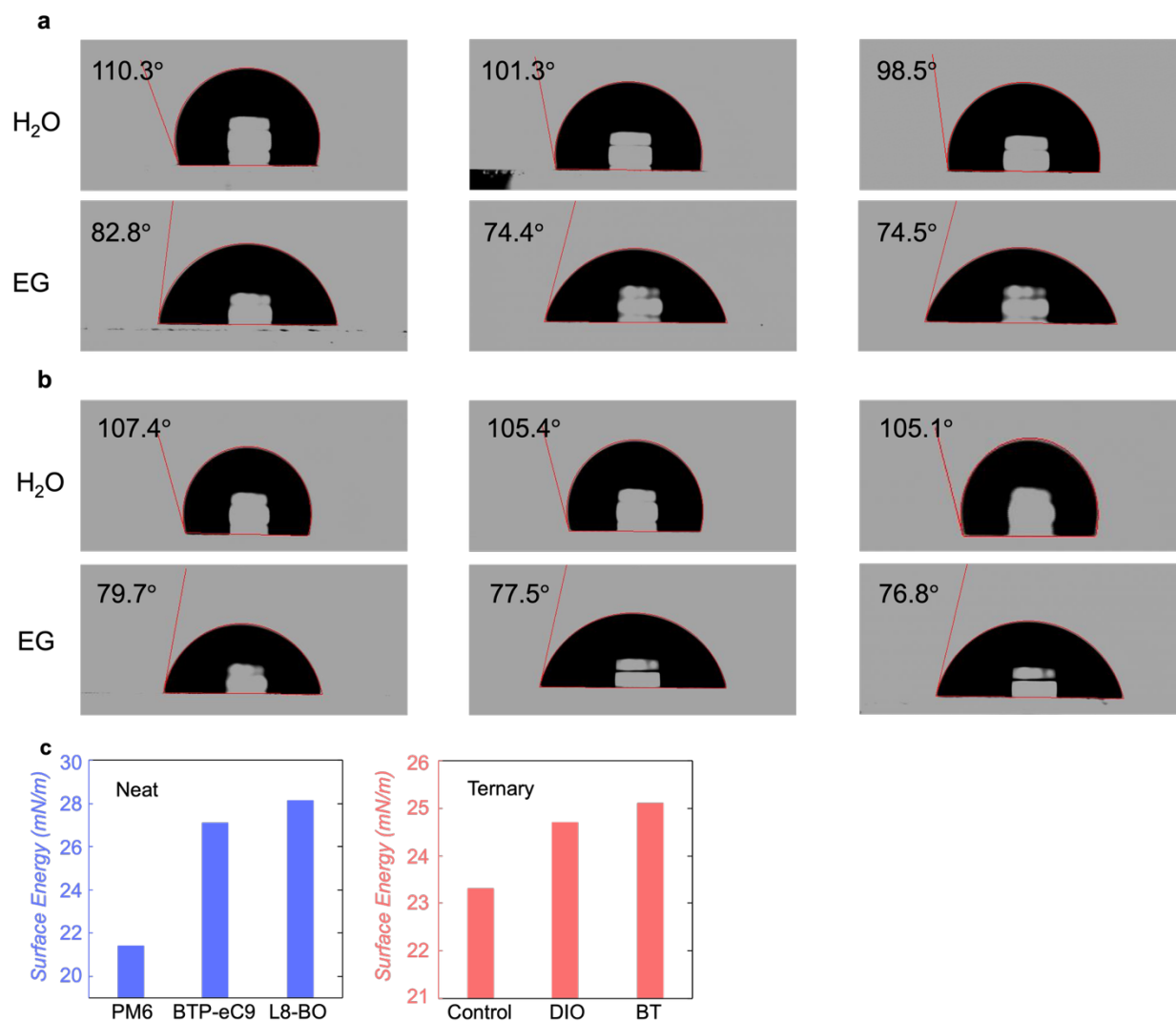
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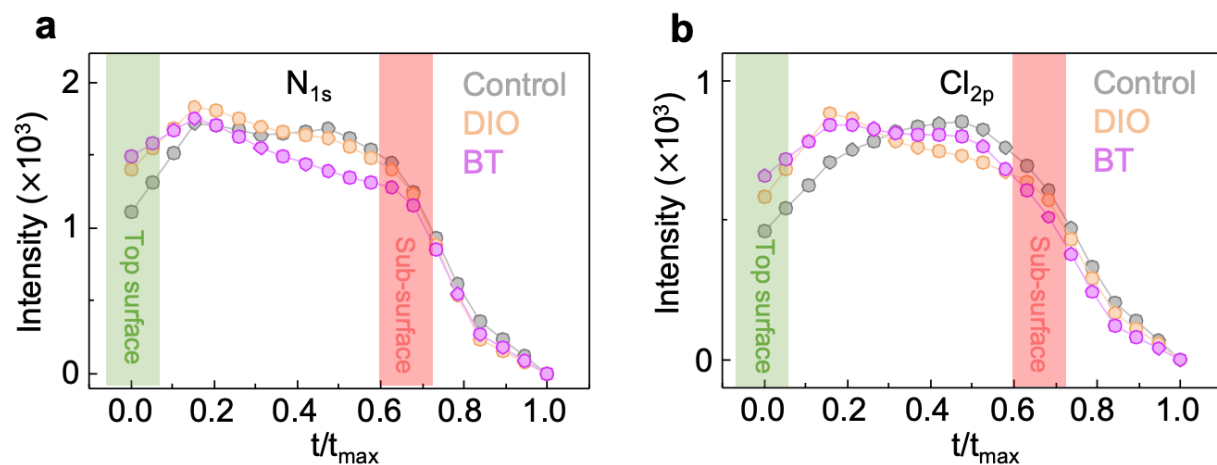
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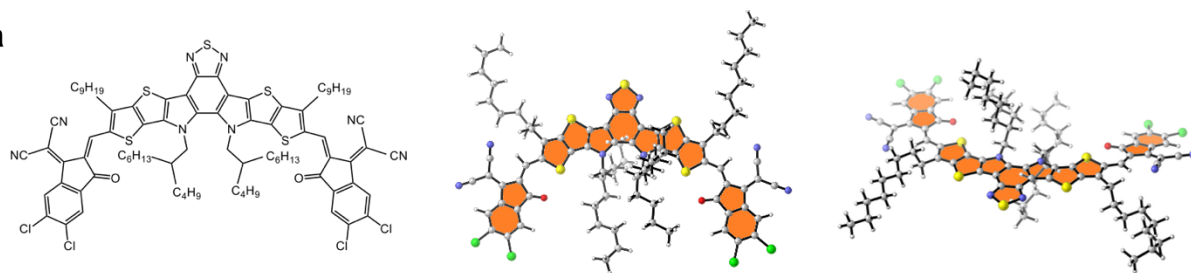
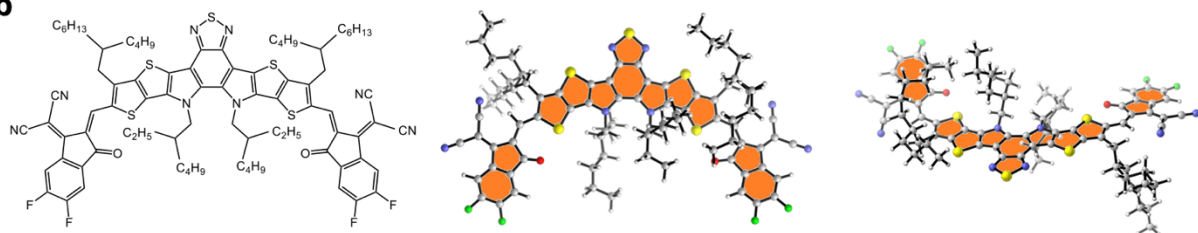
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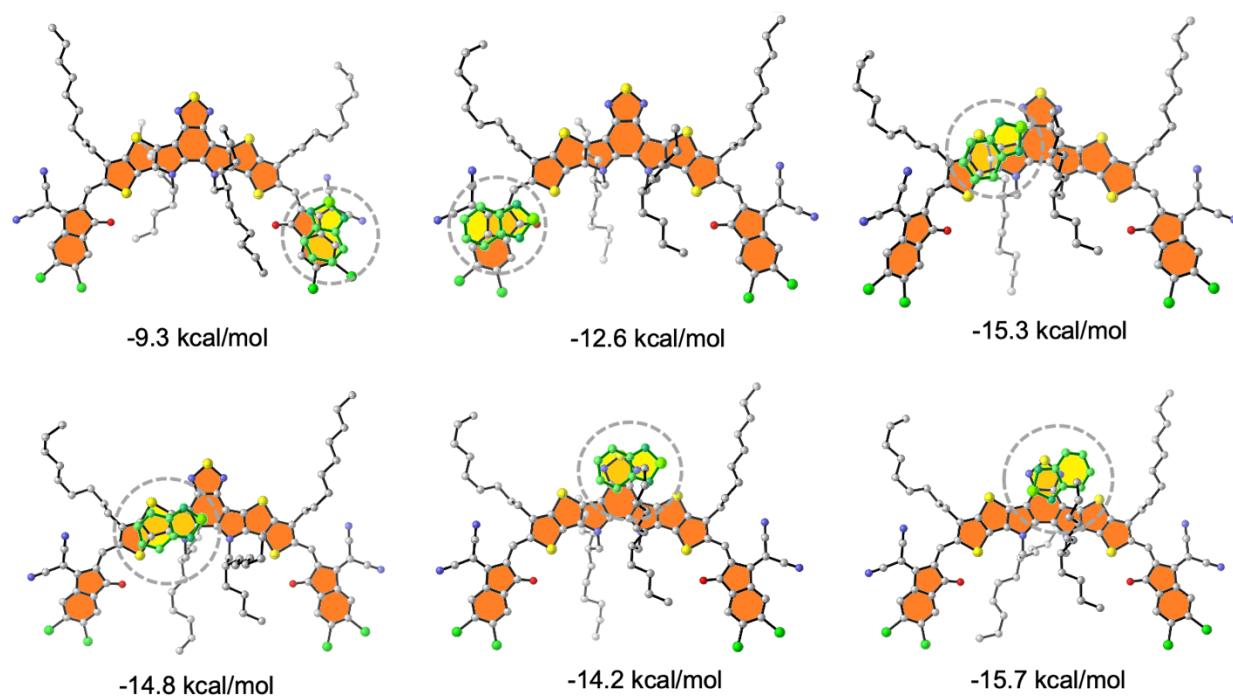
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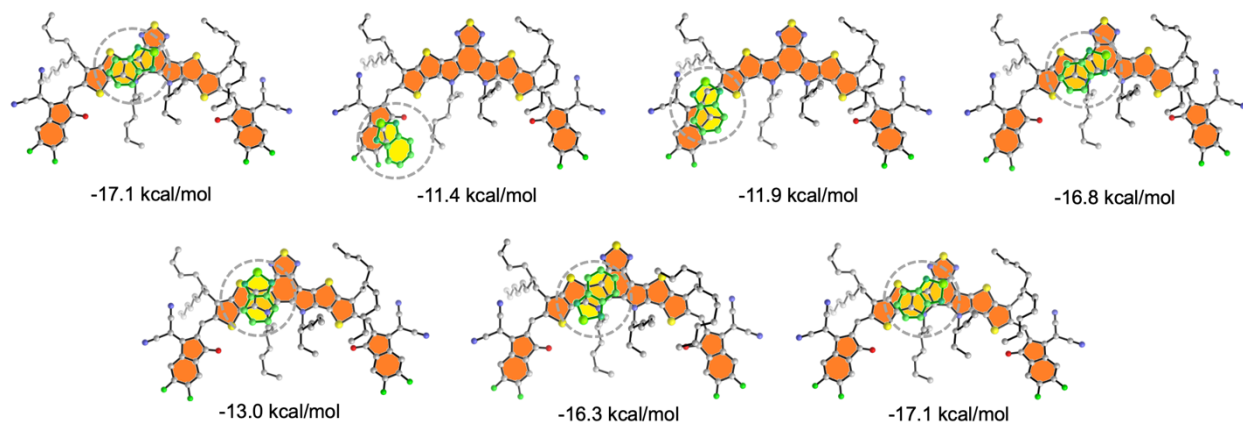
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a**b**

