Electronic Supplementary Information (ESI)

# Nucleation driving force-controlled fibril network formation enables polythiophene solar cells with exceeding 18% efficiency from non-halogenated solvent

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# 1. Experimental Procedures

#### 1.1 Materials

All reagents were purchased from commercial sources (Sigma Aldrich, Acros, and J&K, etc.) and used as received without further purification unless specifically mentioned. The eC9-2Cl and L8-BO-F were purchased from Solarmer Material Inc. PNDIT-F3N and PDINN were purchased from eFlexPV. The different batches of P5TCN-HD ( $M_n$ =73 kg mol<sup>-1</sup>,  $D_M$ =1.9;  $M_n$ =53 kg mol<sup>-1</sup>,  $D_M$ =2.2;  $M_n$ =30 kg mol<sup>-1</sup>,  $D_M$ =1.6) were synthesized according to the procedures reported in our previous work.<sup>1</sup>

# **1.2 Measurements and characterization**

**UV-vis absorption spectra:** UV-vis absorption spectra of the polymers in chlorobenzene solutions and as thin films were recorded on a SHIMADZU UV-3600 spectrophotometer. The solution concentration was 0.02 mg mL<sup>-1</sup>, and the films were spin-coated on glass substrates.

**Solubility tests:** Solubility tests were conducted by dissolving P5TCN-HD in solvents at elevated temperatures to form homogeneous solutions, followed by cooling to room temperature. This process yielded either gels or precipitates. The critical gelation concentration was defined as the minimum concentration required to form a gel. The solubility limit was determined by comparing the absorption spectra of saturated solutions (diluted with known amounts of pure solvent) to those of diluted solutions with known concentrations. The concentration was calculated using the Beer-Lambert law based on the absorbance at the maximum absorption peak.

**In-situ UV-vis absorption spectra:** In-situ UV-vis absorption spectra were recorded by an Ocean Optics QE pro-spectrometer using the transmission mode with the time resolution of 0.5 second. Film formation time was monitored by the Filmetrics F20-EXR spectrometer using the reflection mode with the time resolution of 0.04 second. The measurements were performed on silicon substrates, using the same solutions as device fabrication.

**Steady-state photoluminescence (PL):** The PL quenching measurements were conducted at an excitation wavelength of 530 nm on a Shimadzu RF-6000 spectrometer.

Atomic force microscopy (AFM): AFM images were obtained by Bruker Multimode 8 Microscope AFM in tapping mode.

**Transmission electron microscopy (TEM)**: TEM images were collected from JEM-2100F transmission electron microscope operated at 200 kV.

**Grazing incidence wide-angle X-ray scattering (GIWAXS):** GIWAXS data were obtained at 1W1A Diffuse X-ray Scattering Station, Beijing Synchrotron Radiation Facility (BSRF-1W1A). The monochromatic of the light source was 1.54 Å. The data were recorded by using the two-dimensional image plate detector of Eiger 2M from Dectris, Switzerland.

**Paracrystalline disorder factor (g-parameter):** The Scherrer expression for weakly disordered system gives the coherence length that paracrystalline feature persists. And considering the interplanar distance d, g-parameter could be estimated by:<sup>2-3</sup>

$$g = \frac{1}{2\pi} \sqrt{\Delta q \times d} \#(S1)$$

 $\Delta q$  is the full width at half the maximum of a diffraction peak, defined as:

$$\Delta q = \frac{2\pi}{CCL} \#(S2)$$

Combining the above two equations, we arrive at:

$$g = \sqrt{\frac{d}{2\pi \times CCL}} \#(S3)$$

**Synthetic complexity (SC) analysis:** The synthetic complexity (SC) was assessed by following the protocol reported by Po et al.<sup>4</sup> There are five parameters: (1) the number of synthetic steps (NSS), (2) the reciprocal yields of the monomers (RY), (3) the number of unit operations required for the isolation/purification of the monomers (NUO), (4) the number of column chromatographic purifications required by the monomers (NCC), and (5) the number of hazardous chemicals used for their preparation (NHC), and it can be calculated according to the following equation:

$$SC = 35 \frac{NSS}{NSS_{max}} + 25 \frac{RY}{RY_{max}} + 15 \frac{NUO}{NUO_{max}} + 15 \frac{NCC}{NCC_{max}} \# (S4)$$

An empiric coefficient is assigned to each parameter, which accounts for the relative importance. The weight of NSS, RY, NUO, NCC, and NHC is 35, 25, 15, 15, and 10, respectively.

