Supporting Information for

Additive assisted molecular aggregation manipulation towards efficient thick organic solar cells

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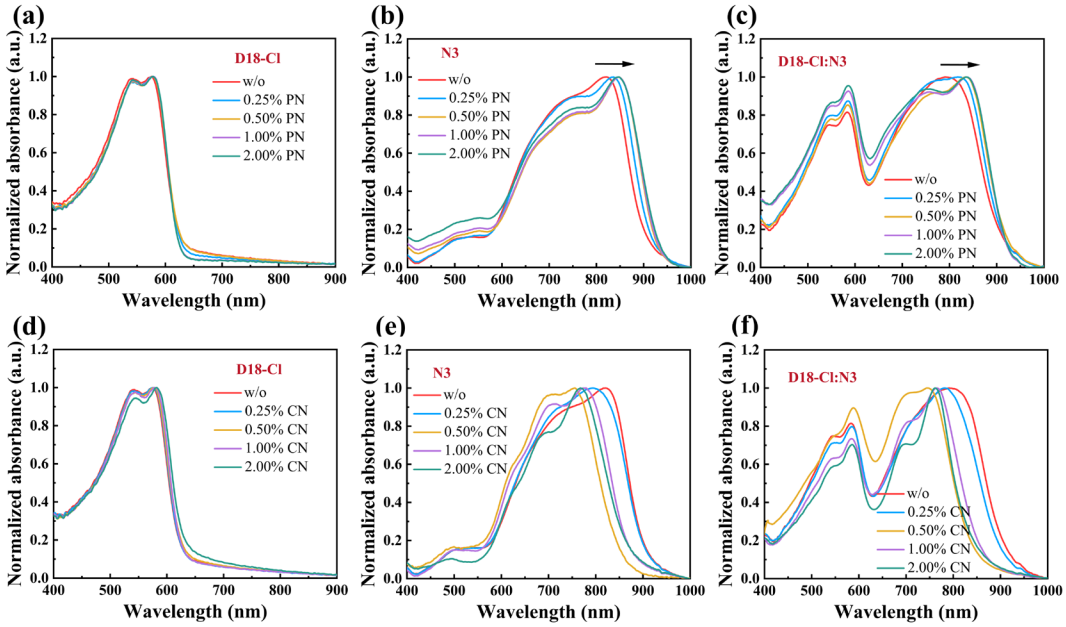

Figure S1. The absorbance of (a) neat D18-Cl films, (b) neat N3 films, and (c) D18-Cl:N3 films with different concentrations of PN. And the absorbance of (d) neat D18-Cl films, (e) neat N3 films, and (f) D18-Cl:N3 films with different concentrations of CN.

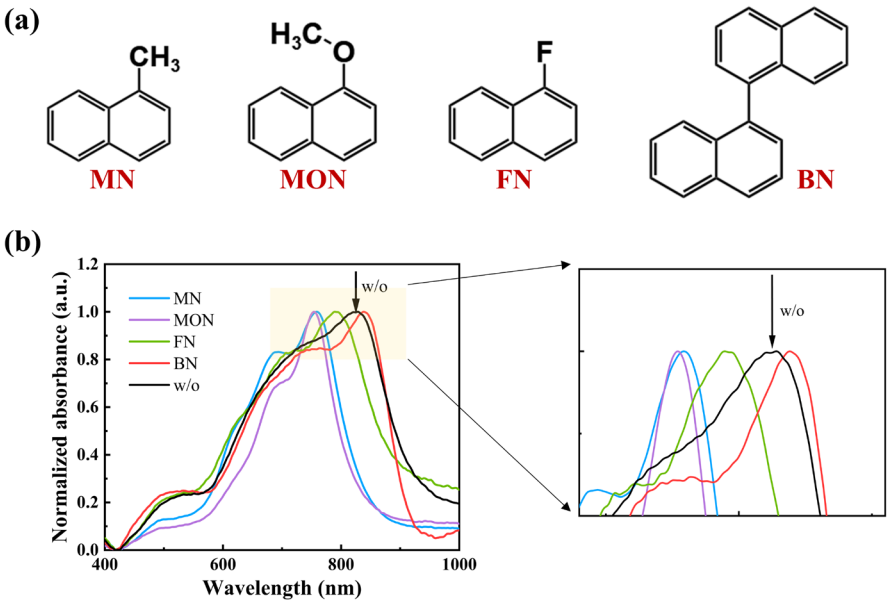

Figure S2. (a) Chemical structures of 1-methylnaphthalene (MN), 1-methoxynaphthalene (MON), 1-fluoronaphthalene (FN) and 1,1'-binaphthalene (BN). (b) The absorbance of N3 processed with MN, MON, FN and BN.

