Electronic Supplementary Information (ESI)

Engineering the Morphology via Processing Additives in Multiple All-Polymer Solar Cells for Improved Performance

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Content

1. Temperature-dependent UV-vis absorption

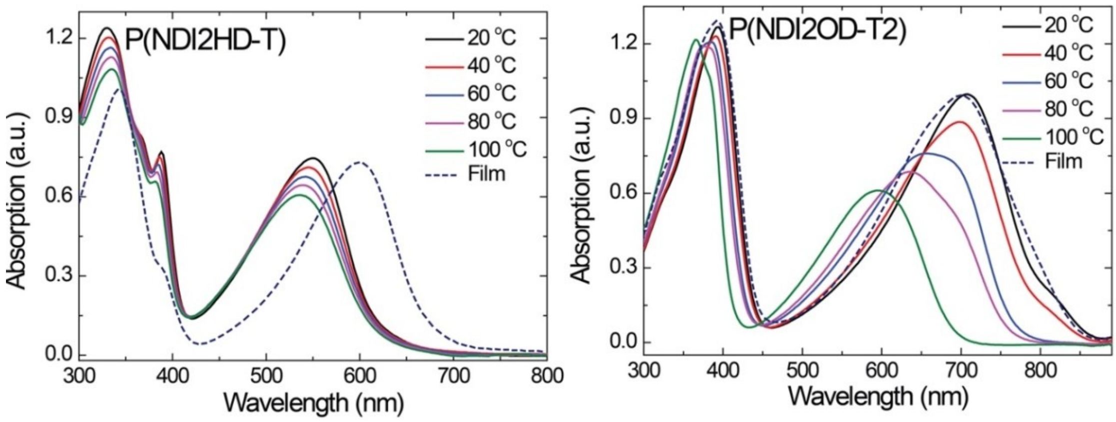

Figure S1. UV–vis absorption spectra of the polymer acceptors in different temperatures in chlorobenzene at a dilute concentration of 0.02 mg/mL.

2. Current-voltage (J-V) characteristics of PTP8/P(NDI2HD-T) solar cells under different processing conditions.

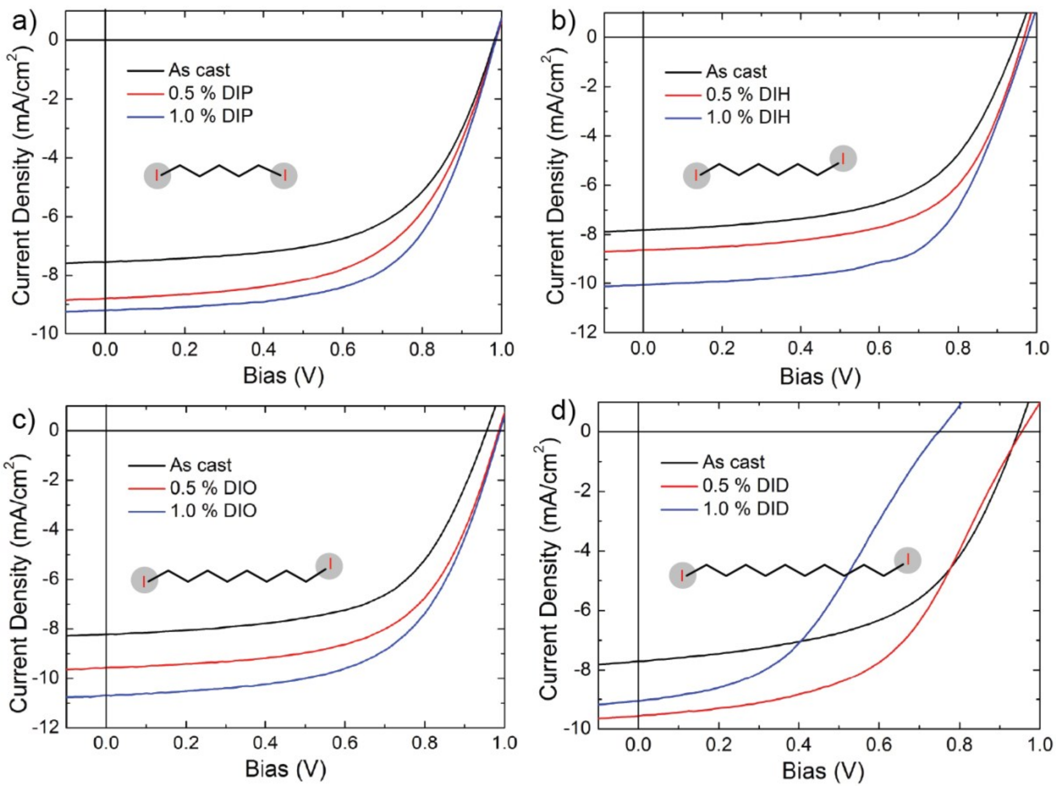

Figure S2. *J-V* curves of PTP8/P(NDI2HD-T) all-polymer solar cells fabricated with 1,x-diiodinealkane additives measured under standard AM 1.5 solar radiation.

