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Supporting Information

Tuning Molar Mass of P3HT via Direct Arylation Polycondensation Yields Optimal Interaction and High Efficiency in Nonfullerene Organic Solar Cells

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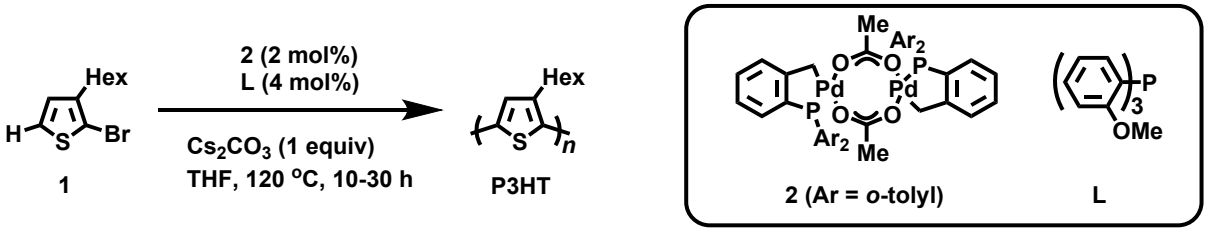
S1. Synthesis of five batches of P3HT via direct arylation polycondensation



Scheme S1. Synthetic route to P3HT via direct arylation polycondensation.

A gastight Schlenk tube (volume is 5 mL) was charged with Herrmann catalyst (9.4 mg, 10.0 μmol), tris(2-methoxyphenyl)phosphine (8.8 mg, 19.9 μmol), anhydrous Cs_2CO_3 (0.326 g, 2.00 mmol), 2-bromo-3-hexylthiophene (199 μL, 1.00 mmol), and THF (0.8 mL). The mixture was gradually heated up to 120 °C, and kept stirring at this temperature for 12-58 h. After reaching the reaction time, the reaction mixture was cooled to room temperature, diluted with $CHCl_3$ (10 mL) to dissolve the polymer deposited from the solution, washed with water (5 mL, 3 times), and then poured into a cool MeOH solvent (40 mL). After stirring for 10 minutes, the precipitation of crude P3HT was obtained. The precipitate was filtered and Soxhlet extracted with methanol, acetone, hexane, and chloroform. The ingredient extracted from chloroform was concentrated, precipitated into 40 mL methanol, filtered and dried under vacuum to give various kinds of heat-to-tail P3HT. The ^{1}H NMR data are consistent with a previous report[32].

P3HT-89K: Deep purple, 83% yield. **Reaction time: 30 hours**. M_n = 35.9 kg/mol, M_w = 89.1 kg/mol, M_w/M_n = 2.49. H-T regioregularity = 90%, based on relative peak integration of the signals at 2.61 (H-H isomer, 0.18H) and 2.80 (H-T isomer, 1.92H).

P3HT-42K: Deep purple, 79% yield. **Reaction time: 26 hours**. M_n = 21.2 kg/mol, M_w = 41.9 kg/mol, M_w/M_n = 1.98. H-T regioregularity = 90%, based on relative peak integration of the signals at 2.61 (H-H isomer, 0.18H) and 2.80 (H-T isomer, 1.82H).

P3HT-26K: Deep purple, 85% yield. **Reaction time: 22 hours**. M_n = 17.2 kg/mol, M_w = 25.5 kg/mol, M_w/M_n = 1.49. H-T regioregularity = 92%, based on relative peak integration of the signals at 2.61 (H-H isomer, 0.14H) and 2.80 (H-T isomer, 1.86H).

P3HT-22K: Deep purple, 68% yield. **Reaction time: 18 hours**. M_n = 14.1 kg/mol, M_w = 22.1 kg/mol, M_w/M_n = 1.57. H-T regioregularity = 90%, based on relative peak integration of the signals at 2.61 (H-H isomer, 0.20H) and 2.80 (H-T isomer, 1.80H).

P3HT-9K: Deep purple, 62% yield. **Reaction time: 10 hours**. M_{n} = 6.04 kg/mol, M_w = 8.9 kg/mol, M_w/M_n = 1.47. H-T regioregularity = 86%, based on relative peak integration of the signals at 2.61 (H-H isomer, 0.20H) and 2.80 (H-T isomer, 1.80H).