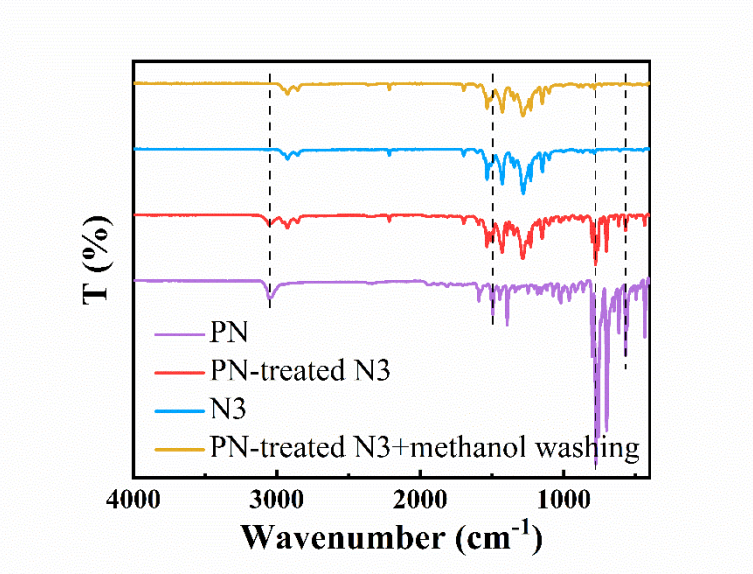

Figure S3. Fourier transform infrared (FTIR) spectra of the N3 films prepared without PN, with PN, and with PN after methanol washing.

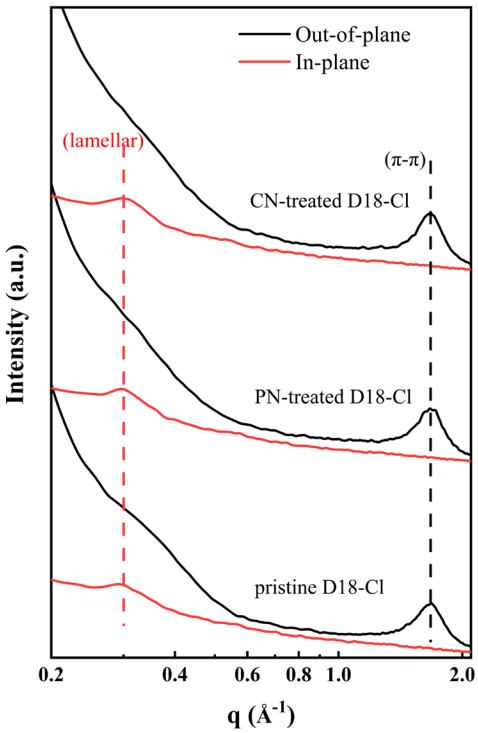

Figure S4. GIXRD profiles of neat D18-Cl without and with different additives (0.5 vol%).

Table S1. The GIXRD (100) peak parameters of blend films processed with or without additive in IP directions. The concentration of additive is 0.5 vol%.

Active layer	Thickness (nm)	Location ($Å^{-1}$)	d-spacing[a] (Å)	CCL[b] (Å)	Intensity (%)
Control		0.29	21.53	27.37	1016
PN	120	0.28	22.63	29.95	1152
CN		0.30	21.29	29.51	1033
Control		0.29	21.53	25.89	1322
PN	300	0.28	22.34	31.47	1659
CN		0.30	21.01	31.08	1504

a). d-spacing=$2\pi/q$, where q is the position of the diffraction peak.

b). CCL=$2\pi K$/FWHM, where K is shape factor, FWHM is the full-width at half-maximum of the peak.