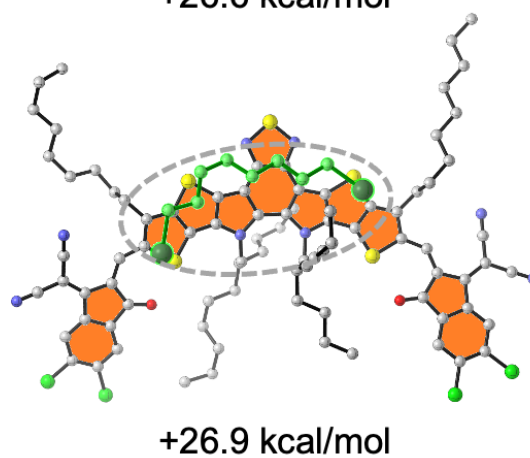
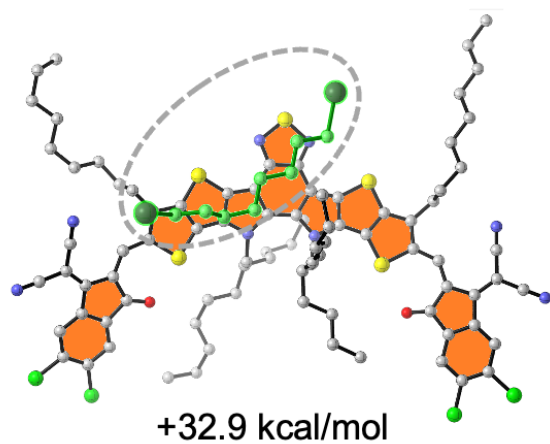
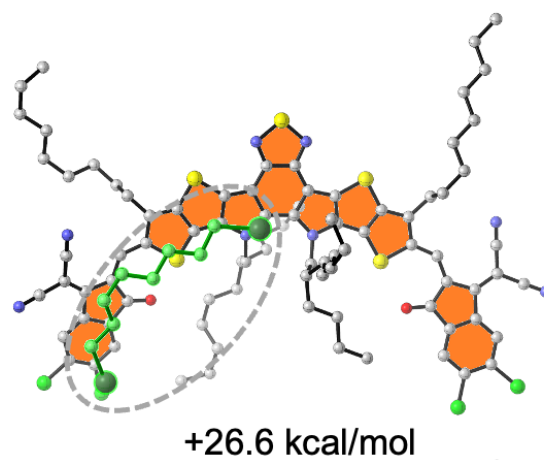
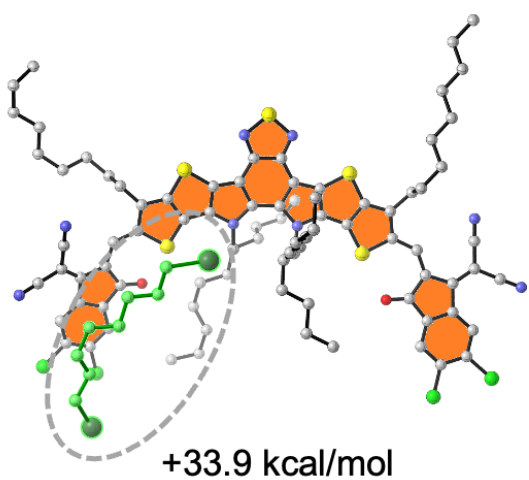
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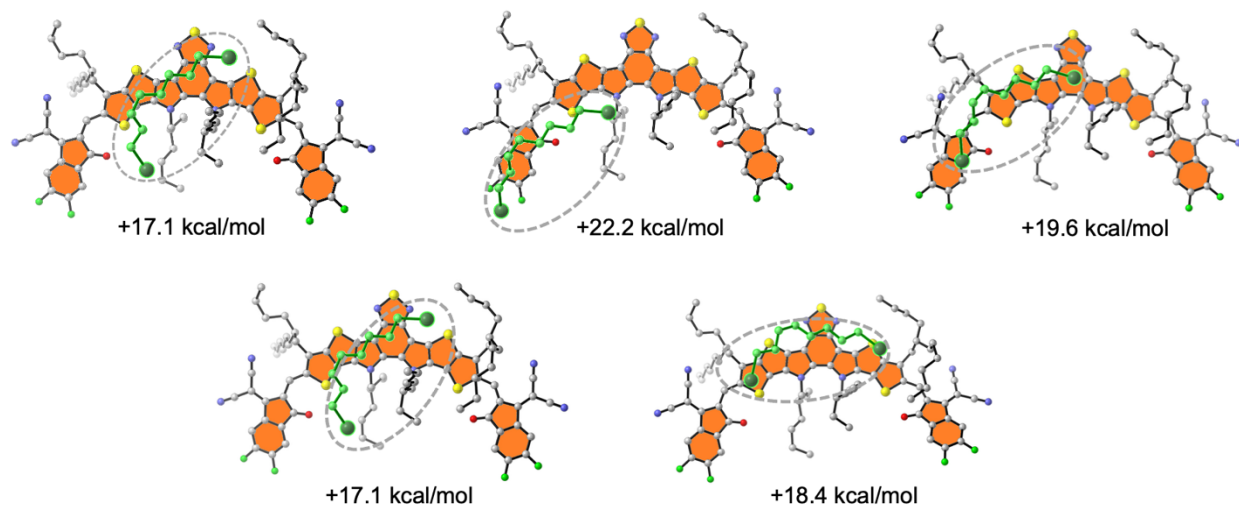
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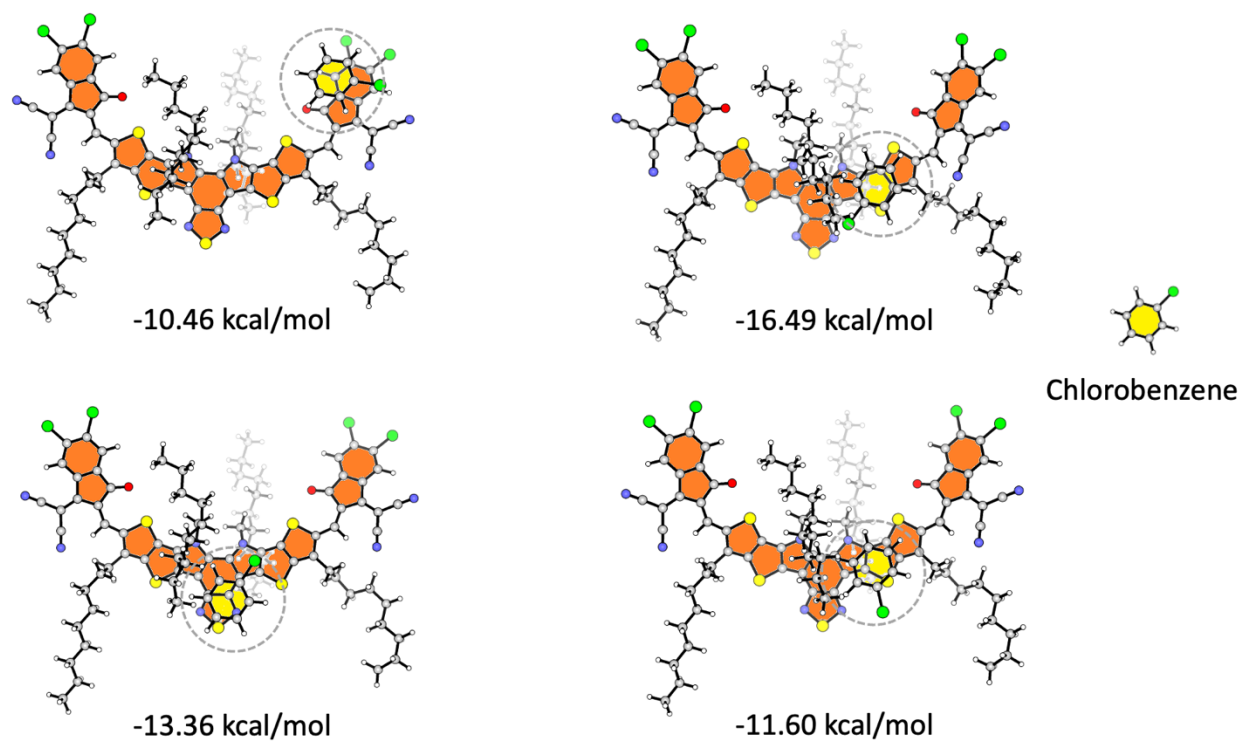
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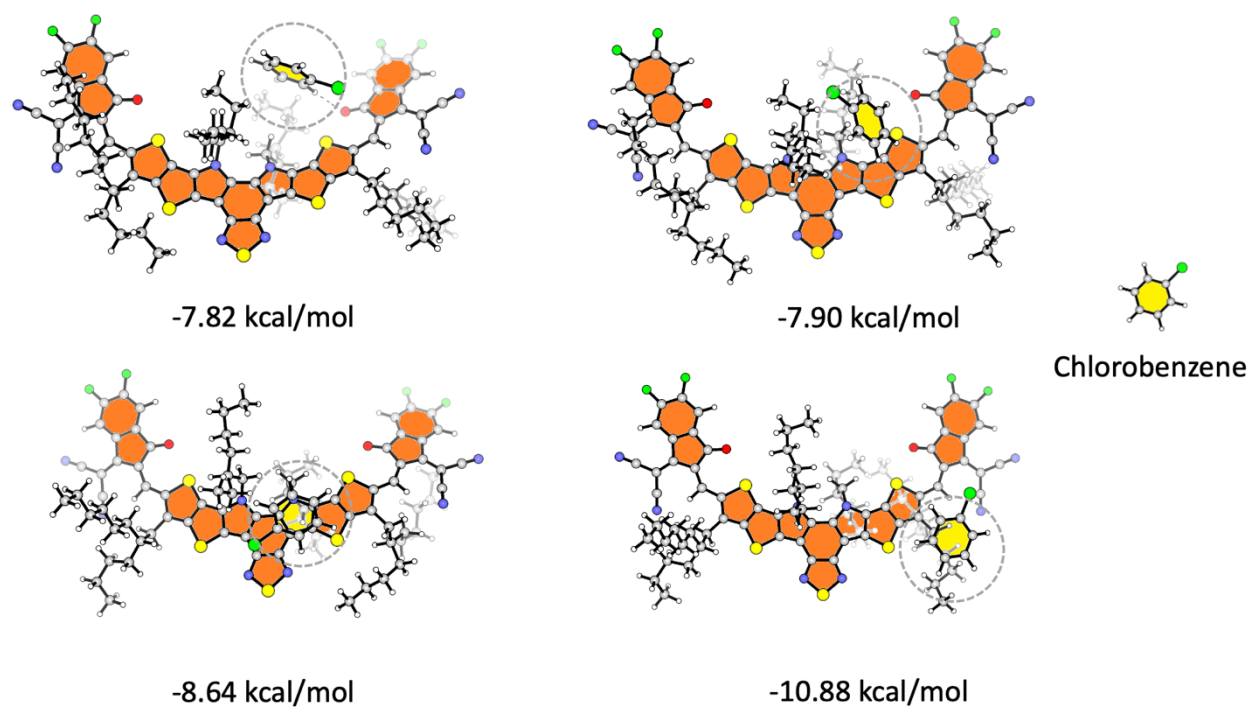
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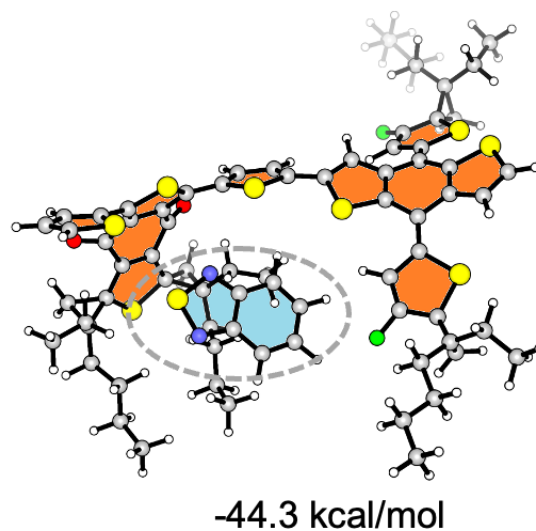
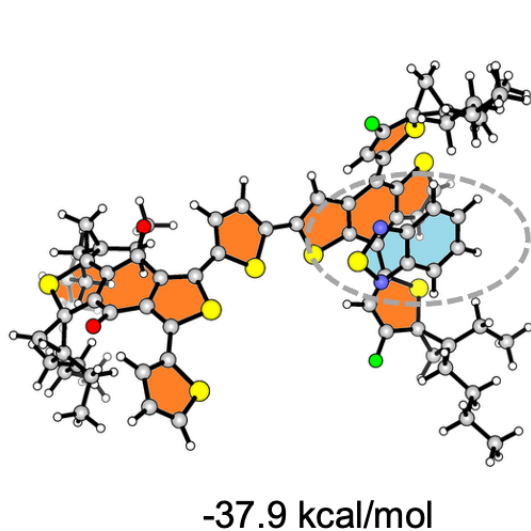
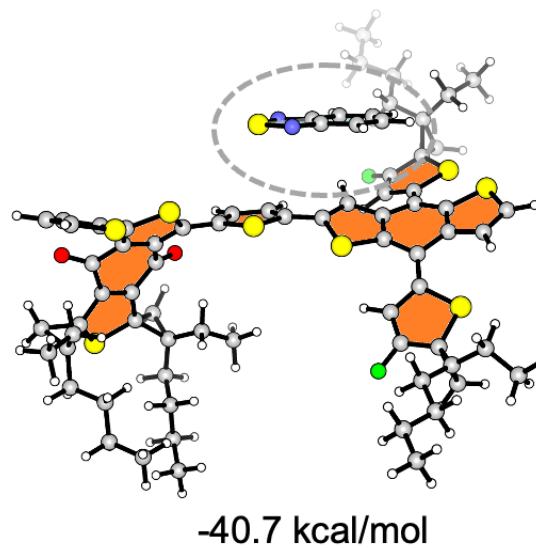
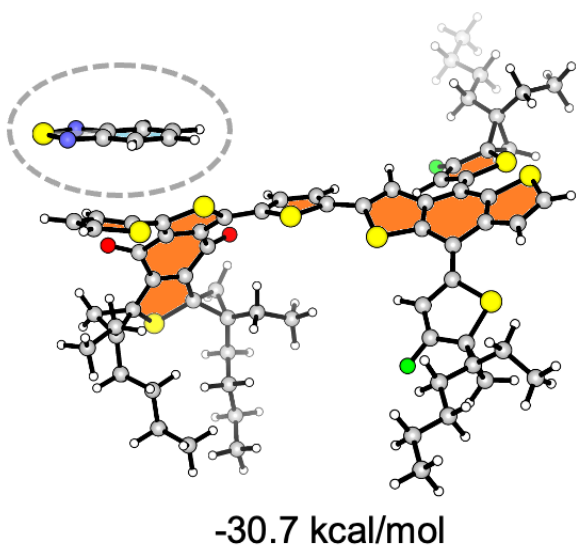
Supplementary Figure 32. The interaction energy between L8-BO and DIO molecule at different positions and optimized structures calculated by DFT.