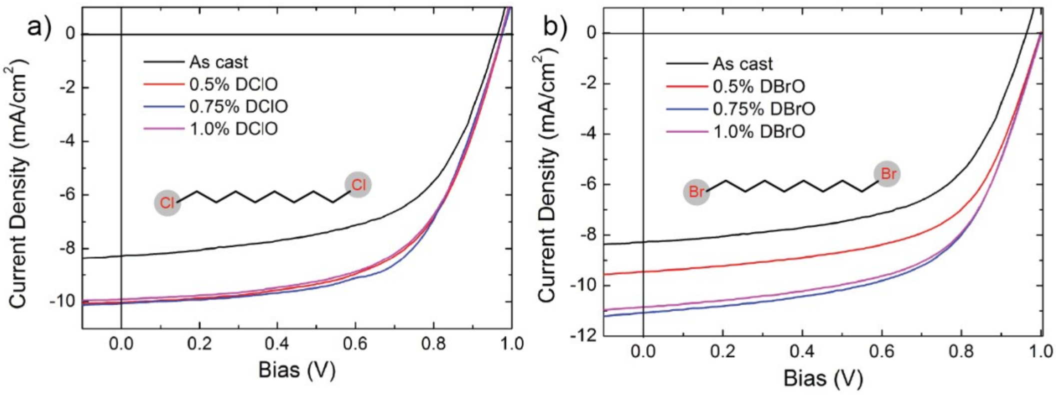

Figure S3. *J-V* curves of PTP8/P(NDI2HD-T) all-polymer solar cells fabricated with 1,8-dichlorooctane (DClO) and 1,8-dibromooctane (DBrO) additives measured under standard AM 1.5 solar radiation.