Table S2. The GIXRD (010) peak parameters of blend films processed with or without additive in OOP directions. The concentration of additive is 0.5 vol%.

Active layer	Thickness (nm)	Location ($Å^{-1}$)	d-spacing (Å)	CCL (Å)	Intensity (%)
Control		1.77	3.55	19.36	1216
PN	120	1.79	3.52	23.19	1372
CN		1.77	3.55	21.17	1299
Control		1.77	3.55	20.13	2426
PN	300	1.79	3.52	25.55	2728
CN		1.76	3.56	22.89	2799

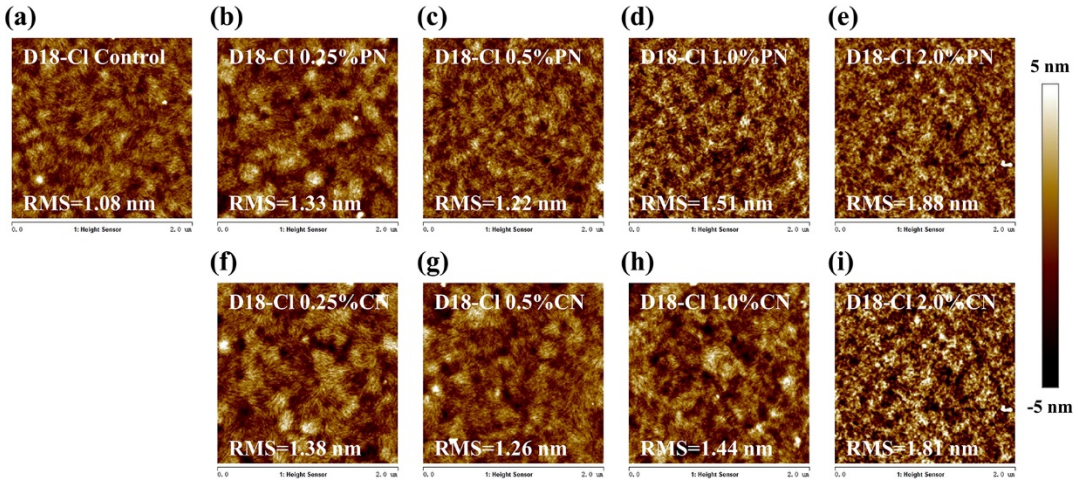

Figure S5. The AFM images of pristine D18-Cl films with (a)-(e) different concentrations of PN and (f)-(i) different concentrations of CN.

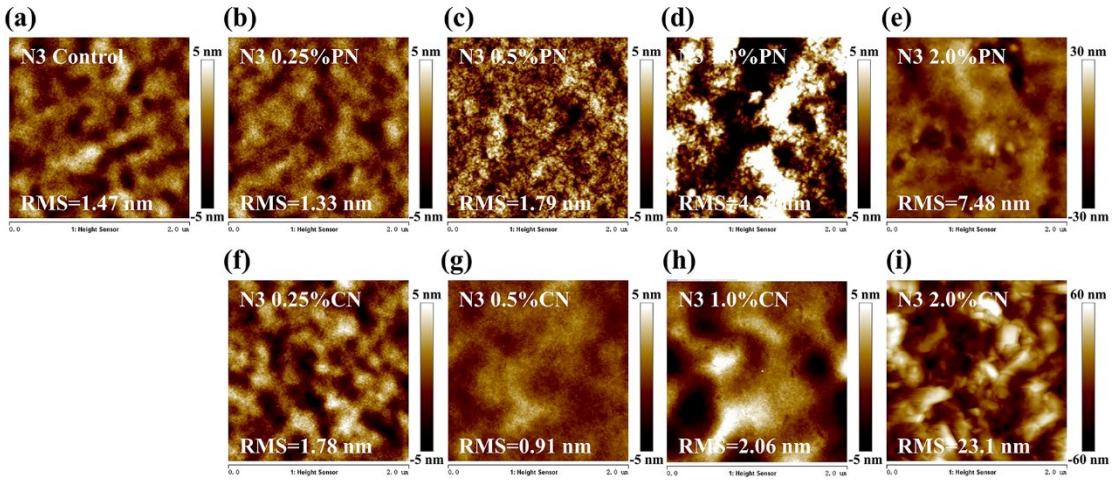

Figure S6. The AFM images of pristine N3 films with (a)-(e) different concentrations of PN and (f)-(i) different concentrations of CN.