S2. GPC curves of P3HT Polymers

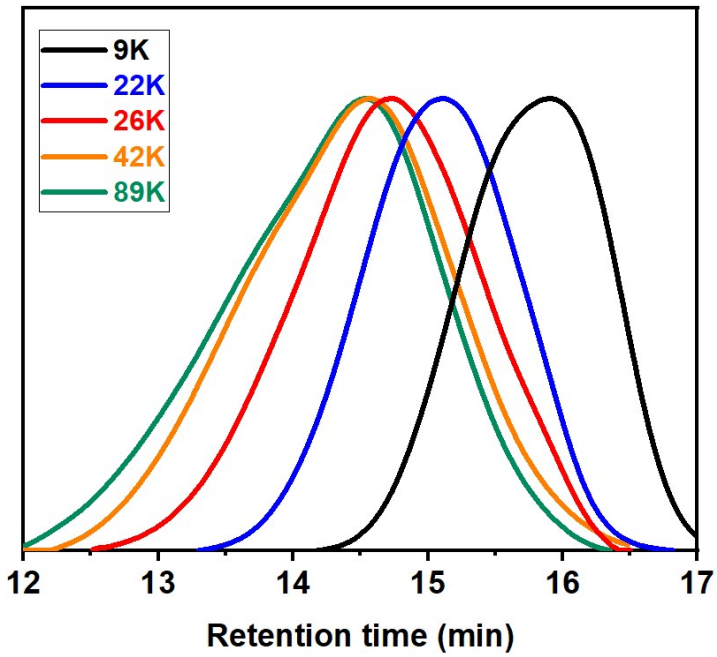
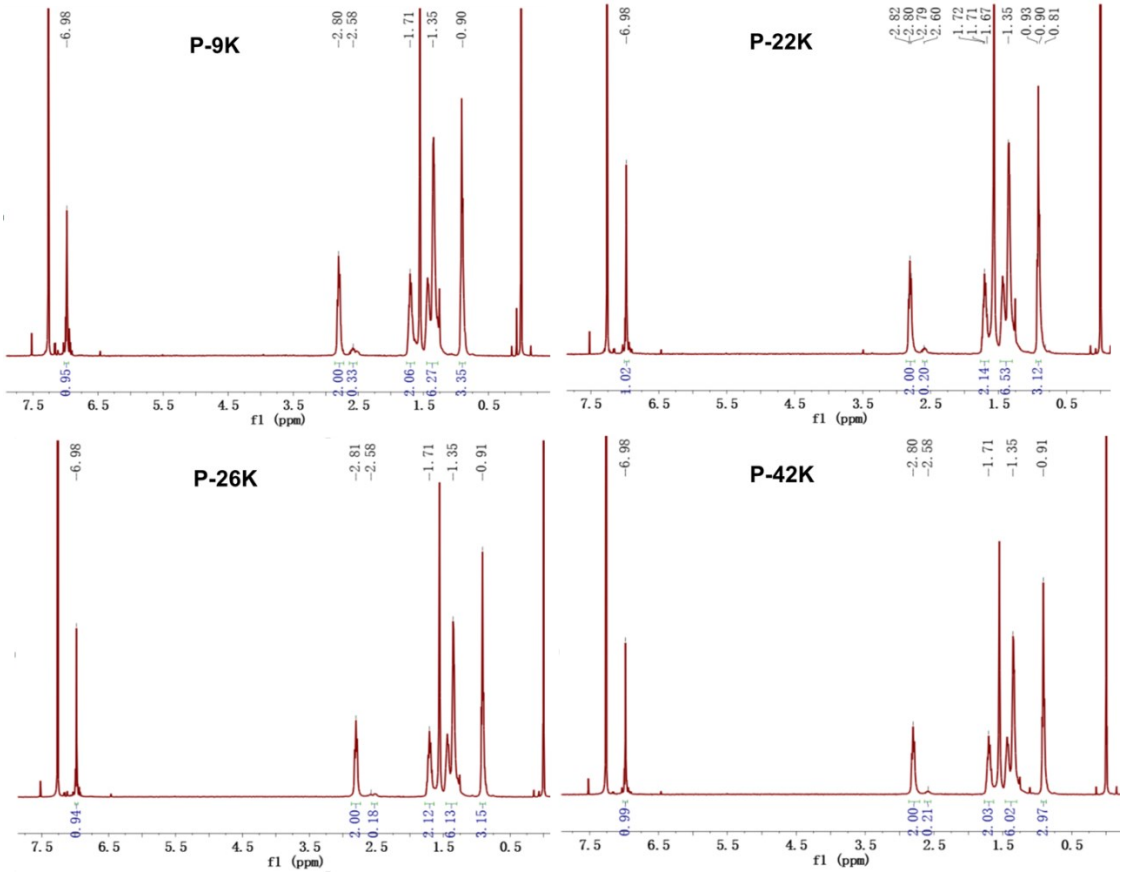