#### **1.3 Device fabrication and characterization**

**Fabrication of solar cells:** The substrates with indium tin oxide (ITO) were cleaned by detergent, sonicated in deionized water, and isopropanol sequentially. After that, the clean substrates were dried in oven at 70 °C. The ITO substrates were subjected to oxygen plasma for 5 minutes. An aqueous solution of PEDOT:PSS (CLEVIOS<sup>™</sup> P VP AI 4083) was spin-

casted onto the ITO substrate at 500 rpm for 10 seconds then 4000 rpm for 30 seconds, followed by drying at 150 °C for 15 minutes in air. The substrates were then transferred into a nitrogenfilled glove box. The optimized active layer preparation conditions for P5TCN-HD:eC9-2Cl binary devices processed with different solvents are as follows. For chloroform (CF), the blend solution contained 0.5 vol% chloronaphthalene (CN) as an additive, a donor concentration of 8.5 mg mL<sup>-1</sup>, and a donor: acceptor weight ratio of 1:1.2. The solution was dissolved by heating at 60 °C for 2 hours and spin-coated after cooling to room temperature. For chlorobenzene (CB), 15 mg mL<sup>-1</sup> 1-bromo-3,5-dichlorobenzene (DCBB) was added as a solid additive,<sup>5</sup> with a donor concentration of 10 mg mL<sup>-1</sup> and a donor:acceptor ratio of 1:1.2. The solution was heated at 80 °C for 2 hours and spin-coated at room temperature. For toluene (Tol), 12 mg mL<sup>-1</sup> DCBB was used, with a donor concentration of 7 mg mL<sup>-1</sup> and a donor:acceptor ratio of 1:1.2. After heating at 100 °C for 2 hours, the solution was cooled to 80 °C for spin-coating. For o-xylene (o-XY), 12 mg mL<sup>-1</sup> DCBB was incorporated, with a donor concentration of 7.5 mg mL<sup>-1</sup> and a donor: acceptor ratio of 1:1.2. The solution was heated at 100 °C for 2 hours and spin-coated at 90 °C. For tetrahydrofuran (THF), 0.5 vol% CN was added, with a donor concentration of 8 mg mL<sup>-1</sup> and a donor:acceptor ratio of 1:1.2. The solution was heated at 60 °C for 2 hours and spin-coated at room temperature. For 2-methyltetrahydrofuran (MTHF), no additive was used. The donor concentration was 6 mg mL<sup>-1</sup> with a donor:acceptor ratio of 1:1.2. The solution was heated at 70 °C for 2 hours and spin-coated at 50 °C. All optimized active layers had a thickness of 110 nm and were annealed at 120 °C for 5 minutes. Afterwards, the electron transport layer of PNDIT-F3N was spin-coated from a methanol:ethanol (1:3) mixture solution (0.5 mg mL<sup>-1</sup>, with 0.5% acetic acid (vol %)) at a speed of 2000 rpm for 30 seconds. Finally, a 100 nm Ag was deposited by thermal evaporation in a vacuum chamber at a pressure of  $5 \times 10^{-6}$  Torr with a shadow mask. The ternary OSC devices were fabricated by introducing L8-BO-F into the binary system with weight ratio of 1:1:0.2 processed with Tol. The ternary devices were fabricated under the same processing conditions as the binary devices, including DCBB addition. Furthermore, the electron transport layer is used by PDINN (1 mg mL<sup>-1</sup>) with 1-bromo-4-chlorobenzene (CBB) as solid additive (50% mass of PDINN).<sup>6</sup>