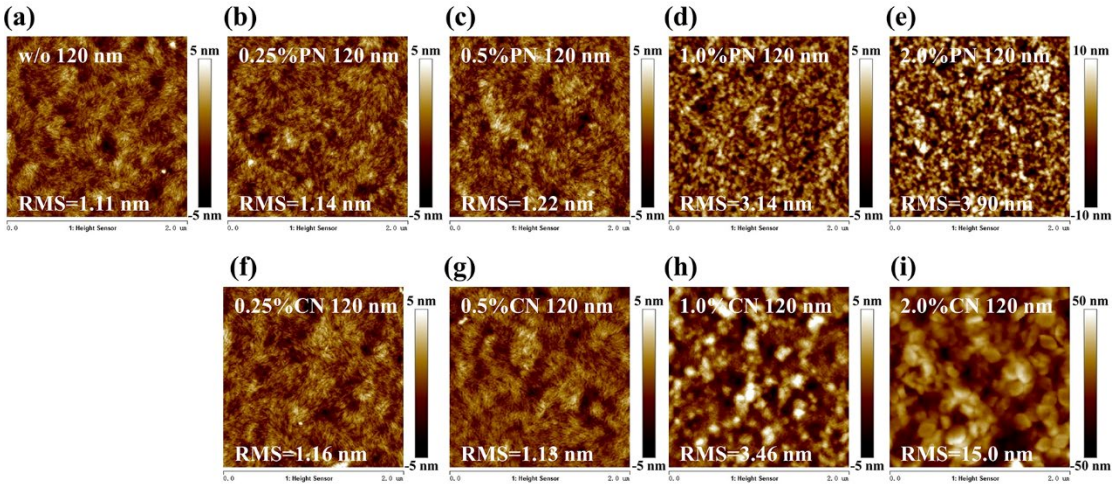

Figure S7. The AFM images of D18-Cl:N3 blend films at a thickness of 120 nm with (a)-(e) different concentrations of PN and (f)-(i) different concentrations of CN.

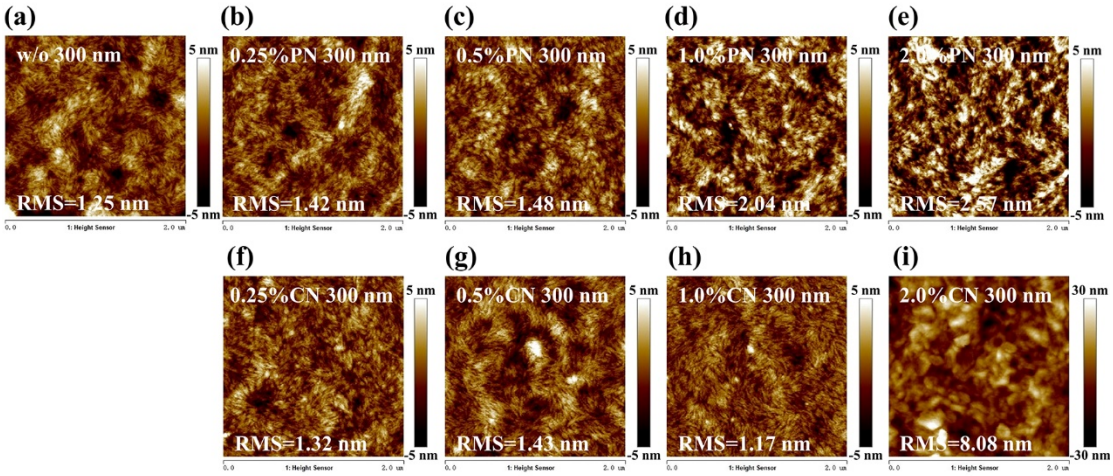

Figure S8. The AFM images of D18-Cl:N3 blend films at a thickness of 300 nm with (a)-(e) different concentrations of PN and (f)-(i) different concentrations of CN.