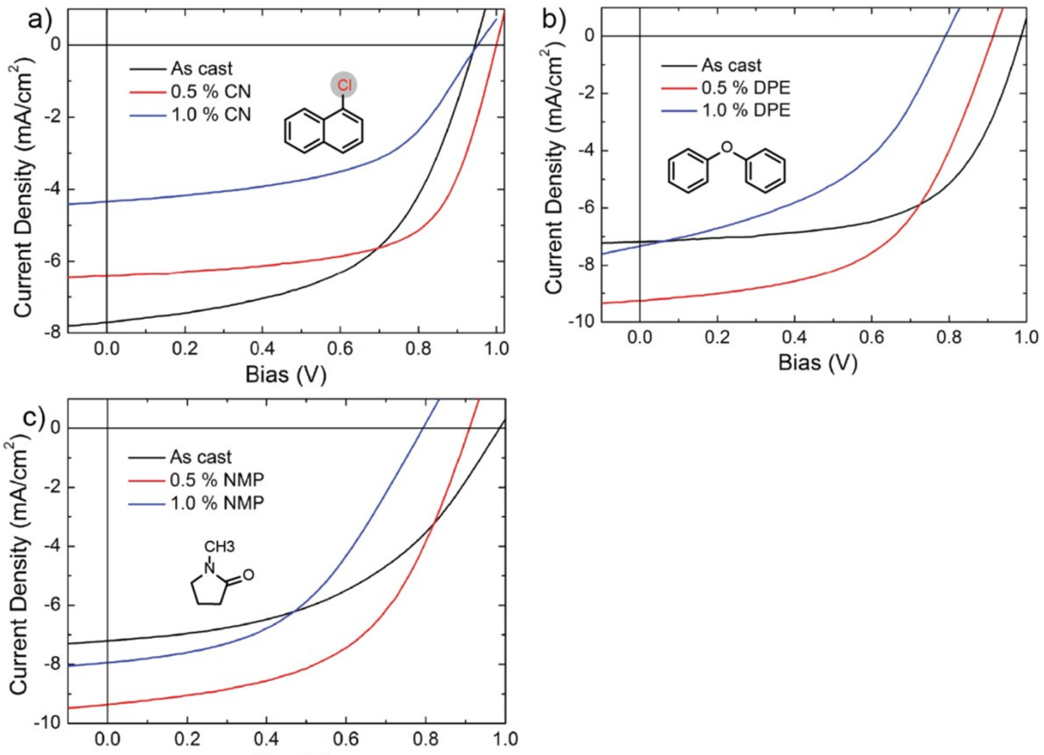

Figure S4. *J-V* curves of PTP8/P(NDI2HD-T) all-polymer solar cells fabricated with 1-chloronaphthalene (CN), diphenyl ether (DPE) and N-methyl-2-pyrrolidone (NMP) additives measured under standard AM 1.5 solar radiation.

3. Additive-dependent UV-vis absorption

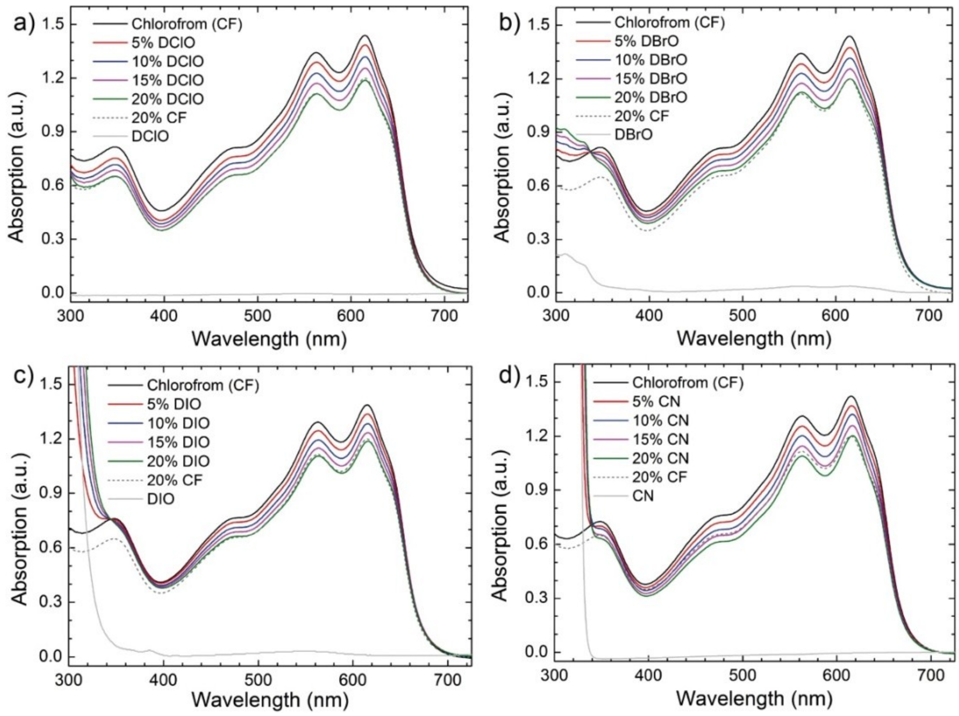

Figure S5. UV-vis absorption of diluted PTP8 solution (~0.02 mg/mL) with different content of DClO (a); DBrO (b), DIO (c) and CN (d).