**Photovoltaic performance measurements**: The photovoltaic performance were measured under AM1.5G irradiation (100 mW cm<sup>-2</sup>) derived from a class solar simulator (Enlitech, Taiwan), which was calibrated by a China General Certification Center-certified reference single-crystal silicon cell (Enlitech). The J-V curves were recorded with a Keithley 2400 source meter. The device area is 0.0516 cm<sup>-2</sup>, and the test was performed with a mask aperture which defined an effective area of 0.04 cm<sup>-2</sup>.

**External quantum efficiencies (EQEs)**: The EQE spectra were measured by a QE system (QE-R3011, Enlitech, Taiwan) with the light intensity calibrated by a standard single-crystal silicon photovoltaic cell (Enlitech).

**Light-intensity dependence measurements:** The light-intensity dependence measurements were carried out with illumination between 10-100 mW cm<sup>-2</sup>, which was calibrated by a standard single-crystal silicon solar cell (Enlitech). The current density and voltage were recorded with a Keithley 2400 source meter.

**Fabrication and characterization of single-carrier devices:** The charge carrier mobilities were measured in single-carrier devices with a structure of ITO/PEDOT:PSS/active layer/MoO<sub>3</sub>/Ag for hole-only devices, and a structure of ITO/ZnO/active layer/PNDIT-F3N/Ag for electron-only devices. The dark current densities were measured by applying a voltage between 0 and 4 V with a Keithley 2400 source meter.

**Charge carrier mobility estimation**: The charge carrier mobility was estimated by fitting the data acquired from single-carrier devices to a space-charge-limit-current (SCLC) model. The mobility was determined by fitting the dark current according to the Mott-Gurney law that considers a Poole-Frenkel-type dependence of mobility on the electric field, given by the following equation:

 $J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 exp(0.89\gamma \sqrt{V/d}) \#(S5)$ 

where J is the dark current density,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the dielectric constant of the polymer which is assumed to be 3 for organic semiconductors,  $\mu_0$  is the zero-filed mobility,  $\gamma$  is a parameter that describes the strength of the field-dependence effect, V is voltage drop across the device, and d is the thickness of the active layer. The hole and electron mobilities are extracted with the fit parameters at an electric field (E) of  $1.0 \times 10^5$  V cm<sup>-1</sup> by the Murgatroyd equation:

$$\mu = \mu_0 exp(\gamma \sqrt{E}) \#(S6)$$

**Femtosecond transient absorption characterization:** TA measurements were conducted by a home-built measurement system. This system is driven by a commercial femtosecond (fs) laser with a repetition rate of 1 kHz, pulse duration of ~170 fs and a wavelength of 800 nm. The amplifier (Legend Elite F 1K HE+II, Coherent, California, USA) is seeded by an oscillator (Mira-HP, Coherent, California, USA) running at 80 MHz. The fundamental laser was split into two beams. One is used to pump a home-built non-collinearly optical parametric amplifier, output of which is used to pump the samples of interest. The pump beam was modulated by a mechanic chopper (MC2000B-EC, Thorlabs, Newton, New Jersey) with a frequency of 500 Hz.

The other beam is employed to generate the super-continuum white light, which is used as the probe beam for differential absorption measurements, by focusing onto a sapphire plate. The probing light was guided into a monochromator (Omni- $\lambda$ 200i, Zolix, Beijing, China) and detected by a CCD detector (Pascher Instruments, Lund, Sweden). The time delay between the pump and probe beams is controlled by a mechanical delay line. For TA measurements, all samples were mounted into an optical chamber filled with nitrogen.

# 2. Additional figures and tables



Figure S1. Chemical structures and performances of polythiophenes investigated in previous works.