Table S3. The summarized solubility parameters (δ) of materials and solvents, and the calculated interaction parameters (χ) as well as the calculation formula.

	δ_D ($MPa^{1/2}$)	δ_P ($MPa^{1/2}$)	δ_H ($MPa^{1/2}$)	δ ($MPa^{1/2}$)	χ_{ij}
D18-Cl				17.94[1]	
N3				19.48[1]	
PN	20.5	2.7	3.4	20.95[2]	
CN	19.9	4.9	2.5	20.65[3]	
D18-Cl-PN					1.04
D18-Cl-CN					0.75
N3-PN					0.51
N3-CN					0.42

The interaction parameters between a nonpolar solvent and nonpolar polymer could be estimated by the following equation according to the Flory–Huggins theory:[1]

$$\boldsymbol{\chi_{ij} = \frac{v_i}{RT}(\delta_i - \delta_j)^2 + 0.34}$$

v_i represents the molar volume of one solvent molecule. R, T, and δ stands for ideal gas constant, Kelvin temperature, and solubility parameters, respectively.

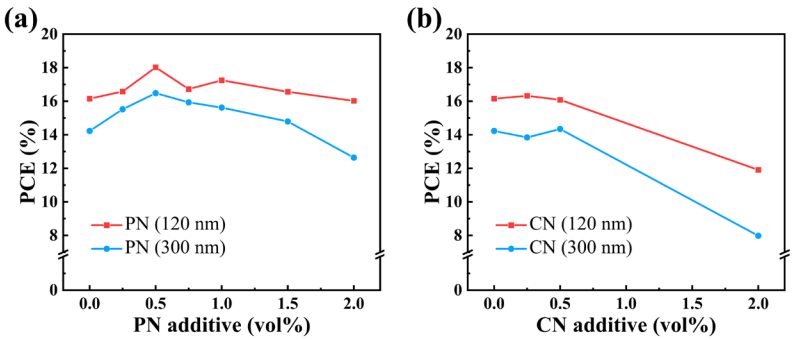

Figure S9. The PCE of varying the volume fraction of (a) PN, and (b) CN from 0.25% to 2% in the devices.

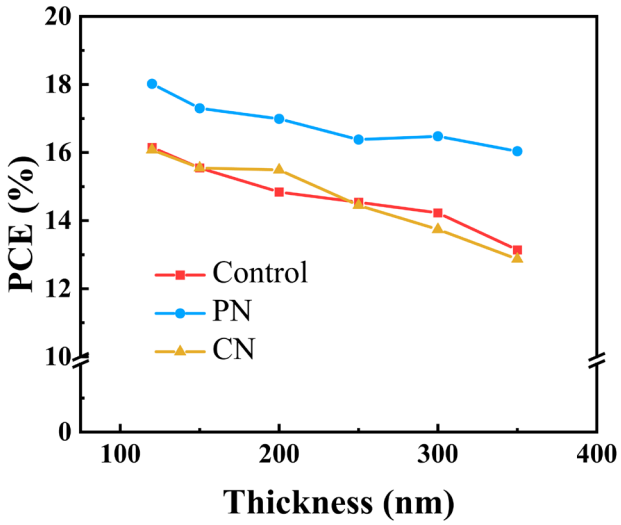

Figure S10. The PCE of control, PN-treated, and CN-treated devices as a function of film thickness.