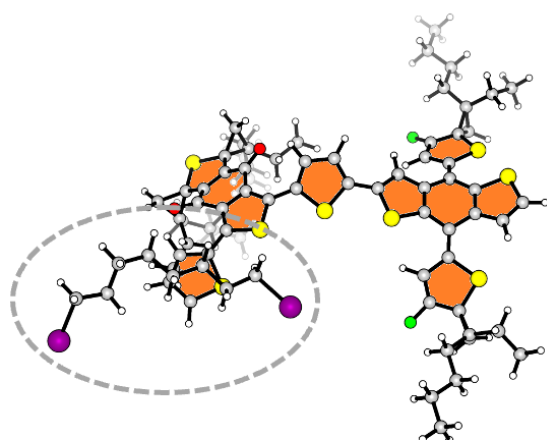
Supplementary Figure 33. Interaction energy between BTP-eC9 and chlorobenzene molecules at different positions and optimized structures calculated by DFT.



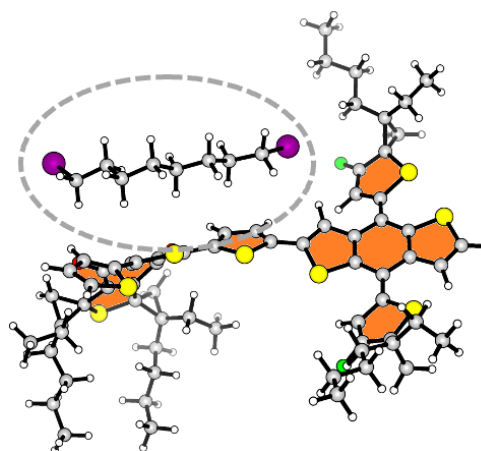
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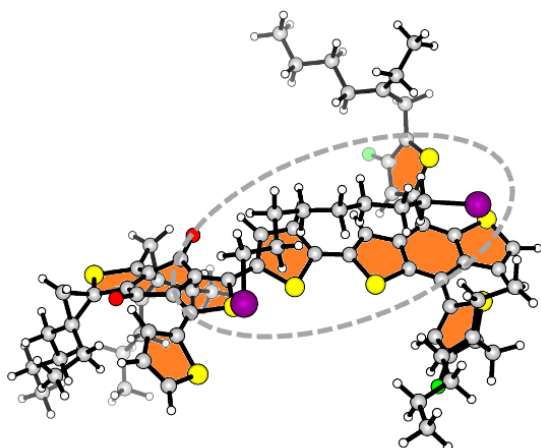
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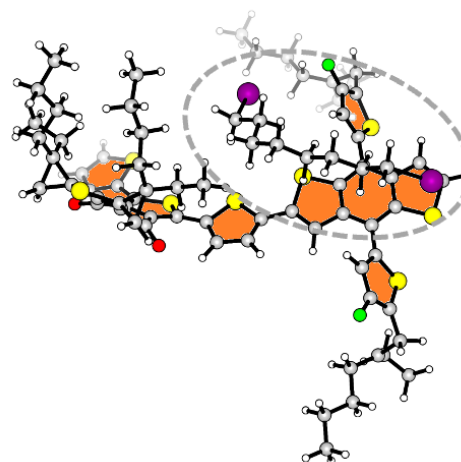
+26.9 kcal/mol