**Figure S2.** (a) Chemical structures of eC9-2Cl and L8-BO-F. (b) UV–vis spectra of eC9-2Cl and L8-BO-F films. (c) Energy level of P5TCN-HD, eC9-2Cl, and L8-BO-F.<sup>1, 7-8</sup>



**Figure S3.** The solubility of P5TCN-HD in different solvents can be inferred by absorption spectrum. UV-vis absorption spectra in (a) CF, (b) CB, (c) Tol, (d) *o*-XY, (e) THF, and (f) MTHF with a determined concentration and the relationship between the absorption and concentration of the corresponding solutions at a certain wavelength. The P5TCN-HD samples were prepared by dilution of 2000 times from the saturated polymer solutions.

Solvent	solubility [mg mL <sup>-1</sup> ]
CF	23.3
CB	38.8
Tol	12.2
o-XY	16.1
THF	22.1
MTHF	5.8

Table S1. The solubility of P5TCN-HD in different solutions at 20 °C.



Figure S4. Tyndall effect measurements for (a) P5TCN-HD and (b) eC9-2C1 in different solvents.



**Figure S5.** AFM phase images (first row) of the P5TCN-HD:eC9-2Cl blend films processed with CF, Tol, and MTHF. The line-cut profiles to obtain the fibril width (second and third row).



**Figure S6.** Photographs of pure acceptor films processed with different solvents at the solution concentration of 8 mg mL<sup>-1</sup> on Glass/ITO/PEDOT:PSS substrates.



**Figure S7** PL spectra of P5TCN-HD and P5TCN-HD:eC9-2Cl films processed with different solvents.



**Figure S8.** Waterfall plots of the in situ UV–vis absorption spectra of the P5TCN-HD:eC9-2Cl blends in (a) CF, (b) Tol, and (c) MTHF solutions during spin-coating.

		OOP (010)	•		OOP (100)	
Sample	q[Å-1]	<i>d</i> -spacing [Å]	CCL [Å]	 q [Å <sup>-1</sup> ]	<i>d</i> -spacing [Å]	CCL [Å]
CF	1.650	3.81	20.58	0.299	21.01	58.28
Tol	-	-	-	0.315	19.94	120.99
MTHF	-	-	-	0.319	19.70	117.55

**Table S2.** GIWAXS parameters of the pure films of P5TCN-HD in OOP direction.

**Table S3.** GIWAXS parameters of the pure films of P5TCN-HD in IP direction.

		IP (010)				IP (100)	
Sample	q[Å-1]	<i>d</i> -spacing [Å]	CCL [Å]	_	q[Å-1]	<i>d</i> -spacing [Å]	CCL [Å]
CF	-	-	-		0.328	19.16	86.17
Tol	1.659	3.79	31.74		-	-	-
MTHF	1.677	3.75	34.56		-	-	-

**Table S4.** The molecular stacking characteristics parameters of P5TCN-HD, including peaks position (q), *d*-spacing, full width at half maximum (FWHM), crystal coherence lengths (CCLs), and *g*-parameter.

Sample	q [Å <sup>-1</sup> ]	<i>d</i> -spacing [Å]	FWHM [Å <sup>-1</sup> ]	CCL [Å]	g [%]
CF	1.650	3.81	0.305	20.58	17.17
Tol	1.659	3.79	0.198	31.74	13.80
MTHF	1.677	3.75	0.182	34.56	13.14

**Table S5.** GIWAXS parameters of the P5TCN-HD:eC9-2Cl blend films in OOP direction.

	OOP (010)			OOP (100)			
Sample	q [Å-1]	<i>d</i> -spacing [Å]	CCL [Å]	 q [Å-1]	<i>d</i> -spacing [Å]	CCL [Å]	
CF	1.667	3.77	31.84	-	-	-	
Tol	1.649	3.81	33.17	0.305	20.60	57.75	
MTHF	1.619	3.88	12.40	0.322	19.51	107.87	

		IP (010)				IP (100)	
Sample	q [Å-1]	<i>d</i> -spacing [Å]	CCL [Å]	_	q [Å <sup>-1</sup> ]	<i>d</i> -spacing [Å]	CCL [Å]
CF	-	-	-	-	0.328	19.16	64.96
Tol	-	-	-		0.331	18.98	61.47
MTHF	1.69	3.718	29.84		0.348	18.06	37.34



**Figure S9.** (a) J-V curves, (b) EQE spectra and integrated  $J_{sc}$  of the OSCs based on P5TCN-HD:eC9-2Cl blend processed with CB, *o*-XY, and THF.