Figure S1. Retention time plots of the DArP P3HT polymers via GPC.

S3. NMR Data of P3HT Polymers (RR included)



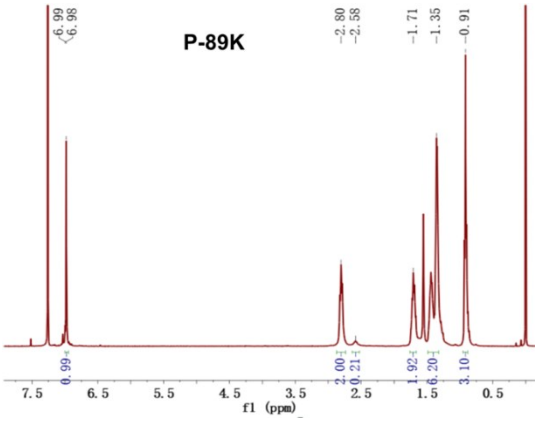


Figure S2. ^{1}H NMR spectra of 5 batches of P3HT polymers.

Table S1. Summary of basic properties of DArP P3HTs.

Batch	M_n[a] (kg/mol)	PDI[a]	T_m (°C)	ΔH_m (J/g)
P-9K	6.0	1.49	168.6	5.5
P-22K	14.1	1.57	190.5	11.4
P-26K	17.2	1.49	200.9	16.4
P-42K	21.2	1.98	201.6	15.2
P-89K	35.8	2.49	203.1	13.6

S4. Absorption spectra of DArP P3HT in dilute THF solutions and thin films

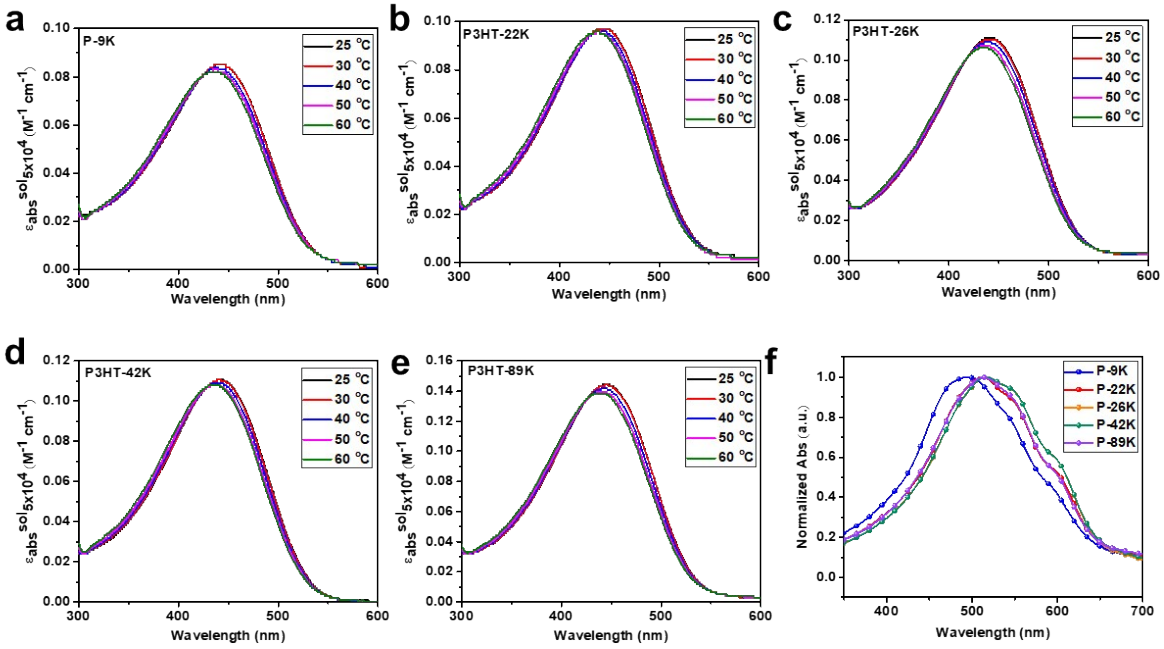


Figure S3. Absorption spectra of P3HT polymers in dilute THF solutions (**a-e**) and thin films

(**f**).