+21.1 kcal/mol

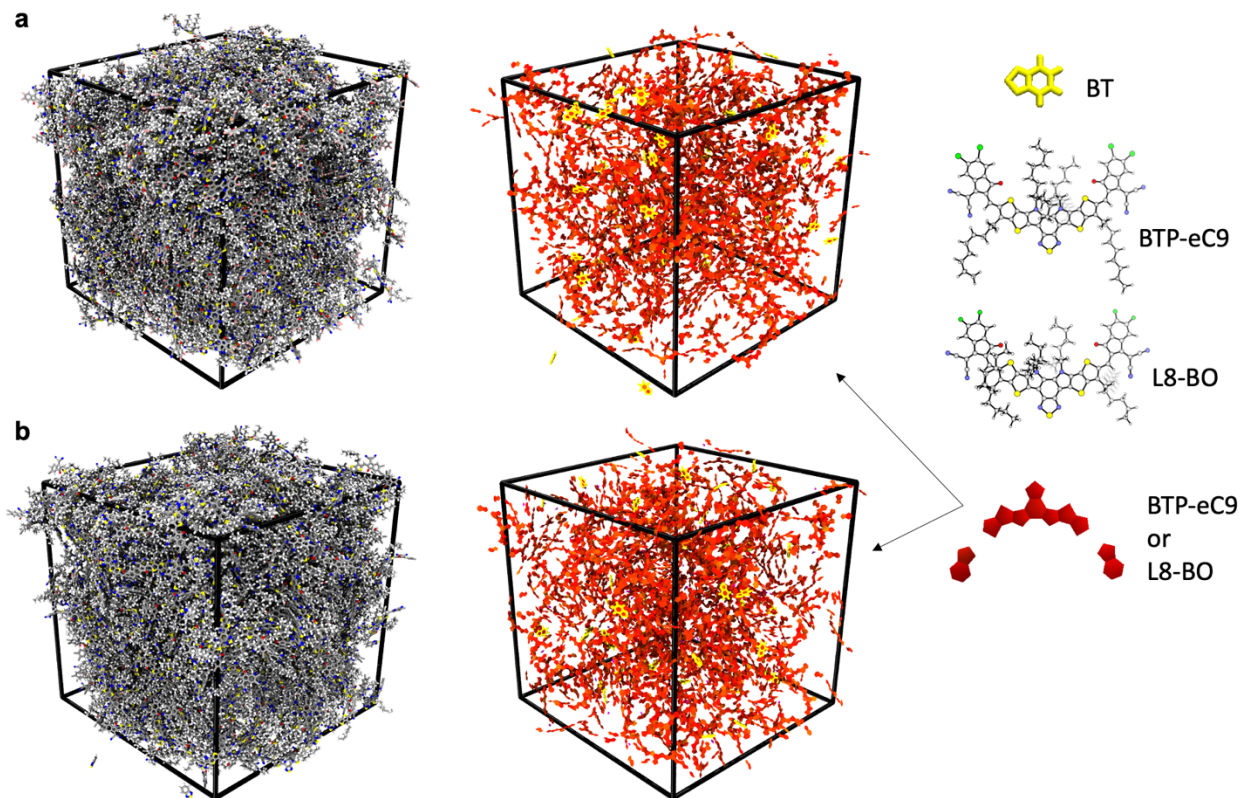


+19.7 kcal/mol

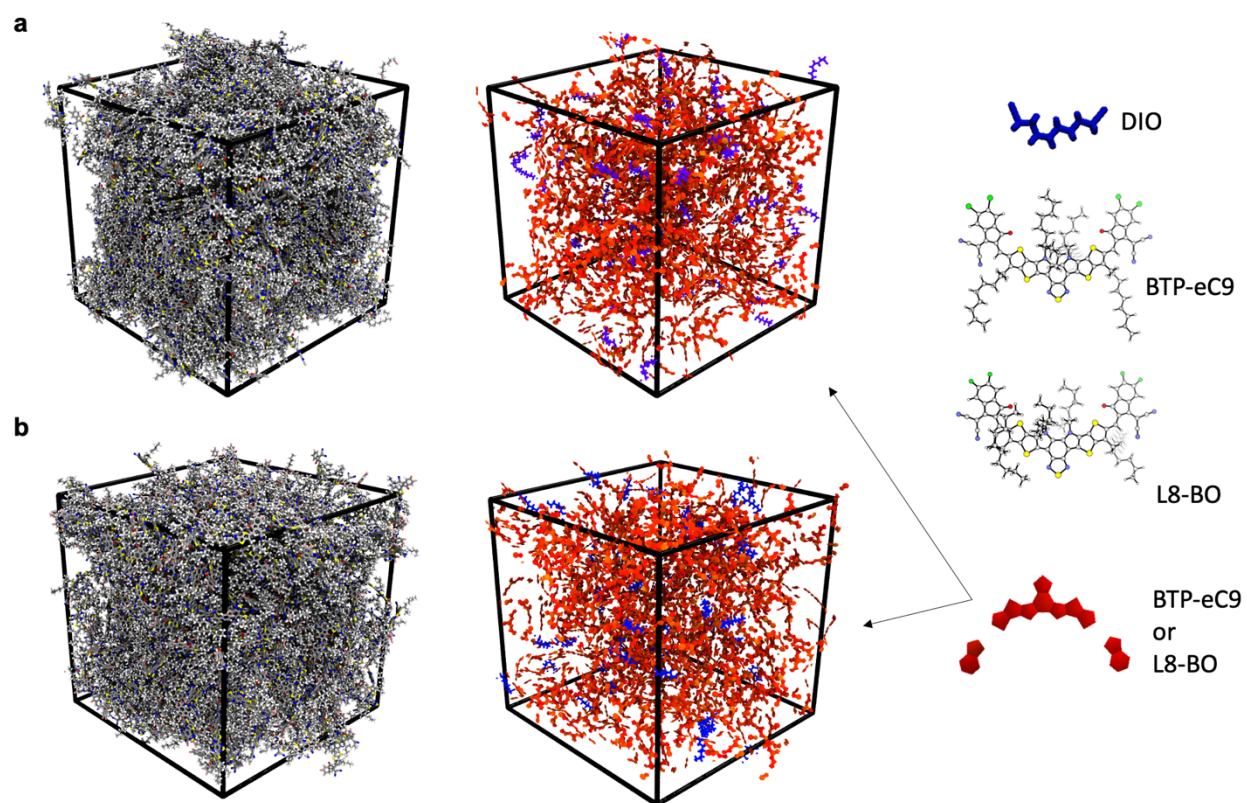


+20.1 kcal/mol

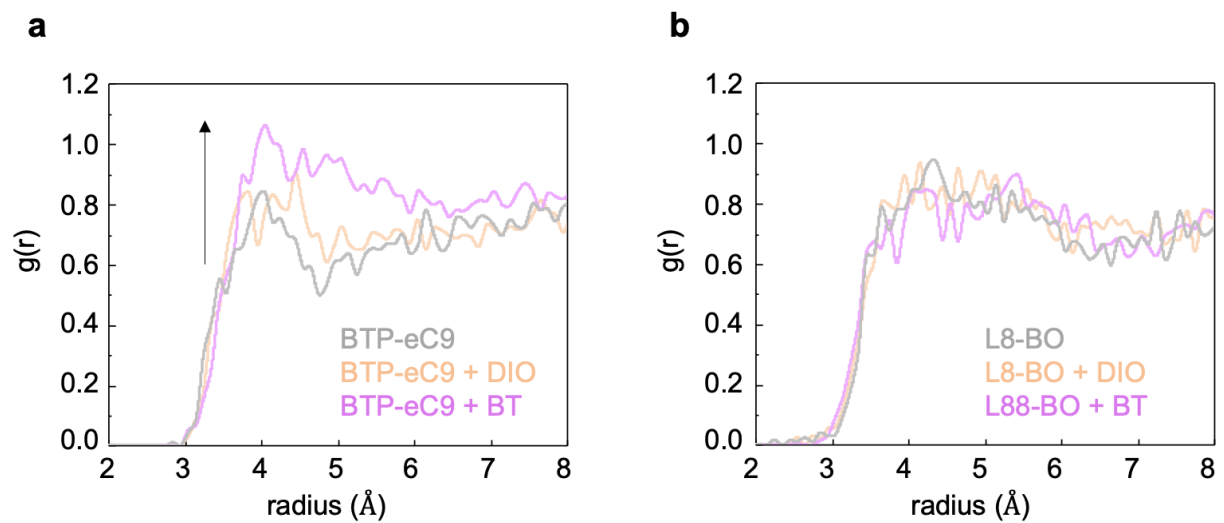
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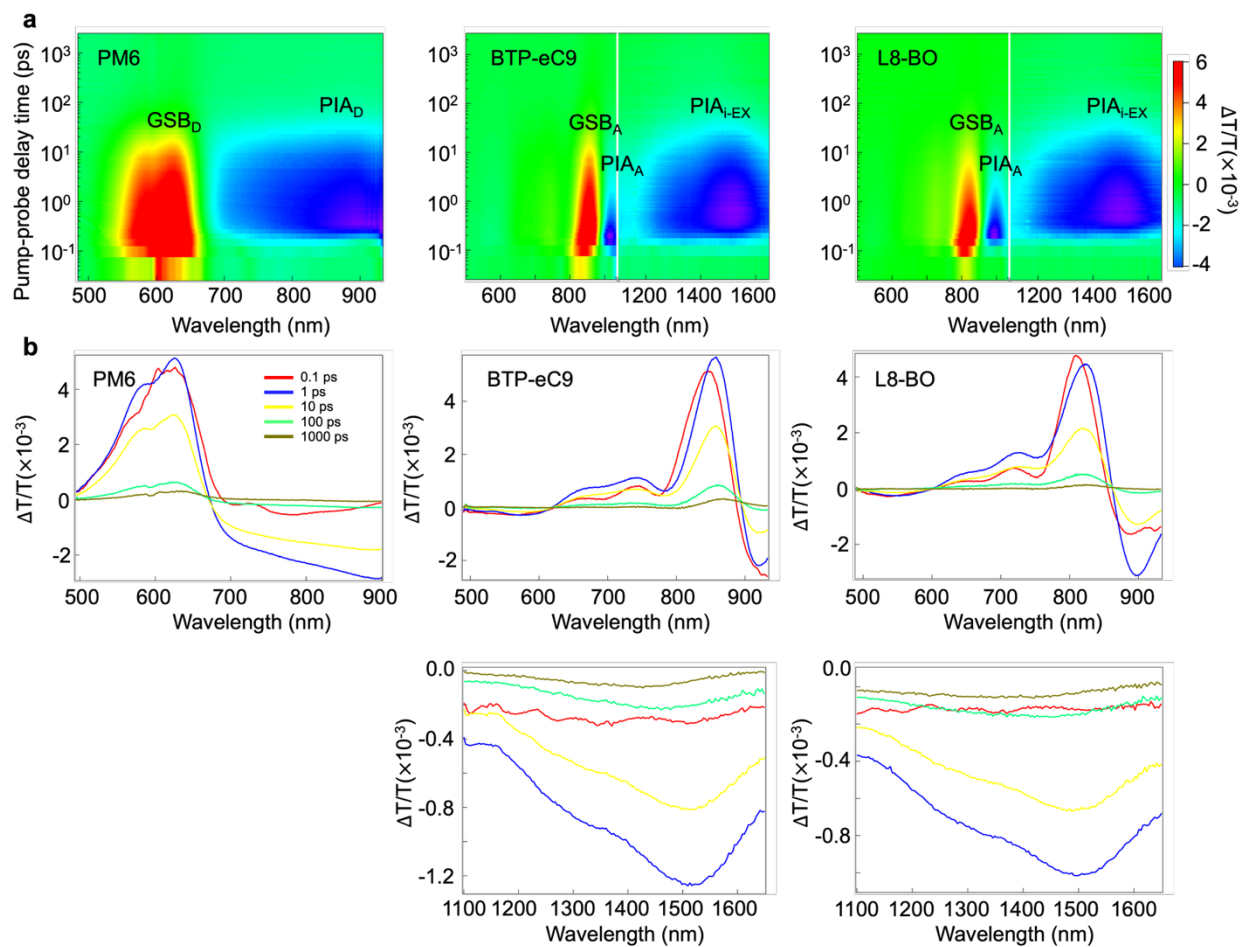
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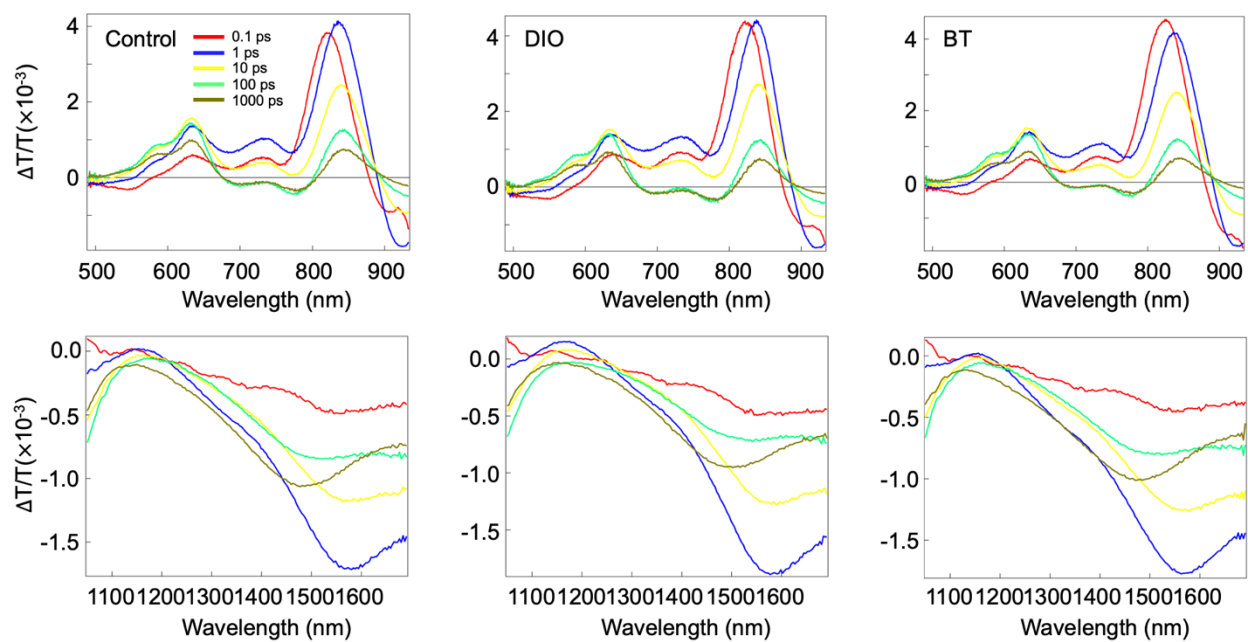
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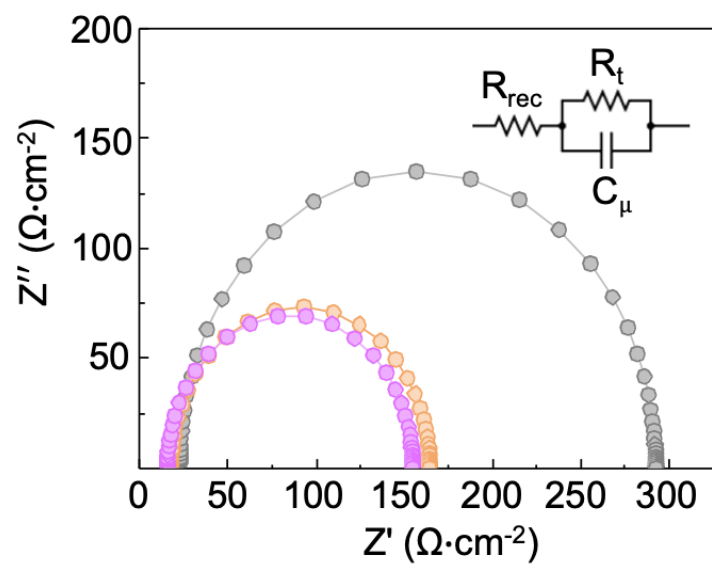
Supplementary Figure 39. Radial Distribution Functions (RDFs) between additive and acceptor aromatic rings in **a**, BTP-eC9 and **b**, L8-BO, indicating additive-specific short-range contact preferences.