**Table S7.** The device parameters of OSCs based on P5TCN-HD:eC9-2Cl blend processed with different solvents.<sup>a</sup>

Solvent	$V_{ m oc}$ [V]	$J_{\rm sc}$ [mA cm <sup>-2</sup> ]	$J_{cal}^{b}$ [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
CB	0.885	20.79	19.49	71.40	$13.14~(13.02\pm0.12)$
o-XY	0.868	24.97	23.89	76.04	$16.48~(16.20\pm0.28)$
THF	0.851	17.48	17.03	68.68	$10.00~(9.82\pm0.18)$

<sup>a</sup> Average values with standard deviation in brackets were acquired from more than eight independent devices; <sup>b</sup> The  $J_{sc}$  values integrated from EQE response.

Table S8. Photovoltaic parameters of P5TCN-HD:eC9-2Cl devices processed with CF.

	1					
D:A	Solvent	Annealing	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
[w/w]	$[\nu/\nu]$	[°C]	[V]	$[mA cm^{-2}]$	[%]	[%]
1.2:1		_	0.881	21.05	68.45	12.69
1:1	CF		0.879	21.89	69.04	13.28
		- 100 -	0.877	22.21	69.54	13.55
	CF + 0.5% DIO	100	0.866	22.50	70.00	13.64
	CF + 0.5% NMP		0.871	19.64	72.75	12.44
	CF + 0.25% CN		0.876	22.85	71.04	14.21
		80	0.877	23.00	68.59	13.84
1:1.2	$CE \pm 0.59$ / CN	100	0.874	23.10	71.23	14.38
	CF + 0.5% CN	120	0.871	23.32	71.33	14.49
		140	0.868	22.01	70.48	13.47
	CF + 0.75% CN		0.869	22.74	70.56	13.94
	CF + 10 mg/mL DCBB	- 100 -	0.879	21.21	71.06	13.25
	CF + 10 mg/mL TCB		0.873	21.07	68.91	12.68
1:1.5	CF		0.874	21.77	68.87	13.10

D:A	Solvent	Annealing	V <sub>oc</sub>	$J_{\rm sc}$	FF	PCE
[w/w]	$[\nu/\nu]$	[°C]	[V]	$[mA cm^{-2}]$	[%]	[%]
1.2:1	_		0.873	23.50	72.56	14.89
1:1	Tol		0.871	23.81	73.34	15.34
	-		0.870	24.32	74.98	15.86
	Tol + 0.5% DIO		0.860	22.05	71.05	13.75
	Tol + 0.5% NMP	100	0.853	21.46	71.48	13.08
	Tol + 0.5% CN	· · · · ·	0.866	24.28	73.56	15.47
	Tol + 0.5 DPE		0.844	20.04	68.88	11.65
1 1 0	Tol + 10 mg/mL DCBB		0.870	24.90	76.78	16.63
1:1.2			0.870	25.08	77.02	16.81
	Tol + 12 mg/mL DCBB	120	0.869	25.23	77.93	17.10
		140	0.853	23.12	75.54	14.90
	Tol + 14 mg/mL DCBB		0.865	25.10	76.51	16.61
	Tol + 10 mg/mL TCB	100	0.859	23.45	73.48	14.80
	Tol + 10 mg/mL DIB	100	0.850	22.50	71.56	13.69
1:1.5	Tol		0.868	23.20	72.00	14.50

 Table S9. Photovoltaic parameters of P5TCN-HD:eC9-2Cl devices processed with Tol.