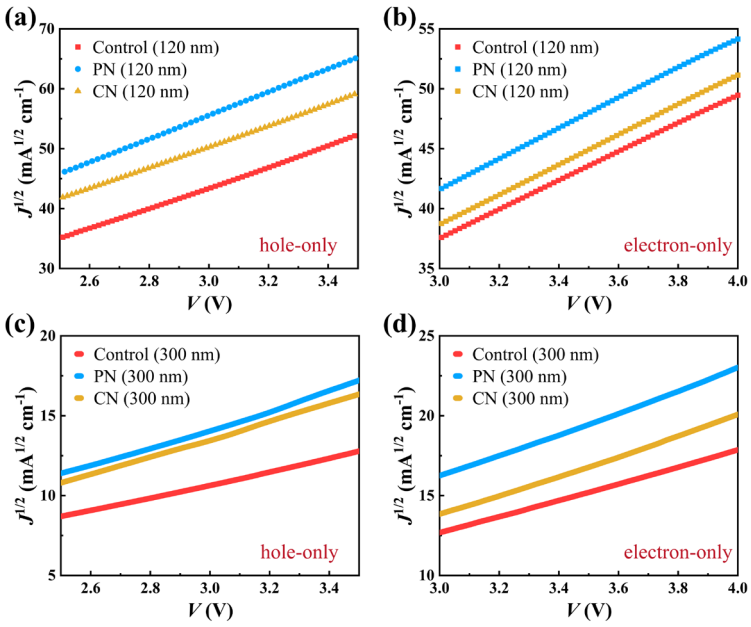

Figure S11. The $J^{1/2}$-V curves of (a) hole- and (b) electron-only devices based on 120-nm-thick active layers without and with different additives; (c) hole- and (d) electron-only devices based on 300-nm-thick active layer without and with different additives. The hole-only devices were fabricated with a structure of ITO/PEDOT:PSS/active layer/MoO_3/Ag and electron-only devices were prepared using a structure of ITO/ZnO/active layer/PFN-Br/Al. The concentration of additive is 0.5 vol%.

Table S4. The parameters of the OSCs are based on the control, PN-treated, and CN-treated devices. The thickness of active layers are 120 nm and 300 nm, respectively.

	Thickness (nm)	η_{diss}	η_{coll}	S	α
D18-Cl:N3	120	96.89	86.12	1.03kT/q	96.08
D18-Cl:N3-PN	120	97.50	87.60	1.01kT/q	96.97
D18-Cl:N3-CN	120	97.15	87.12	1.02kT/q	96.40
D18-Cl:N3	300	97.01	80.56	1.15kT/q	92.84
D18-Cl:N3-PN	300	97.61	87.30	1.09kT/q	95.04
D18-Cl:N3-CN	300	97.54	84.79	1.16kT/q	93.98

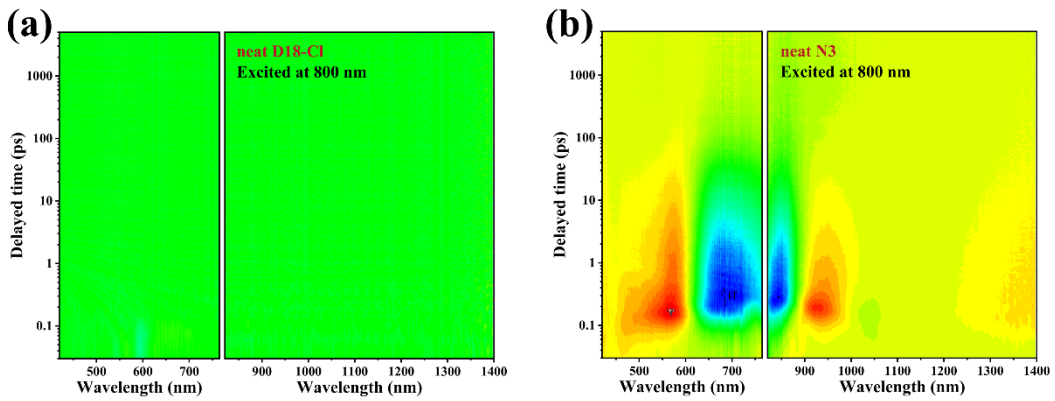

Figure S12. Broadband TA data of the (a) neat D18-Cl, (b) neat N3 films with pump at 800 nm.