S5. Molecular packing parameters of DArP P3HTs.

Table S2. Molecular packing parameters obtained from GIXRD measurements.

Batch	$q_{(010)}$(Å^{-1})	$d_{(010)}$(Å)	$L_{c(010)}$(Å)
P-9K	1.66	3.80	14.5
P-22K	1.66	3.81	15.2
P-26K	1.66	3.80	19.6
P-42K	1.66	3.80	13.3
P-89K	1.68	3.77	16.7

S6. DSC heat-only thermograms of ZY-4Cl

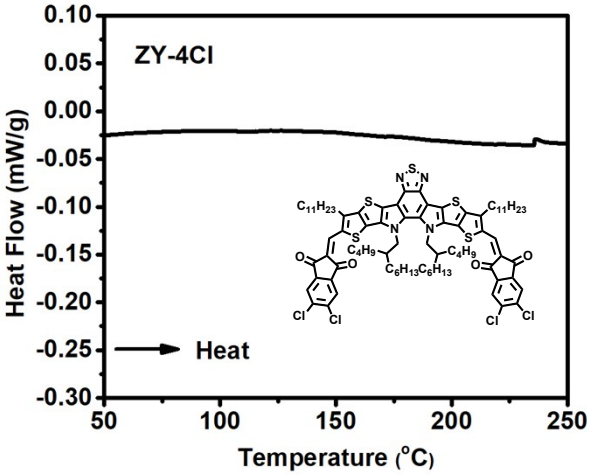


Figure S4. DSC heat-only thermogram of ZY-4Cl.

S7. 2D GIXRD pattern of the as-cast ZY-4Cl film

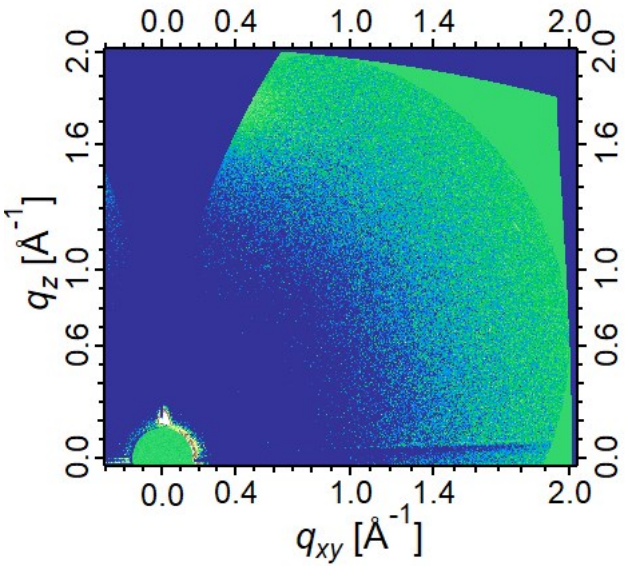


Figure S5. 2D GIXRD pattern of the as-cast ZY-4Cl film. It displays a highly amorphous feature in as-cast film.