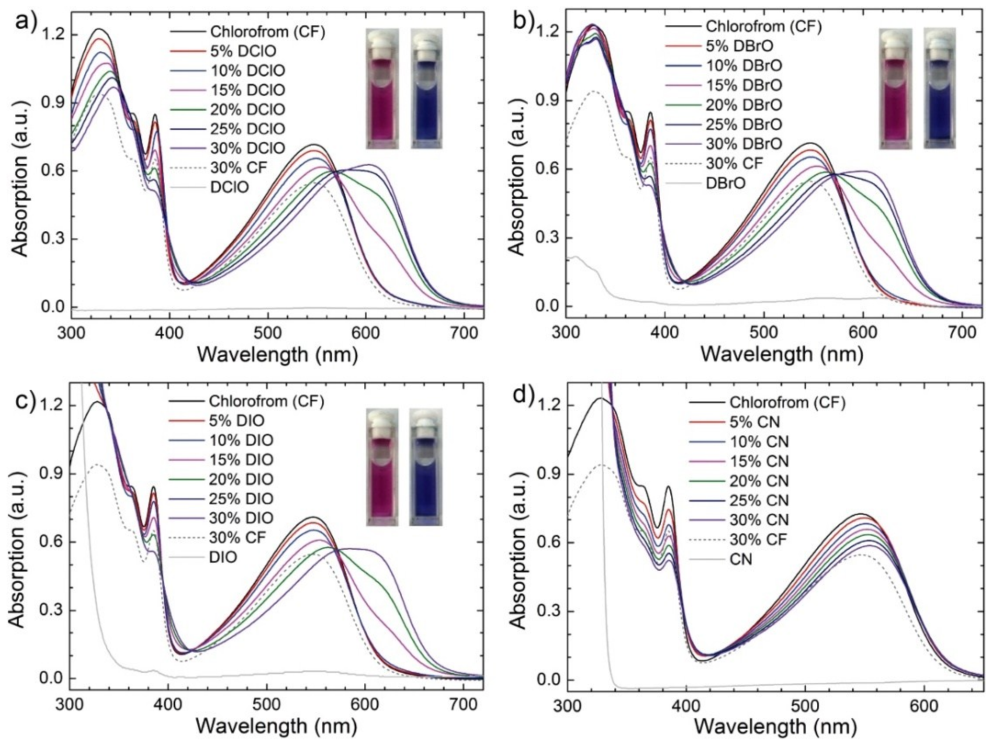

Figure S6. UV-vis absorption of diluted P(NDI2HD-T) solution (~0.02 mg/mL) with different content of DClO (a); DBrO (b), DIO (c) and CN (d).

4. Mobility measurements by space charge limited current method

Hole-only and electron-only devices were fabricated to measure the hole and electron mobility using the space charge limited current (SCLC) method. The hole-only device structure is ITO/PEDOT:PSS/blend/MoOx (6 nm)/Ag (80 nm) and the electron-only device structure is ITO/ZnO/blend/LiF (0.6 nm)/Al (80 nm). The thickness was measured by profilometer. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation:

$$J = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu_h \frac{V^2}{d^3},$$

Where J is the current, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, μ is the zero-field mobility, d is the thickness of the polymer layer, V is the applied voltage. Then hole and electron mobilities were calculated from the fitting slope of the $J^{1/2}$-V curves.

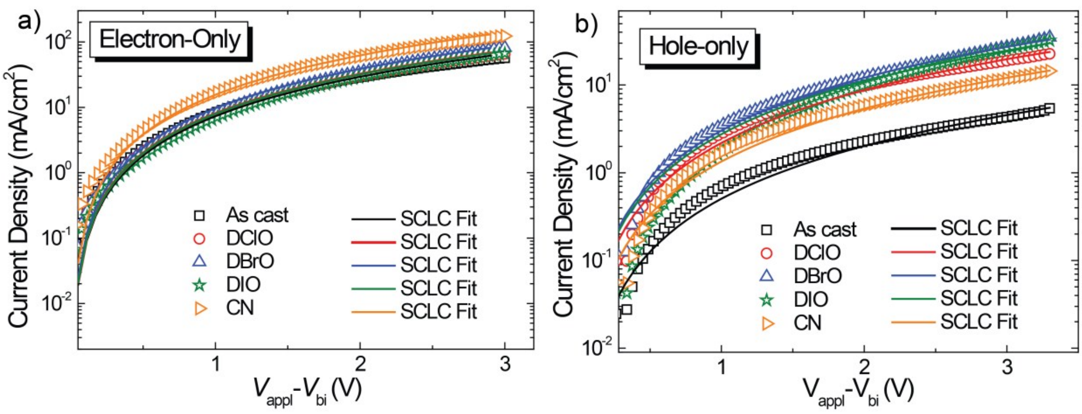

Figure S7 *J-V* curves of PTP8/P(NDI2HD-T) all-polymer processed from pure solvent and with optimal additive: (a) electron-only and hole-only (b) diodes devices.