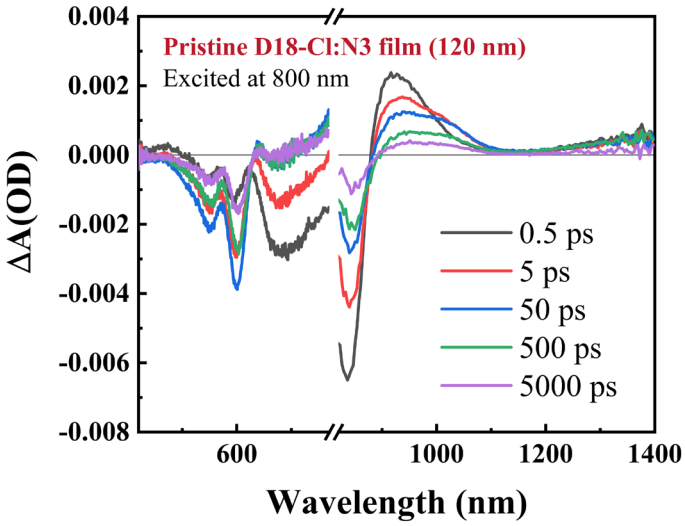

Figure S13. The line-cuts of TA spectroscopy with pump at 800 nm at an indicated delay time of the control film.

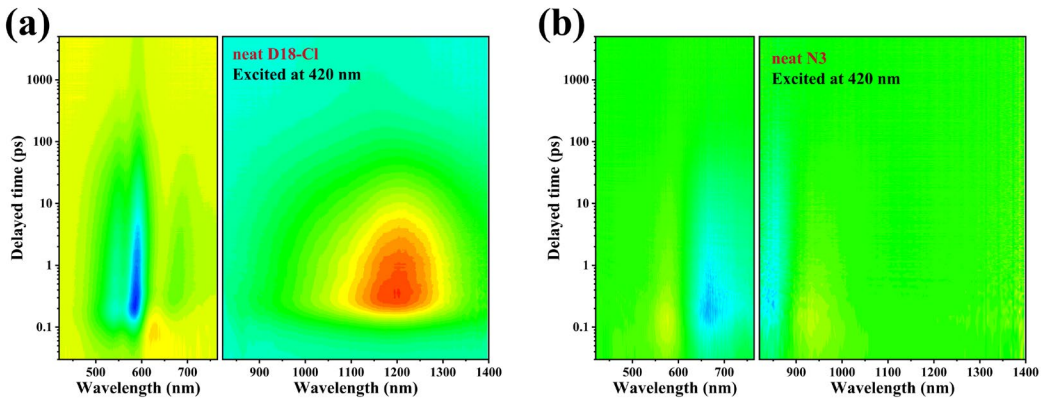

Figure S14. Broadband TA data of the (a) neat D18-Cl, (b) neat N3 film with pump at 420 nm.

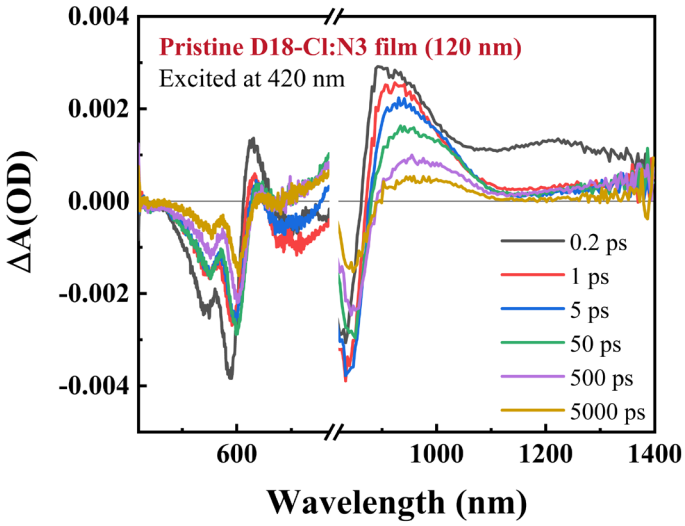

Figure S15. The line-cuts of TA spectroscopy with pump at 420 nm at an indicated delay time of the control film.

Table S4. The fitted time and relative population of exciton dynamics for OSCs based on the control, PN-treated, and CN-treated devices.