 Table S10. Photovoltaic parameters of P5TCN-HD:eC9-2Cl devices processed with MTHF.

D:A	Solvent	Annealing	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
[w/w]	$[\nu/\nu]$	[°C]	[V]	$[mA cm^{-2}]$	[%]	[%]
1.2:1			0.849	15.20	55.27	7.13
1:1		100	0.848	15.55	56.64	7.47
	MTHE	-	0.842	16.03	58.96	7.96
	МІПГ	70	0.846	16.58	55.72	7.82
		80	0.845	17.38	60.61	8.91
1:1.2		120	0.837	15.04	60.11	7.57
	MTHF + 0.5% DIO		0.837	15.02	54.12	6.80
	MTHF + 0.5% NMP		0.840	14.33	55.48	6.68
	MTHF + 0.5% CN		0.839	14.87	55.34	6.91
	MTHF + 10 mg/mL DCBB	100	0.845	15.63	59.12	7.81
	MTHF + 10 mg/mL TCB	_	0.847	15.71	57.08	7.60
1:1.5	MTHF		0.840	16.04	57.45	7.74



**Figure S10.** The GPC traces of P5TCN-HD batches measured with 1,2,4 trichlorobenzene as the eluent and polystyrene as a standard at 150 °C.



Figure S11. Solubility measurements in toluene of P5TCN-HD with different molecular weights.

Table S11. The solubility of different batches of P5TCN-HD in toluene at 20	) °C.
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Batch	$\frac{M_{\rm n}}{[\rm kg\ mol^{-1}]}$	$D_{\mathrm{M}}$	Solubility [mg mL <sup>-1</sup> ]
p30	30	1.6	21.4
p53	53	2.2	15.9
P73	73	1.9	12.2



**Figure S12.** (a) TEM and (b) AFM images of the P5TCN-HD:eC9-2Cl binary blend films based on P5TCN-HD with different molecular weights.



**Figure S13.** (a) J-V curves, (b) EQE spectra and integrated  $J_{sc}$  of the P5TCN-HD:eC9-2C1 binary OSCs based on P5TCN-HD with different molecular weights.

**Table S12.** Photovoltaic performances of P5TCN-HD:eC9-2Cl binary OSCs based on P5TCN-HD with different molecular weights.

$M_{ m n}$	$V_{\rm oc}$	$J_{ m sc}$	$J_{ m cal}$	FF	PCE
[kg mol <sup>-1</sup> ]	[V]	[mA cm <sup>-2</sup> ]	$[mA cm^{-2}]$	[%]	[%]
30	0.882	22.72	22.22	67.53	13.54
53	0.871	24.14	23.87	76.80	16.14
73	0.869	25.23	24.61	77.93	17.10