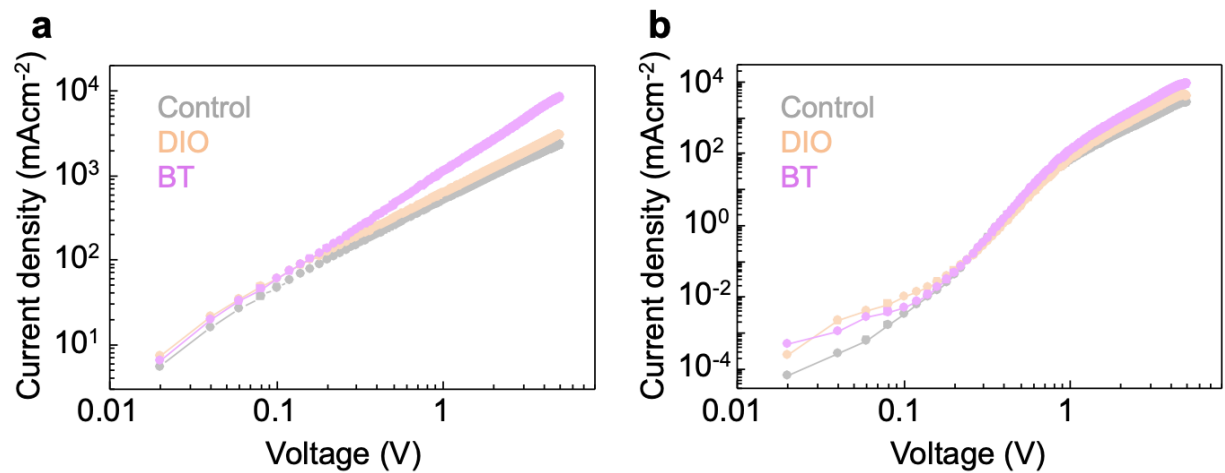
Supplementary Figure 40. a, Contour plots of TA spectra of neat films of PM6, BTP-eC9, and L8-BO. PM6 had an excitation wavelength of 600 nm, while BTP-eC9 and L8-BO had an excitation wavelength of 790 nm. **b**, TA spectra of different neat films at indicated delay times.



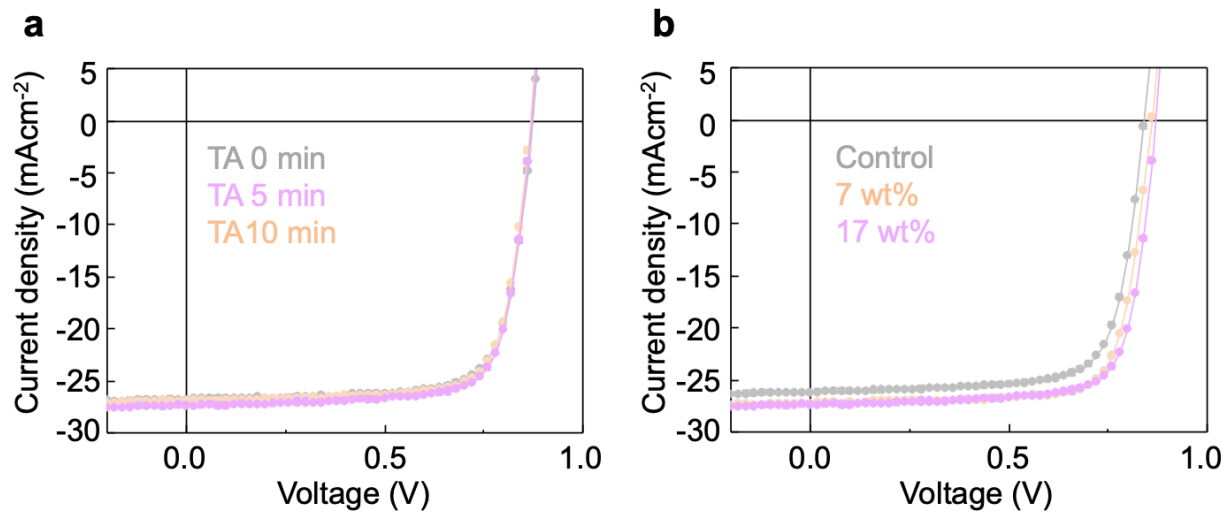
Supplementary Figure 41. TA spectra of the ternary blend films at indicated delay times.



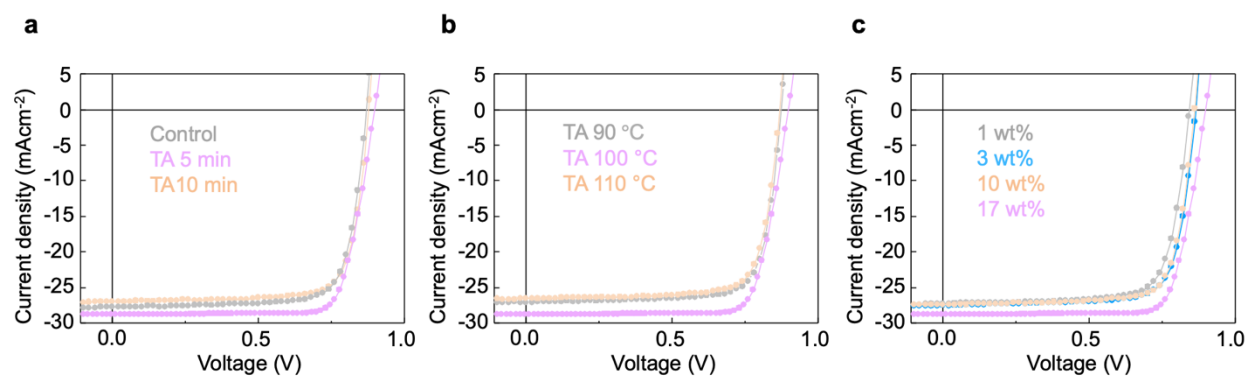
Supplementary Figure 42. Electrochemical impedance spectroscopy measurement of the binary blend devices.



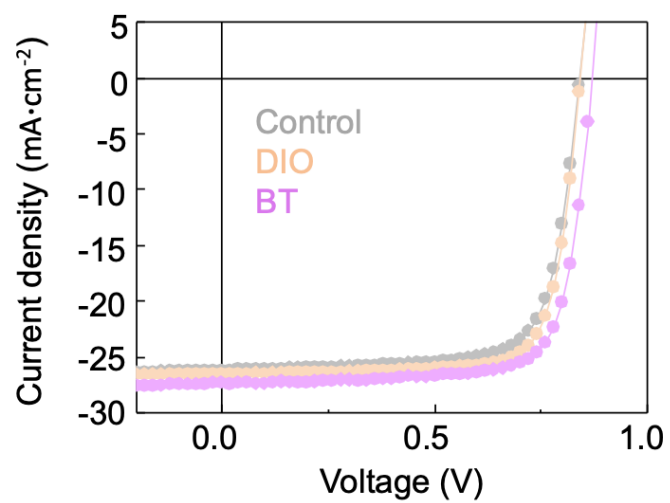
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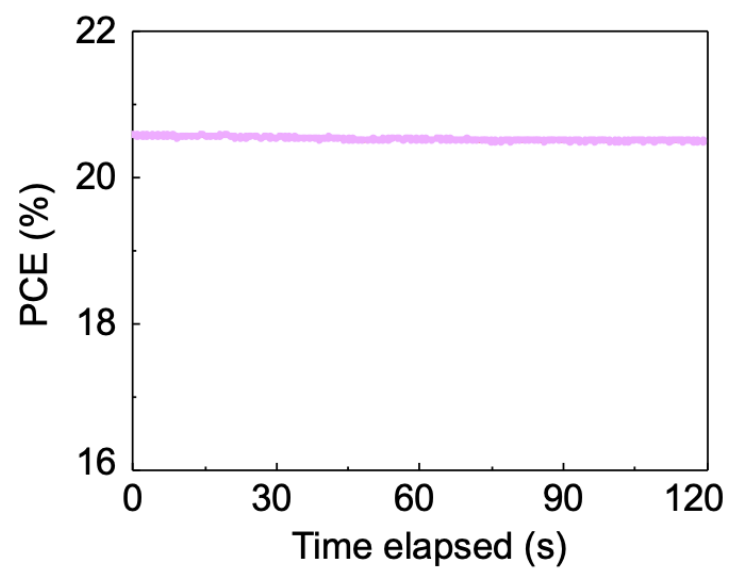
Supplementary Figure 44. IV curves of binary devices (PM6:BTP-eC9) to optimize the effect of **a**, the thermal annealing time and **b**, BT concentration on the device performance.



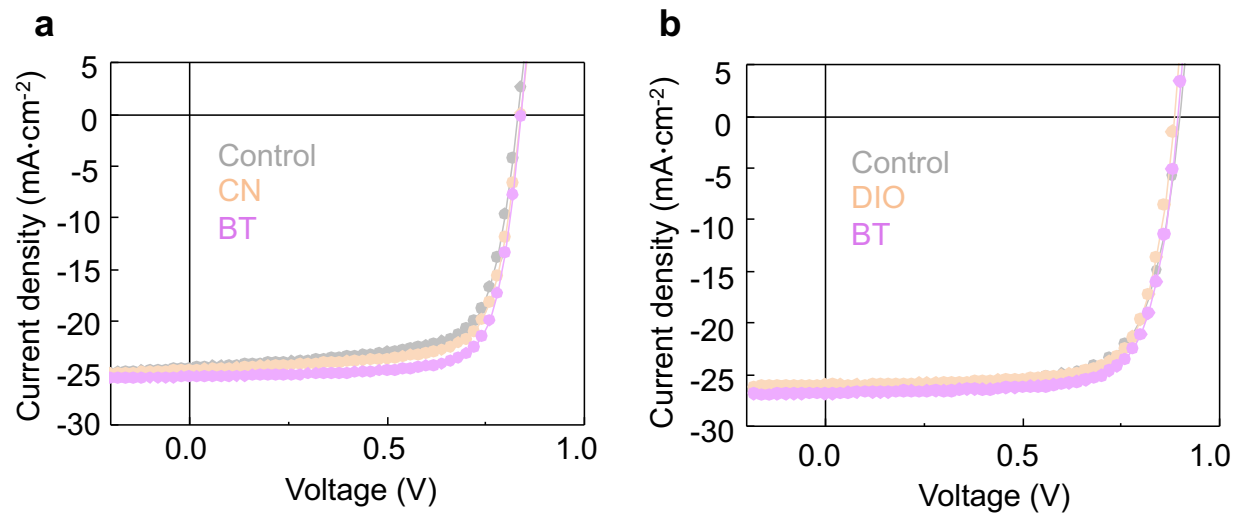
Supplementary Figure 45. IV curves of ternary devices (PM6:BTP-eC9:L8-BO) to optimize the effect of **a**, the thermal annealing time, **b**, temperature, and **c**, BT concentration on the device performance.