S8. Melting point depression of P3HT:ZY-4Cl blends

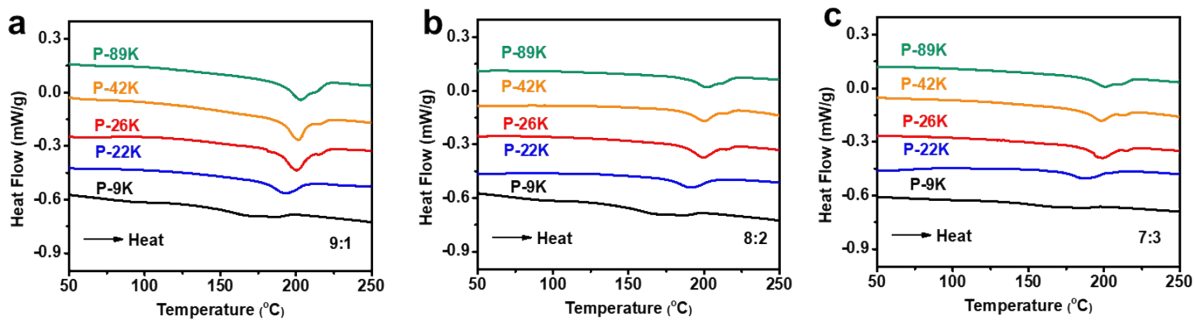


Figure S6. DSC heat-only thermograms of P3HT:ZY-4Cl blends with different blend ratios.

S9. Contact angle measurements of the P3HT and ZY-4Cl films

Table S3. Contact angle measurements of P3HT and ZY-4Cl.

Organic layer	contact angle [water] (°)	contact angle [EG] (°)	γ^d (mN/m)	γ^p (mN/m)	surface tension (mN/m)	$\left(\sqrt{\gamma_{Donor}}-\sqrt{\gamma_{Acc}}\right.$
ZY-4Cl	88.62	82.38	74.28	72.16	146.44	

P-9K	96.73	81.90	64.26	73.01	137.27	0.15
P-22K	97.59	82.40	63.18	72.46	135.64	0.21
P-26K	96.88	85.35	64.07	69.18	133.25	0.31
P-42K	96.27	92.88	64.84	60.78	125.62	0.79
P-89K	99.88	92.21	60.30	61.53	121.83	1.13

$(\sqrt{\gamma_{Donor}} - \sqrt{\gamma_{Accptor}})^2$ is proportional to the value of χ.