Voor D:A		Calarat	V <sub>oc</sub>	$J_{\rm sc}$	FF	PCE	Def
Y ear	D:A	Solvent	[V]	$[mA cm^{-2}]$	[%]	[%]	Rei
2018	PDCBT-2F:ITIC-4F	CF	0.93	18.10	0.710	11.8	9
2018	PDCBT:O-NTNC	CB	0.94	15.51	0.679	10.0	10
2018	PDCBT:IDTT-BH	CF	0.88	17.15	0.686	10.4	11
2019	PDCBT-Cl:ITIC-Th1	CF	0.94	18.50	0.712	12.4	12
2020	P3HT:ZY-4Cl	THF	0.88	16.49	0.650	9.5	13
2020	PTOBT-Z:ITIC	CF	0.82	19.86	0.550	9.0	14
2021	P3HT:ZY-4Cl	THF	0.90	17.00	0.670	10.2	15
2021	P4T2F-HD:Y6-BO	o-XY	0.72	24.39	0.753	13.7	16
2021	P302:Y5	CF	0.84	20.24	0.570	9.7	17
2021	PDCBT-Cl:IDIC-4F	CF	0.83	15.00	0.725	9.0	18
2021	PDCBT-Cl-Si5:ITIC-Th1	CF	0.93	19.27	0.717	12.9	19
2022	PT-4F:BTP-eC9:L8-BO	CF	0.84	25.27	0.770	16.4	20
2022	P5TCN-2F:Y6	CF	0.85	25.07	0.750	16.1	21
2022	P5TCN-F25:Y6:[70]PCBM	CF	0.80	27.55	0.777	17.2	1
2023	P5TCN-F25:Y6-BO	o-XY	0.80	26.88	0.729	15.7	22
2023	PDCBT-2F:Tz	Tol	0.88	21.1	0.718	13.3	23
2023	PDCBT:PY-IT	CF	0.93	22.8	0.722	15.3	24
2024	P3HT:ZY-4Cl:BTP-2Br	THF	0.89	17.78	0.725	11.4	25
2024	DETCN UD CO 2C1	Tal	0.860	25.22	0.770	171	This
2024	PSICN-HD:eC9-2CI	101	0.809	23.23	0.779	1/.1	work
2024	P5TCN-HD:eC9-2Cl·L8-BO-F	Tol	0.874	26.18	0.792	18.1	This
2027	1 5 1 C1 - 11D. CC 7-2C1. L0-D0-1	101	0.074	20.10	0.772	10.1	work

Table S13. Photovoltaic parameters of representative PT-based OSCs in literatures.



**Figure S14.** (a) J-V curves, (b) EQE spectra and integrated  $J_{sc}$  of the P5TCN-HD:eC9-2Cl:L8-BO-F ternary OSCs.

**Table S14.** Photovoltaic performances of P5TCN-HD:eC9-2C1:L8-BO-F ternary OSCs with different blend ratios (PDINN with CBB as ETL).

DSTCN HD:aC0 2C1.1 8 BO F	$V_{\rm oc}$	$J_{ m sc}$	$J_{ m cal}$	FF	PCE
151CN-HD:CC9-2CI:L8-BO-F	[V]	$[mA cm^{-2}]$	$[mA cm^{-2}]$	[%]	[%]
1:1.1:0.1	0.871	25.80	24.83	0.776	17.51
1:1:0.2	0.874	26.18	25.21	0.792	18.12
1:0.9:0.3	0.879	25.85	24.77	0.779	17.70



Chart S1. Chemical structures of the monomers.



Chart S2. Chemical structures of the polymers.

Scheme S1. Synthetic routes of the monomers M1-M7 (The unit operations are represented by codes: 1 =Quenching/neutralization, 2 =Extraction, 3 =Column chromatography, 4 =Recrystallization, 5 =Distillation/sublimation):





**Table S15**. The summarized NSS, RY, NUO, NCC, NHC and SC of the monomers. The letters "A" and "N" represent the absolute value and the normalized value, respectively, where the values used for the normalization are  $NSS_{max} = 13$ ,  $RY_{max} = 77$ ,  $NUO_{max} = 25$ ,  $NCC_{max} = 9$  and  $\underline{NHC}_{max} = 36.^{26}$ 

Manaman	N	SS	R	Y	N	UO	Ν	CC	N	HC	SC	Def
Monomer	А	Ν	А	N	А	N	А	Ν	А	Ν	(%)	Kel
M1	1	0.08	1.25	0.05	1	0.04	0	0	2	0.05	5.13	27
M2	5	0.38	3.05	0.25	10	0.40	2	0.22	13	0.36	32.82	28-29
M3	5	0.38	1.54	0.10	8	0.32	3	0.33	13	0.36	29.10	1
M4	8	0.62	16.67	0.65	20	0.80	4	0.44	13	0.36	60.01	30
M5	6	0.46	3.13	0.26	14	0.56	4	0.44	11	0.31	40.84	31
M6	9	0.69	5.37	0.39	18	0.72	6	0.67	20	0.56	60.26	32