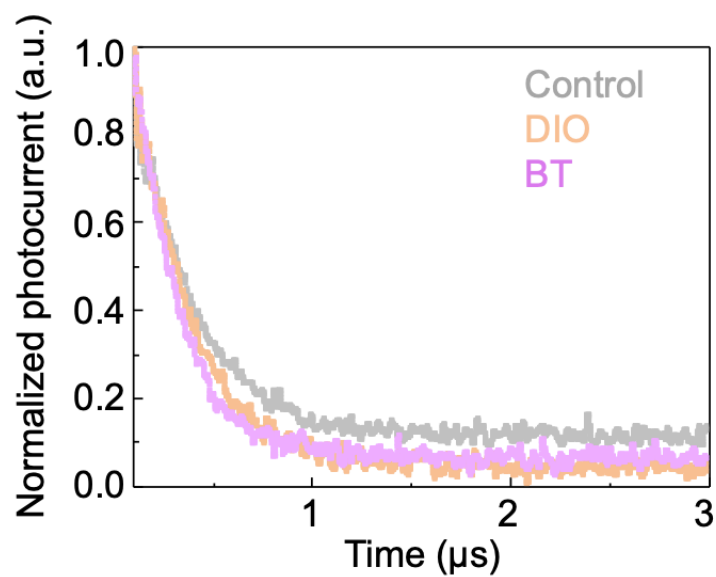
Supplementary Figure 46. IV curve of the optimized binary OPV devices fabricated in control, DIO, and BT blend system.



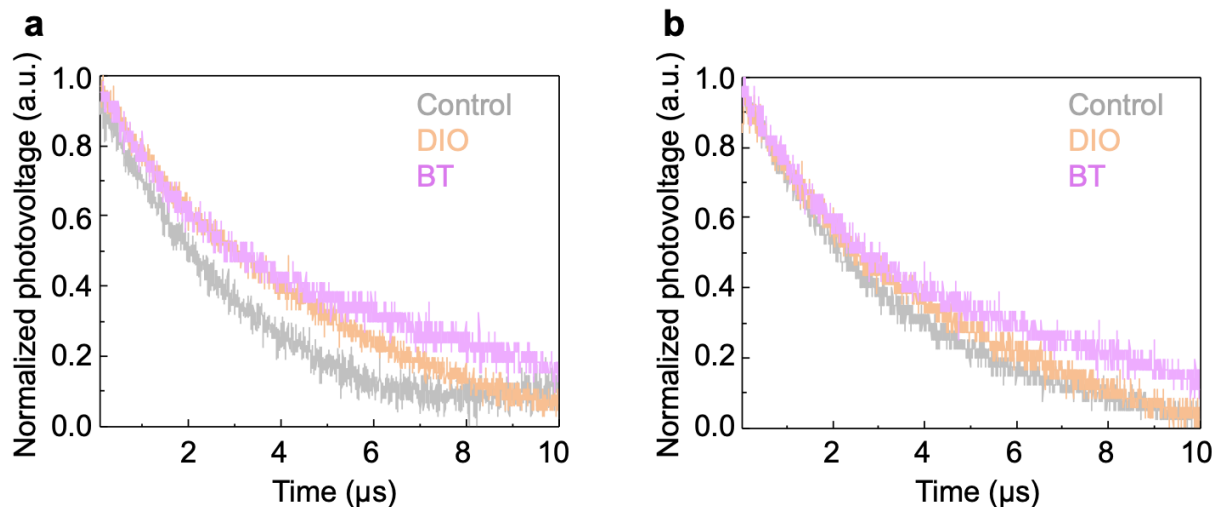
Supplementary Figure 47. The steady-state PCE of OPV devices fabricated in BT ternary system.



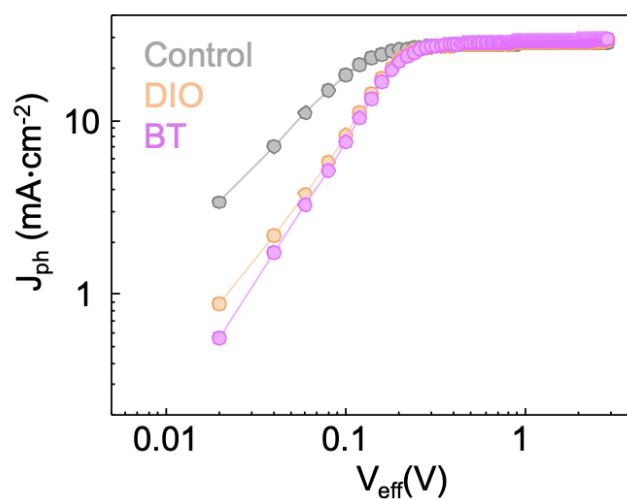
Supplementary Figure 48. IV curves of **a**, PM6:Y6 devices fabricated in control, CN (chloronaphthalene), and BT blends, and **b**, PM7:BTP-eC9:L8-BO devices fabricated in control, DIO, and BT blend systems.



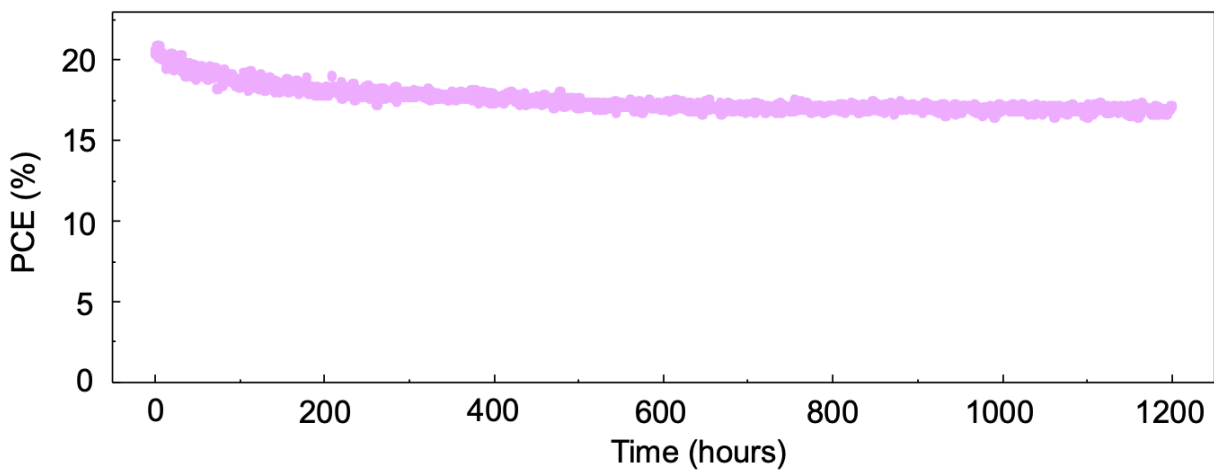
Supplementary Figure 49. Transient photocurrent decay curve of the binary blend devices. The decay times were 0.34 μs , 0.27 μs , and 0.21 μs for control, DIO, and BT binary blends, respectively, indicating faster charge extraction in the BT blend.



Supplementary Figure 50. Transient photovoltage (TPV) measurements of devices without additive, with DIO and BT additives in **a**, binary and **b**, ternary system. The TPV measurements were conducted under open-circuit condition. When the solar cell was illuminated under pulse light, there were photon-generated electrons and holes, followed by the generation of photovoltage. After the pulsed light was off, the voltage decreased owing to the recombination of electrons and holes at various sites such as defects.



Supplementary Figure 51. Photocurrent as a function of the effective voltage of the binary blend devices. The probability of exciton dissociation $P(E, T)$ was 97.0%, 97.6%, and 97.8% for control, DIO, and BT binary blends, respectively. It indicates that the BT blend has lower geminated recombination than DIO and control blends.



Supplementary Figure 52. MPP tracking traces of OPV device fabricated in BT blend system over 1,200 hours under ISOS-L-3 condition at 85 °C. The PCE decreased from 20.5% to 17.0% (reduction of 17.2%).

Supplementary Tables

Supplementary Table 1. Thermal properties of benzothiadiazole and other reference additives. Benzothiadiazole can reach 100 wt% loss at about 75% of boiling point. They can be melted into liquid before leaving the active layer completely. It can be removed efficiently by sublimation and volatilization. Given that the additive evaporation rate in the blend is usually much higher than that in the neat state because of a larger specific surface area of the additive, a 5 wt% loss point was adopted as an indication for the temperature to completely remove the solid additive from the active layer.^[3]

	T _m (°C)	T _b (°C)	Temperature @5wt% loss (°C)	Temperature @100wt% loss (°C)
Benzothiadiazole (Air)	42	206	82.5	150.6
Benzothiadiazole (N ₂)	42	206	77.2	144.3
*2-Chloronphthalene (2-CN)	59	256	76	128
*Dibromobenzene (DBB)	88	219	67	109
*Dichlorobenzene (DCB)	55	173	41	76

^[3] Fan, B., et al. Understanding the role of removable solid additives: selective interaction contributes to vertical component distributions. *Adv. Mater.* **35**, 2302861 (2023).

Supplementary Table 2. Absorbance ratio between peaks at 610 nm and 740 nm of samples 1 – 4 and their standard deviation.

Absorbance ratio (610 nm : 740 nm)	Sample 1	Sample 2	Sample 3	Sample 4	Standard Deviation
Liquid Precursor State	2.13:2.08	1.98:1.88	1.87:1.91	1.70:1.95	0.09 ~ 0.18
Thin Film State	0.58:0.66	0.58:0.66	0.59:0.66	0.58:0.66	0 ~ 0.005

Supplementary Table 3. Summary of d -spacing and crystal coherence lengths of the (010) peak in the out-of-plane for neat and blend films.

Active layer	q ($\text{\AA}^{-1}$)	d -spacing ($\text{\AA}$)	FWHM ($\text{\AA}^{-1}$)	CCL ($\text{\AA}$)
PM6	1.703	3.689	0.2590	21.590
BTP-eC9	1.768	3.553	0.2708	20.650
L8-BO	1.788	3.512	0.3002	18.627
Binary Control	1.744	3.602	0.2825	19.794
Binary DIO	1.751	3.588	0.2766	20.217
Binary BT	1.756	3.578	0.2510	22.279
Ternary Control	1.741	3.608	0.2731	20.476
Ternary DIO	1.750	3.590	0.2590	21.590
Ternary BT	1.752	3.586	0.2413	23.174

Supplementary Table 4. Summary of d -spacing and crystal coherence lengths of the (100) peak in the in-plane for neat and blend films.