	Thickness (nm)	τ_1 (ps)	A_1 (%)	τ_2 (ps)	A_2 (%)
D18-Cl:N3	120	0.54	39.51	7.00	50.95
D18-Cl:N3-PN	120	0.54	42.33	5.53	53.17
D18-Cl:N3-CN	120	0.52	48.27	5.78	39.85

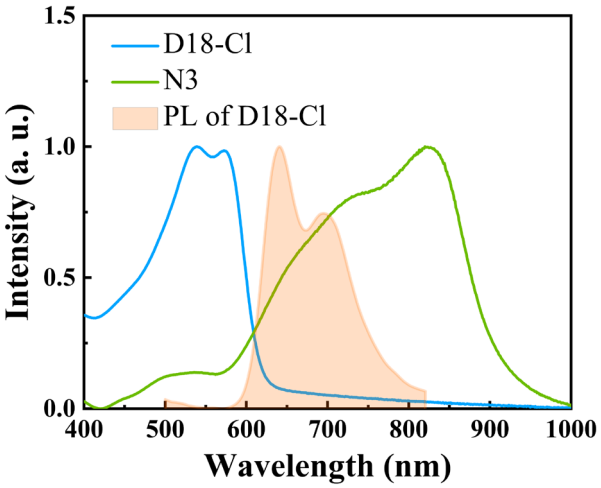

Figure S16. The absorption of D18-Cl and N3 film, and the photoluminescence (PL) of D18-Cl film.

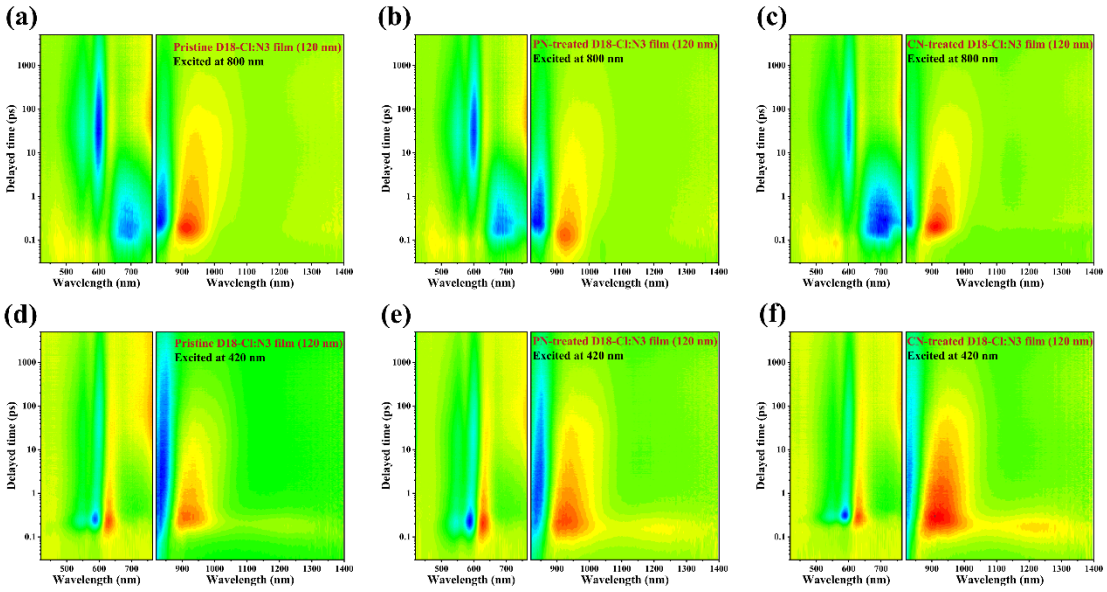

Figure S17. The 2D plots of TA spectra of the blend films (a) without additive, (b) with PN and (c) with CN additive pump at 800 nm. The 2D plots of TA spectra of the blend films (a) without additive, (b) with PN and (c) with CN additive pump at 420 nm.

References

1. X. He, C. C. S. Chan, X. Zou, S. Zhang, P. W. K. Fong, J. Kim, G. Li, X. Hu, W. Ma, K. S. Wong and W. C. H. Choy, *Adv. Energy Mater.*, 2023, **13**, 2203697.
2. L. Ye, Y. Xiong, M. Zhang, X. Guo, H. Guan, Y. Zou and H. Ade, *Nano Energy*, 2020, **77**, 105310.
3. K. Yao, Y. X. Xu, X. Wang, F. Li and J. Yuan, *RSC Adv.*, 2015, **5**, 93689-93696.