5. GIWAXS measurements

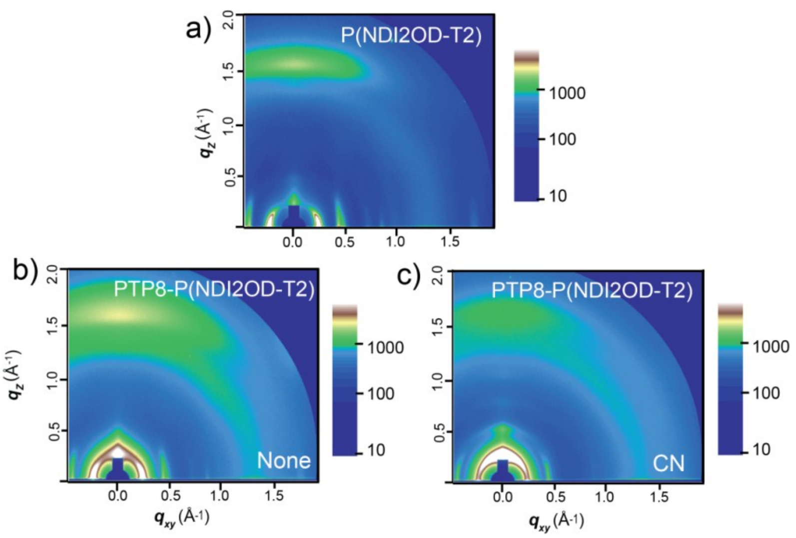

Figure S8. Two-dimensional GIWAXS images of the neat P(NDI2OD-T2) film (a), PTP8/P(NDI2OD-T2) blend films without additive treatment (b) and with optimal CN (c) additive treatment.

6. Summary of the additive properties

Table S1. The information of commercial available solvent additive used in this work.

Solvent Additive	**MW**	**Boiling-point (°C)**
DIP (C5)	323.94	101-102 °C (3mm Hg)
DIH (C6)	337.96	141-142 °C (10 mmHg)
DIO (C8)	366.02	313-315°C (760 mmHg)
DBrO (C8)	272.02	270-272 °C (760 mmHg)
DClO (C8)	183.10	241°C (760 mmHg)
DID (C10)	394.07	349.7 °C (760 mmHg)
CN (C10)	162.26	259-263 °C (760 mmHg)
DPE (C12)	170.22	257 °C (760 mmHg)
NMP	99.1	202 °C (760 mmHg)

7. Solar cell performance summary

Table S2. Effect of blend ratios on the performance of as-cast devices based on PTP8/P(NDI2HD-T).

PTP8/P(NDI2HD-T) (As-cast)	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF*	*PCE* (%)
70:30	0.976	7.05	0.54	3.77
65:35	0.976	7.10	0.57	3.92
60:40	0.975	7.96	0.60	4.66
55:45	0.963	7.40	0.62	4.43
50:50	0.948	7.22	0.57	3.89

Table S3. Effect of solvent additives on the performance of all-PSC devices based on PTP8/P(NDI2HD-T).

Additive	Vol%	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF*	*PCE* (%)
None	0.0%	0.975	7.53	59.2	4.34
DIP	0.5%	0.975	8.79	58.1	4.99
DIP	1.0%	0.975	9.19	61.4	5.52
DIP	1.5%	0.975	9.01	59.6	5.24
None	0.0%	0.950	7.82	57.5	4.26
DIH	0.5%	0.963	8.61	60.9	5.10
DIH	1.0%	0.975	10.06	61.6	6.05
DIP	1.5%	0.975	9.85	59.8	5.74
None	0.0%	0.950	8.21	59.5	4.64
DIO	0.5%	0.975	9.56	60.5	5.64
DIO	1.0%	0.988	10.58	59.3	6.20
DIO	1.5%	0.988	10.05	59.0	5.84
None	0.0%	0.938	7.70	54.4	3.90
DID	0.5%	0.950	9.54	51.6	4.68
DID	1.0%	0.738	9.03	42.8	2.86
None	0.0%	0.963	8.25	58.6	4.66
DClO	0.5%	0.975	10.01	59.6	5.84
DClO	0.75%	0.980	10.06	61.0	6.02
DClO	1.0%	0.963	9.90	60.3	5.75
None	0.0%	0.938	7.70	54.4	3.90
DBrO	0.5%	0.990	9.45	60.8	5.67
DBrO	0.75%	1.000	11.05	59.1	6.55
DBrO	1.0%	1.000	10.83	59.6	6.45
None	0.0%	0.938	7.70	54.4	3.90

CN	0.5%	0.990	6.42	64.9	4.15
CN	1.0%	0.950	4.33	53.4	2.20
None	0.0%	0.975	7.17	60.6	4.20
DPE	0.5%	0.913	9.25	54.4	4.60
DPE	1.0%	0.788	7.29	45.3	2.61
None	0.0%	0.975	7.20	48.0	3.33
NMP	0.5%	0.900	9.34	53.5	4.50
NMP	1.0%	0.788	7.92	47.1	2.94