Active layer		q ($\text{\AA}^{-1}$)	d -spacing ($\text{\AA}$)	FWHM ($\text{\AA}^{-1}$)	CCL ($\text{\AA}$)
PM6		0.293	21.443	0.0769	72.718
BTP-eC9		0.401	15.668	0.0781	71.600
L8-BO		0.369	17.027	0.0897	62.341
Binary Control	Donor	0.296	21.226	0.0599	93.356
	Acceptor	0.379	16.578	0.1071	52.213
Binary DIO	Donor	0.297	21.155	0.0561	99.679
	Acceptor	0.380	16.534	0.1042	53.666
Binary BT	Donor	0.300	20.943	0.0613	91.224
	Acceptor	0.382	16.448	0.1035	54.029
Ternary Control	Donor	0.294	21.371	0.0661	84.599
	Acceptor	0.379	16.578	0.1153	48.499
Ternary DIO	Donor	0.296	21.226	0.0595	93.983
	Acceptor	0.382	16.448	0.1075	52.018
Ternary BT	Donor	0.299	21.013	0.0651	85.899
	Acceptor	0.387	16.235	0.1041	53.717

Supplementary Table 5. Domain area percentages in donor dominating, acceptor dominating, and D/A intermixed regions in the top surface and sub-surface of the photoactive layer.

Domain Area	Binary						Ternary					
	Donor bottom	Acceptor Bottom	D/A Intermixed bottom	D/A Intermixed top	Donor top	Acceptor top	Donor bottom	Acceptor bottom	D/A Intermixed bottom	D/A Intermixed top	Donor top	Acceptor top
Control	7.57	24.13	68.30	72.51	11.12	16.37	9.55	21.63	68.82	70.99	10.83	18.18
DIO	9.80	21.33	68.87	66.76	13.62	19.62	14.17	17.82	68.01	67.03	11.71	21.26
BT	8.88	20.83	70.29	67.59	9.61	22.80	14.32	16.63	69.05	68.32	7.77	23.91

Supplementary Table 6. The contact angles and surface tension of the neat and ternary blend films.

Films	θ_{H_2O} (°)	θ_{EG} (°)	γ (mN/m)
PM6	110.3	82.8	21.4
BTP-eC9	101.3	74.4	27.1
L8-BO	98.5	74.5	28.1
Ternary Control	107.4	79.7	23.3
Ternary DIO	105.4	77.5	24.7
Ternary BT	105.1	76.8	25.1

Supplementary Table 7. Element intensity from the beginning to the end of measurement by depth profiling XPS.

Films	$t/t_{\max}$	$N_{1s} (\times 10^3)$	$Cl_{2p} (\times 10^3)$
Control	0.0	1.111	0.460
	0.16	1.723	0.724
	0.33	1.625	0.830
	0.51	1.687	0.859
	0.66	1.410	0.654
	0.83	0.391	0.217
	1	0	0
DIO	0.0	1.403	0.585
	0.16	1.825	0.902
	0.33	1.672	0.772
	0.51	1.613	0.720
	0.66	1.345	0.613
	0.83	0.246	0.175
	1	0	0
BT	0.0	1.491	0.658
	0.16	1.776	0.853
	0.33	1.531	0.809
	0.51	1.359	0.802
	0.66	1.265	0.556
	0.83	0.285	0.129
	1	0	0

Supplementary Table 8. The rise times of the hole transfer process in blend films extracted from the biexponential fitting, where A_i are the amplitudes, τ_i are the rise times of the two components.

	A_1	τ_1 (ps)	A_2	τ_2 (ps)
Con	0.451	0.433 ± 0.025	0.549	7.906 ± 0.341
DIO	0.423	0.218 ± 0.020	0.578	7.331 ± 0.327
BT	0.649	0.188 ± 0.011	0.351	5.620 ± 0.342

Supplementary Table 9. Recombination resistance, charge transfer resistance, and capacitance values of binary and ternary systems, measured by electrochemical impedance spectroscopy.

Binary	Control	DIO	BT
R_{rec}	22.4 Ω	17.8 Ω	15.5 Ω
R_{t}	270.0 Ω	146.6 Ω	139.2 Ω
Capacitance	3.75 nF	4.21 nF	3.62 nF
Ternary	Control	DIO	BT
R_{rec}	16.8 Ω	14.8 Ω	12.6 Ω
R_{t}	170.2 Ω	125.7 Ω	96.6 Ω
Capacitance	4.08 nF	4.91 nF	4.96 nF

Supplementary Table 10. Summary of photovoltaic performances of binary devices (PM6:BTP-eC9) in optimizing the effect of the thermal annealing time and BT concentration.

TA time effect	V_{oc}	J_{sc}	PCE	FF
TA100°C 0min	-0.870 (-0.871±0.004)	26.82 (26.709±0.124)	17.68 (17.652±0.127)	75.68 (75.836±0.128)
TA100°C 5min	-0.868 (-0.869±0.003)	27.35 (27.286±0.176)	18.23 (17.968±0.228)	76.81 (76.647±0.228)
TA100°C 10min	-0.865 (-0.859±0.00)	26.93 (26.958±0.147)	17.83 (17.506±0.201)	76.45 (76.115±0.317)
BT concentration effect	V_{oc}	J_{sc}	PCE	FF
Control	-0.842 (-0.840±0.003)	26.19 (26.282±0.374)	16.43 (16.381±0.212)	74.58 (73.803±0.433)
7 wt%	-0.859 (-0.853±0.004)	27.26 (27.215±0.125)	17.97 (17.680±0.179)	76.75 (76.443±0.201)
17 wt%	-0.868 (-0.869±0.003)	27.35 (27.286±0.176)	18.23 (17.968±0.228)	76.81 (76.647±0.228)

Supplementary Table 11. Summary of photovoltaic performances of ternary devices (PM6:BTP-eC9:L8-BO) in optimizing the effect of the thermal annealing time, temperature, and BT concentration.

TA time effect	V_{oc}	J_{sc}	PCE	FF
TA100°C 0min	-0.876 (-0.876±0.003)	27.04 (27.190±0.307)	18.41 (18.402±0.077)	77.63 (77.405±0.597)
TA100°C 5min	-0.885 (-0.885±0.002)	29.87 (28.745±0.240)	20.73 (20.435±0.054)	78.39 (78.772±0.180)
TA100°C 10min	-0.868 (-0.869±0.003)	27.75 (27.736±0.148)	18.69 (18.655±0.069)	77.52 (77.323±0.203)
TA temperature effect	V_{oc}	J_{sc}	PCE	FF
TA90°C 5min	-0.872 (-0.870±0.004)	27.12 (27.068±0.116)	18.37 (18.191±0.315)	77.66 (77.241±0.383)
TA100°C 5min	-0.885 (-0.885±0.002)	29.87 (28.745±0.240)	20.73 (20.435±0.054)	78.39 (78.772±0.180)
TA110°C 5min	-0.867 (-0.868±0.002)	26.52 (26.413±0.106)	17.88 (17.784±0.089)	77.71 (77.566±0.141)
BT concentration effect	V_{oc}	J_{sc}	PCE	FF
1 wt%	-0.855 (-0.842±0.006)	27.27 (27.089±0.405)	17.47 (17.219±0.187)	76.05 (75.525±0.812)
3 wt%	-0.863 (-0.854±0.005)	27.49 (27.430±0.138)	18.47 (18.038±0.267)	78.13 (77.268±0.661)
13 wt%	-0.888 (-0.874±0.012)	27.41 (27.760±0.219)	19.01 (18.917±0.088)	78.10 (77.791±0.467)
17 wt%	-0.885 (-0.885±0.002)	29.87 (28.745±0.240)	20.73 (20.435±0.054)	78.39 (78.772±0.180)

Supplementary Table 12. Summary of photovoltaic performances of binary devices (PM6:BTP-eC9) and ternary devices (PM6:BTP-eC9:L8-BO) in control, DIO, and BT blend system.

Binary	V_{oc}	J_{sc}	PCE	FF
Control	-0.842 (-0.840±0.003)	26.19 (26.282±0.374)	16.43 (16.381±0.212)	74.58 (73.803±0.433)
DIO	-0.843 (-0.837±0.005)	26.52 (26.610±0.180)	17.28 (17.060±0.249)	77.30 (76.588±0.552)
BT	-0.868 (-0.869±0.003)	27.35 (27.286±0.176)	18.23 (17.968±0.228)	76.81 (76.647±0.228)
Ternary	V_{oc}	J_{sc}	PCE	FF
Control	-0.850 (-0.845±0.010)	27.01 (27.072±0.146)	17.51 (17.431±0.215)	76.21 (75.790±0.377)
DIO	-0.856 (-0.847±0.007)	27.38 (27.287±0.120)	18.22 (17.933±0.296)	77.76 (77.056±0.513)
BT	-0.885 (-0.885±0.002)	29.87 (28.745±0.240)	20.73 (20.435±0.054)	78.39 (78.772±0.180)

Supplementary Table 13. Summary of the PM6:BTP-eC9 based ternary OSCs.

Active layer	Ratio	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)	Ref
PM6:BTP-eC9	1:1.2	0.85	26.8	77.5	17.6	[1]
PM6:BTP-eC9:BTP-F	1:1.02:0.18	0.86	27.0	79.7	18.5	
PM6:BTP-F	1:1.2	0.90	24.1	75.0	16.2	
PM6:BTP-eC9	1:1.2	0.84	26.6	78.1	17.5	[2]
PM6:L8-BO-F	1:1.2	0.93	23.4	76.9	16.8	
PM6:BTP-eC9:L8-BO-F	1:1.02:0.18	0.85	27.4	80.0	18.7	
PM6:BTP-eC9	1:1.2	0.84	27.0	76.1	17.4	[3]
PM6:BTP-eC9:MOIT-M	1:1.2:0.3	0.87	27.4	77.3	18.5	
PM6:MOIT-M	1:1.2	1.01	15.8	64.3	10.3	
PM6:Y6	1:1.2	0.84	24.9	71.0	14.9	[4]
PM6:BTP-eC9	1:1.2	0.86	23.2	69.0	13.3	
PM6:Y6:BTP-eC9	1:0.48:0.72	0.85	26.4	73.0	16.4	
PM6:BTP-ICB1F	1:1.2	0.97	21.8	65.0	13.8	[5]
PM6:BTP-ICB2F	1:1.2	0.94	25.0	68.6	16.2	
PM6:BTP-ICB3F	1:1.2	0.91	26.0	74.6	17.7	
PM6:BTP-ICBCF3	1:1.2	0.93	25.9	74.0	17.8	[6]
PM6:BTP-eC9:BTP-ICBCF3	1:1.2:0.24	0.85	27.4	77.8	18.2	
PM6:ZH1	1:1.2	1.057	6.9	52.8	3.9	
PM6:ZH2	1:1.2	0.96	20.0	68.3	13.0	
PM6: BTP-eC9	1:1.2	0.84	27.0	76.5	17.4	
PM6:BTP-eC9:ZH1	1:1.1:0.1	0.85	27.1	77.3	17.8	