S10. Determination of χ_{ca} of the P3HT:ZY-4Cl blends

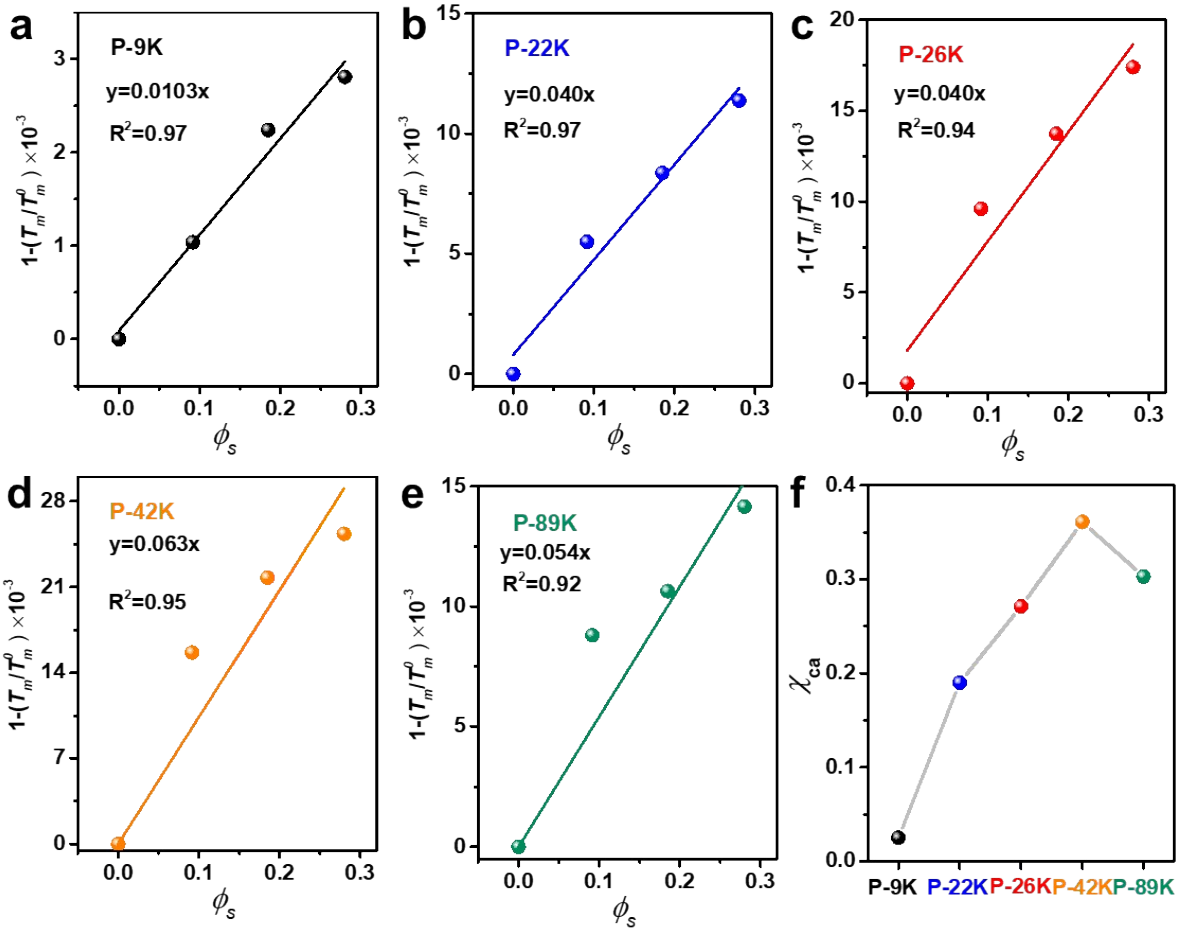


Figure S7. Estimates of χ_{ca} parameters from DSC measurements of melting point depression of the P3HT:ZY-4Cl blends. Plot of changes of the inverse of melting point as a function of the volume fraction of ZY-4Cl: (a) P-9K, (b) P-22K, (c) P-26K, (d) P-42K, (e) P-89K. (f) Plot of χ_{ca} of the P3HT:ZY-4Cl blends with the polymer molar mass.

S11. Device performance of the P3HT:ZY-4Cl solar cells based on P3HT via GRIM

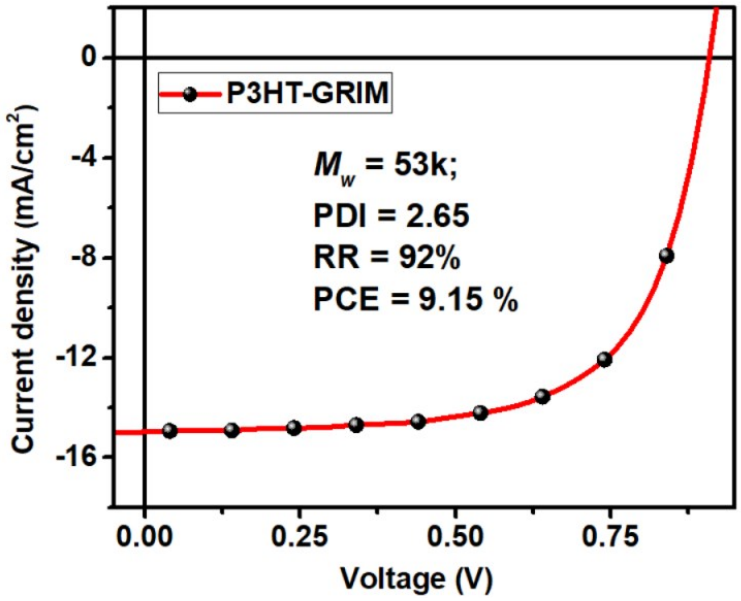
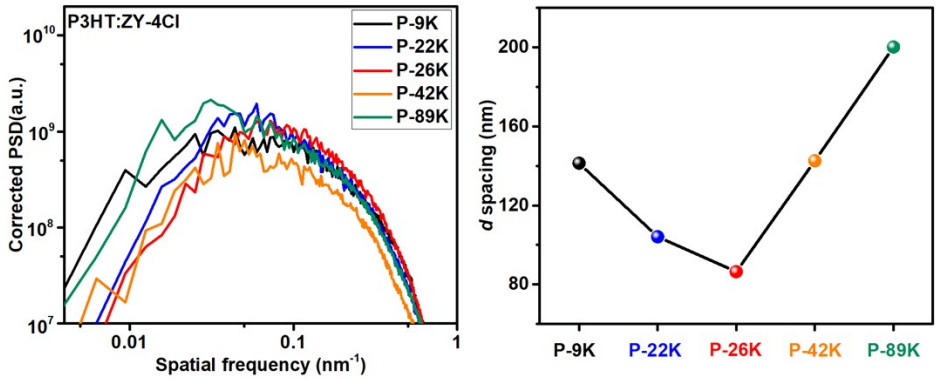


Figure S8. *J-V* characteristic of the P3HT:ZY-4Cl blend employing Traditional GRIM method prepared P3HT (M_w = 50-70 kg/mol; PDI = 2.0-2.5; Regioregularity = 91-94%). The P3HT was purchased from Rieke Metals.