**Table S16.** The summarized NSS, RY, NUO, NCC, NHC and SC of the polymers. The letters "A" and "N" represent the absolute value and the normalized value, where the values used for the normalization are  $NSS_{max} = 22$ ,  $RY_{max} = 86.9$ ,  $NUO_{max} = 39$ ,  $NCC_{max} = 13$  and  $NHC_{max} = 44.^{26}$ 

Dalarraa	Manaman	NSS		R	RY N		NUO N		NCC N		HC	SC
Polymer	Monomer	Α	Ν	А	N	А	Ν	А	Ν	А	Ν	(%)
P5TCN-HD	M1, M3	7	0.32	3.01	0.24	9	0.23	3	0.23	15	0.34	27.50
P5TCN-F25	M1, M2, M3	12	0.55	6.47	0.43	19	0.49	5	0.38	28	0.64	49.16
P3HT <sup>[4]</sup>	/	3	0.14	1.10	0.02	4	0.10	0	0	4	0.09	7.75
PM6	M4, M5	15	0.68	19.72	0.67	34	0.87	7	0.54	24	0.55	67.17
D18	M4, M6	18	0.82	33.67	0.79	38	0.97	9	0.69	33	0.75	80.83



**Figure S15.** Macroscopic factor matrix of SC, FOM, and PCE based on P5TCN-HD, P5TCN-F25, P3HT, PM6, and D18.

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Polymer	SC	PCE	FOM	Ref
P5TCN-HD	27.50	18.1	65.82	This work
P5TCN-F25	49.16	17.2	34.99	1
РЗНТ	7.75	11.4	147.10	4
PM6	67.17	19.6	29.18	33
D18	80.83	20.2	24.99	34

Table S17. SC and FOM calculation for the investigated polymers.



**Figure S16.** SCLC measurements of (a-c) hole-only devices processed with (a) CF, (b) Tol, and (c) MTHF; (d-f) Electron-only devices processed with (d) CF, (e) Tol, and (f) MTHF.

**Table S18.** Charge carrier mobilities of the P5TCN-HD:eC9-2Cl blends acquired from singlecarrier devices.

Sample	$[\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}]$	$\mu_{\rm e}$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	$\mu_{ m h}/\mu_{ m e}$
CF	$6.02 \times 10^{-4}$	$8.23 \times 10^{-4}$	0.73
Tol	$8.06 \times 10^{-4}$	$8.88  imes 10^{-4}$	0.91
MTHF	$5.03 \times 10^{-4}$	$2.84 \times 10^{-4}$	1.77



Figure S17. Transient photovoltage (TPV) of the P5TCN-HD:eC9-2Cl solar cells processed with different solvents.



**Figure S18.** (a-c) TA spectra of blend films processed with (a) CF, (b) Tol, and (c) MTHF under 520 nm excitation at selected delay times. (d-f) The extracted dynamics at 600, 615, and 810 nm of blend films processed with (d) CF, (e) Tol, and (f) MTHF under 520 nm excitation.

**Table S19.** The detailed fitting parameters of the rising process in 600 nm for the P5TCN-HD:eC9-2Cl blend films processed with different solvents after excitation at 800 nm.

Blend film	Probed [nm]	$A_1$	$ au_1$ [ps]	$A_2$	$ au_2$ [ps]
CF	600	0.72	0.3	0.28	5.6
Tol	600	0.66	0.3	0.34	8.3
MTHF	-	-	-	-	-



**Figure S19.** TA kinetics and fitting curves of the P5TCN-HD:eC9-2Cl blend films processed with CF and Tol after excitation at 800 nm and probed at 600 nm.

Blend film	Probed [nm]	А	τ [ps]
CF	600	0.71	2380
Tol	600	0.83	2955

**Table S20.** The detailed fitting parameters of charge recombination process for the P5TCN-HD:eC9-2Cl blend films processed with CF and Tol after excitation at 800 nm and probed at 600 nm.

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