Active layer	Ratio	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)	Ref
PM6:BTP-eC9:ZH2	1:1.1:0.1	0.86	27.3	79.7	18.8	[7]
PM6:BTP-eC9	1:1.2	0.85	26.8	77.6	17.5	
PM6:BTP-eC9:AFIC	1:1.2:0.1	0.85	27.7	79.0	18.7	
PM6:AFIC	1:1.2	0.90	18.1	76.0	12.4	
PM6:BTP-eC9	1:1.2	0.85	26.0	76.0	16.9	[8]
PM6:IT-M	1:1.2	1.02	15.2	60.1	9.4	[9]
PM6:BTP-eC9:IT-M	1:1.02:0.18	0.87	27.0	79.5	18.7	
PM6:G6-EH	1:1.2	0.89	24.3	77.1	16.7	
PM6:G6-BO	1:1.2	0.91	24.2	77.3	17.1	
PM6:G6-EHep	1:1.2	0.90	23.1	76.0	15.8	[10]
PM6:G6-BO:BTP-eC9	1:0.96:0.24	0.85	27.6	77.7	18.1	
PM6:BTP-eC9	1:1.2	0.86	25.8	76.0	16.9	
PM6:ITIC	1:1.2	1.00	15.1	59.4	9.5	
PM6:BTP-eC9:ITIC	1:1.08:0.12	0.87	26.8	78.2	18.3	[11]
PM6:BTP-eC9	1:1.2	0.84	26.5	78.4	17.4	
PM6:EH-C8F17	1:1.2	0.60	25.5	55.6	8.3	
PM6:BTP-eC9:EH-C8F17	1:1.1:0.1	0.84	27.3	79.2	18.0	
PM6:BTP-eC9	1:1.2	0.86	27.0	77.5	18.0	[12]
PM6:isoIDTIC	1:1.2	0.89	5.75	32.3	1.7	[13]
PM6:BTP-eC9:isoIDTIC	1:1.1:0.1	0.87	27.3	80.4	19.0	
PM6:BTP-eC9	1:1.2	0.85	27.2	76.8	17.7	

Active layer	Ratio	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)	Ref
PM6:LA21	1:1.2	0.97	18.5	70.7	12.6	
PM6:LA22	1:1.2	0.84	19.8	74.0	12.3	
PM6:LA23	1:1.2	0.93	19.7	70.4	13.0	
PM6:BTP-eC9:LA21	1:1.2:0.2	0.86	27.8	78.0	18.7	
PM6:BTP-eC9:LA22	1:1.2:0.2	0.84	27.5	78.0	18.1	[14]
PM6:BTP-eC9:LA23	1:1.2:0.2	0.86	28.0	79.5	19.1	
PM6:BTP-eC9	1:1.2	0.84	26.8	76.9	17.2	
PM6:PhC6-IC-F	1:1.2	0.83	20.1	64.1	10.7	
PM6:BTP-eC9:PhC6-IC-F	1:1:0.2	0.86	27.1	78.9	18.3	[15]
PM6:BTP-eC9	1:1.3	0.84	26.8	78.2	17.7	
PM6:ZY-4Cl	1:1.3	1.01	5.1	45.4	2.3	
PM6:BTP-eC9:ZY-4Cl	1:1.144:0.156	0.86	27.4	79.0	18.7	
PM6:IT-4F	1:1.2	0.85	21.5	73.4	13.5	[16]
PM6:BTP-eC9	1:1.2	0.85	27.2	74.2	17.1	
PM6:BTP-eC9:IT-4F	1:1.02:0.18	0.86	27.8	76.5	18.2	
PM6:BTP-eC9	1:1.2	0.85	27.8	76.4	18.1	
PM6:ITOA:BTP-eC9	1:0.05:1.2	0.87	28.3	78.8	19.3	[17]
PM6:BTP-eC9	1:1.2	0.85	28.8	78.4	19.3	
PM6:SMA	1:1.2	0.92	25.5	76.4	17.9	
PM6:BTP-eC9:SMA	1:1.08:0.12	0.86	29.1	80.5	20.2	
PM7-Si:BTP-eC9	1:1.2	0.90	14.4	41.7	5.4	[19]

Active layer	Ratio	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)	Ref
PM6:BTP-eC9	1:1.2	0.84	26.4	76.6	17.0	[20]
PM6:PM7-Si:BTP-eC9	0.9:0.1:1.2	0.86	26.4	77.6	17.7	
PM6:BTPeC9	1:1.2	0.85	26.6	77.3	17.3	
BPR-SCl:BTPeC9	1:1.2	0.90	4.9	20.4	0.9	
PM6:BPR-SCl:BTPeC9	0.8:0.2:1.2	0.86	27.1	77.6	18.0	[21]
PM6:BTP-eC9	1:1.2	0.90	25.7	74.5	17.4	
PM6:PTO2:BTP-eC9	1:0.1:1.2	0.90	27.1	73.3	18.0	
PM6:BTP-eC9	1:1.2	0.84	26.7	77.0	17.4	[22]
BTR-Cl:BTP-eC9	1:1.2	0.73	20.1	48.8	18.3	
PM6:BTR-Cl:BTP-eC9	1:0.15:1.2	0.84	27.7	79.0	7.1	[23]
PM6:BTP-eC9	1:1.2	0.84	27.6	75.1	17.3	
PM6:PCN3:BTP-eC9	0.9:0.1:1.2	0.86	26.9	78.2	18.1	
PM6:BTPeC9	1:1.2	0.83	26.1	78.7	17.1	[24]
FY1:BTP-eC9	1:1.2	0.85	23.9	70.8	14.5	
FY2:BTP-eC9	1:1.2	0.84	22.6	66.9	12.6	
FY3:BTP-eC9	1:1.2	0.85	21.8	64.7	12.0	[25]
FY1:PM6:BTPeC9	0.05:0.95:1.2	0.85	27.5	79.1	18.5	
PM6:BTP-eC9	1:1.2	0.84	26.5	77.5	17.3	
PM6:D18-SiCl: BTP-eC9	0.9:0.1:1.2	0.85	27.7	79.0	18.7	[26]
PM6:BTP-eC9	1:1.2	0.84	26.7	77.7	17.4	
PM6:TB-S	1:1.2	0.95	20.7	72.4	14.2	

Active layer	Ratio	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)	Ref
PM6:TB-S1	1:1.2	1.03	13.8	44.9	6.4	
PM6:TB-S1-O	1:1.2	1.12	13.6	60.0	9.1	
PM6:BTP-eC9:TB-S	1:1.05:0.15	0.83	26.4	73.9	16.2	
PM6:BTP-eC9:TB-S1	1:1.05:0.15	0.83	27.3	71.6	16.2	
PM6:BTP-eC9:TB-S1-O	1:1.05:0.15	0.86	27.4	77.2	18.1	
PM6:AITC	1:1.2	1.07	14.3	71.6	11.0	[27]
PM6:BTP-eC9	1:1.2	0.87	27.2	79.7	18.8	
PM6:AITC:BTP-eC9	1:0.3:1.2	0.84	26.9	76.5	17.2	
PM6:BTP-eC9	1:1.2	0.85	26.7	75.6	17.2	[28]
PM6:ITIC-Th	1:1.2	0.98	16.4	71.4	11.5	
PM6:BTP-eC9:ITIC-Th	1:1.02:0.18	0.87	28.0	77.0	18.7	

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Supplementary Table 14. Summary of photovoltaic performances of PM6:Y6 devices fabricated in control, CN, and BT blends, and PM7:BTP-eC9:L8-BO devices fabricated in control, DIO, and BT blend systems.

PM6:Y6	V_{oc}	J_{sc}	PCE	FF
Control	-0.832 (-0.831±0.001)	24.52 (24.415±0.163)	14.51 (14.415±0.111)	71.09 (69.750±0.252)
CN	-0.840 (-0.835±0.005)	24.71 (24.557±0.219)	15.19 (15.123±0.070)	73.18 (72.980±0.134)
BT	-0.840 (-0.837±0.003)	25.49 (25.432±0.078)	15.88 (15.835±0.064)	74.13 (73.860±0.381)
PM7:BTP-eC9:L8-BO	V_{oc}	J_{sc}	PCE	FF
Control	-0.890 (-0.889±0.011)	26.13 (25.960±0.030)	16.85 (16.638±0.268)	70.80 (71.285±0.159)
DIO	-0.889 (-0.885±0.007)	26.10 (26.045±0.077)	17.19 (17.145±0.063)	74.84 (74.460±0.537)
BT	-0.895 (-0.897±0.003)	26.87 (26.880±0.014)	17.90 (17.895±0.021)	74.69 (74.495±0.257)

Supplementary Table 15. The device performance of semi-transparent OPVs.

PCE (%)	AVT (%)	LUE (%)	Reference
13.5	21.5	2.9	1
13.7	22.2	3.0	2
12.9	22.4	2.9	3
12.2	22.2	2.7	4
12.0	20.0	2.4	5
9.1	40.0	3.6	6
13.1	22.4	2.9	7
8.1	43.3	3.5	8
10.0	34.0	3.4	9
9.8	32.0	3.1	10
9.3	21.0	1.9	11
11.0	30.0	3.3	12
10.3	37.4	3.8	13
7.7	37.0	2.8	14
9.4	24.6	2.3	15
8.5	26.2	2.2	16
14.9	25.1	3.7	This work

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Supplementary Table 16. Summary of the stability for PM6:BTP-eC9 based OSCs.

Active layer	PCE (%)	Storage conditions	Time (h)	PCE/PCE ₀ (%)	Ref
PM6:BTP-eC9:L8-BO-F	18.7	1 sun AM 1.5 G	50	80	[1]
PM6:BTP-eC9:BTP-F	18.5	1 sun AM 1.5 G	142	80	[2]
PM6:BPR-SCl:BTPeC9	18.0	1 sun AM 1.5 G	100	78	[3]
PM6:AITC:BTPeC9	16.7	1 sun AM 1.5 G	1300	84	[4]
PM6:BTP-eC9:ZY-4Cl	18.7	1 sun AM 1.5 G	62.5	80	[5]
PM6:BTP-eC9:isoIDTIC	19.0	1 sun AM 1.5 G	254	80	[6]
PM6:BTP-eC9:AFIC	18.7	white LED	130	80	[7]
PM6:BTP-eC9:ZH1	17.8	1 sun AM 1.5 G	35.2	80	[8]
PM6:BTP-eC9:ZH2	18.8	1 sun AM 1.5 G	39.9	80	
FY1:PM6:BTP-eC9	18.5	LED illumination	100	80	[9]
PM6:BTP-eC9:L8-BO-F	19.1	1 sun AM 1.5 G	1140	87	[10]
PM6:BTP-eC9	19.3	1 sun AM 1.5 G	1000	78	[11]
PM6:BTP-eC9:L8-BO-X	19.0	1 sun AM 1.5 G	1200	82	[12]
PM6:BTP-eC9:PC71BM	18.3	100 °C	13	80	[13]
PM6:L8-BO:BTP-eC9	18.9	60 °C	48	91	[14]
PM6:BTP-eC9:LA23	19.1	60 °C	60	86	[15]
PM6:BTP-eC9	12.6	85 °C	400	90	[16]
		1 sun AM 1.5 G	400	85	
PM6:BTP-eC9:PhC6-IC-F	18.3	85 °C	200	70	[17]
		1 sun AM 1.5 G	200	78	
PM6:BTP-eC9	16.6	150 °C	72	63	[18]

Active layer	PCE (%)	Storage conditions	Time (h)	PCE/PCE ₀ (%)	Ref
PM6:Y6:BTP-eC9	16.4	N2-filled glovebox	150	86	[19]
PM6:BTP-eC9:MOIT-M	18.5	N2-filled glovebox	864	80	[20]
PM6:BTP-eC9	18.3	N2-filled glovebox	350	82	[21]
PM6:BTP-eC9	15.5	N2-filled glovebox	200	94	[22]
PM6:BTP-eC9	15.3	N2-filled glovebox	650	86	[23]
PM6:BTP-eC9	19.1	N2-filled glovebox	7438	80	[24]

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