S12. PSD analysis of the AFM phase images of the P3HT:ZY-4Cl blend films



P3HT:ZY-4Cl	P-9K	P-22K	P-26K	P-42K	P-89K
d (nm)	141.3	104.1	86.4	142.6	200.2

Figure S9. PSD Analysis of the AFM images of 5 batches of P3HT:ZY-4Cl blend films.

Table S4. Molecular packing parameters of blend films obtained from GIXRD measurements.

Batch	P3HT:ZY-4Cl Films (P3HT Peak)				
	$q_{(010)}$(Å^{-1})	$d_{(010)}$(Å)	Peak Height	Peak Area	π-π intensity
P-9K	1.70	3.69	608.90	68.20	0.66
P-22K	1.70	3.70	743.00	79.44	0.77
P-26K	1.70	3.69	742.56	103.60	1
P-42K	1.70	3.69	478.70	49.27	0.48
P-89K	1.70	3.70	591.65	62.78	0.61
Batch	**P3HT:ZY-4Cl Films (ZY-4Cl Peak)**				
	$q_{(010)}$(Å^{-1})	$d_{(010)}$(Å)	π-π intensity	FWHM (Å^{-1})	$L_{c(010)}$(Å)
P-9K	1.84	3.42	0.64	0.105	15.05
P-22K	1.83	3.43	0.65	0.123	12.84
P-26K	1.85	3.40	1	0.090	17.45
P-42K	1.84	3.42	0.45	0.095	16.57
P-89K	1.84	3.42	0.45	0.101	15.51

Note: The fitted (010) peak area was selected to describe relative π-π intensity.

S13. Electron-only devices of the P3HT:ZY-4Cl blend films

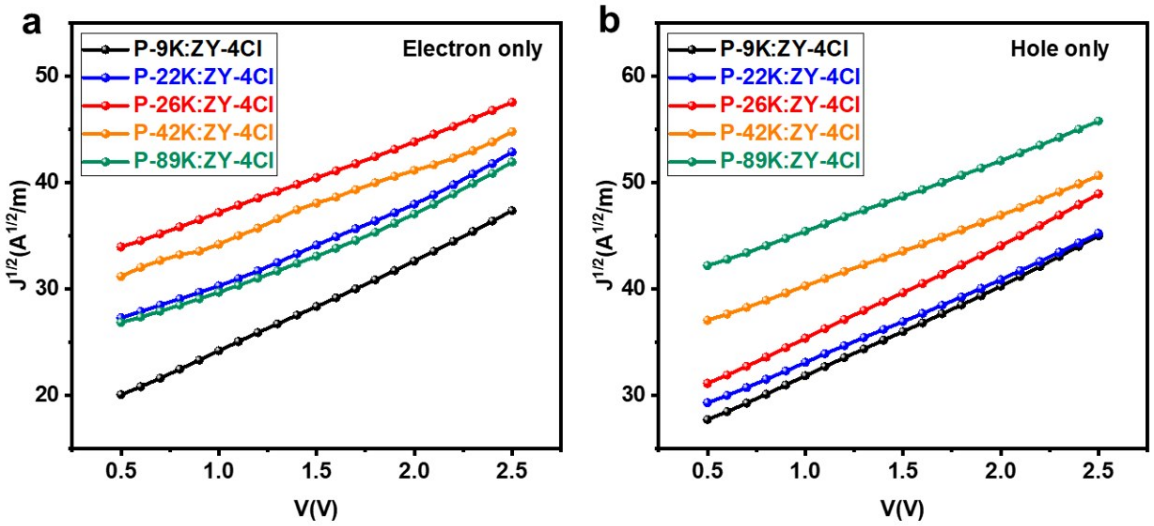


Figure S10. *J-V* characteristics of (a) hole-only devices and (b) electron-only devices based on 5 batches of P3HT:ZY-4Cl.

Table S5. The μ_h, μ_e and μ_h/μ_e in blend films with different P3HT batches.

P3HT:ZY-4Cl	**P-9K**	**P-22K**	**P-26K**	**P-42K**	**P-89K**
Electron Mobility (10^{-4} cm^2 V^{-1} S^{-1})	0.99	2.35	4.29	3.18	2.13
Hole Mobility (10^{-4} cm^2 V^{-1} S^{-1})	3.27	4.11	5.62	6.58	8.32
μ_h/μ_e	3.30	1.75	1.31	2.06	3.90

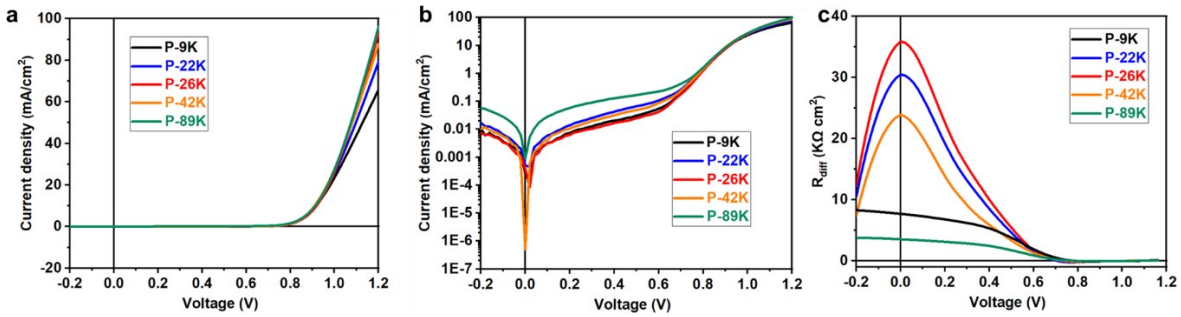


Figure S11. *J-V* characteristics of the 5 batches of P3HT:ZY-4Cl in the dark (a) and (b), differential resistance of the P3HT:ZY-4Cl solar cells in the dark (c).

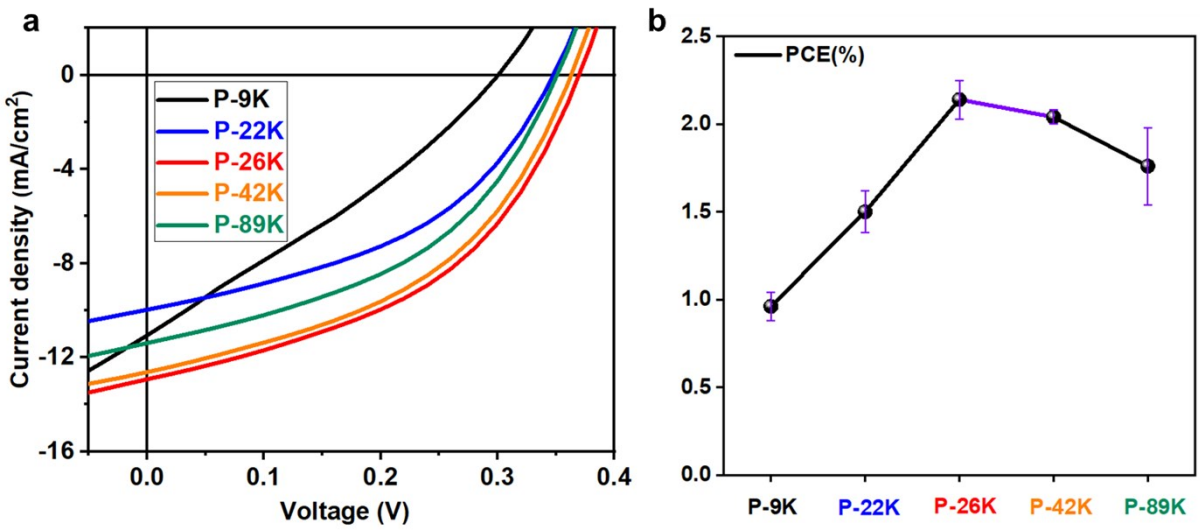


Figure S12. *J-V* characteristics of devices based on 5 batches of P3HT:Y6 (a). PCE of P3HT:ZY-4Cl film blends (b).