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Supporting Information

Boiling Water Tolerant Organic Field-Effect Transistors Enabled by a Short-Chain Polymer Blending Approach

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Figure S1 The average mobility of PNDI2OD-2T, extracted in the saturation regime, as a function of 4 kDa PS content.



Figure S2 Output characteristics of OFETs fabricated with (a) neat PNDI2OD-2T and PS blended films with different molecular weights (MWs): (b) 4 kDa, (c) 400 kDa and (d) 1000 kDa.



Figure S3 (a) Average saturation mobility of neat and PS-blended PNDI2OD-2T OFETs with varying MWs. Open dots represent fresh samples, while closed dots denote samples after one day of water immersion at 25 °C. Output characteristics of (b) neat, (c) 4 kDa, (d) 400 kDa and (e) 1000 kDa PS-blended devices after one day of immersion in 25 °C water. (f) Photographs of OFET devices during immersion in hot (50 °C) and boiling (100 °C) water.



Figure S4 Optical microscopy images of (a) PNDI2OD-2T and (b) 4 kDa PS blended films before and after water immersion. Note that the PNDI2OD-2T/4 kDa PS blended film retained a more uniform morphology after a day-long soak, unlike the neat PNDI2OD-2T film, which developed many pinholes (highlighted by red circles).



Figure S5 Atomic force microscopy images of (a) PNDI2OD-2T and (b) 4 kDa PS blended films before and after water immersion. Note that the PNDI2OD-2T/4 kDa PS blended film retained a more uniform morphology after a day-long soak, unlike the neat PNDI2OD-2T film, which developed cracks.



Figure S6 (a) Schematic illustration of the experimental setup configuration used for absorption measurements. In keeping with the device configuration, the active layers were directly spincoated onto SiO₂ wafers. (b) The spectrum of light source for the absorption test. (c) Absorption spectra of PNDI2OD-2T and PNDI2OD-2T/PS films before and after one day of water immersion. The shaded areas highlight spectral differences between fresh and water-soaked samples. Note that the neat PNDI2OD-2T film displayed significant spectral alterations after immersion, likely due to increased defect states and degradation at the molecular level from water exposure. In contrast, the 4 kDa PS blended film exhibited only minor spectral variations under identical experimental conditions, demonstrating exceptional stability against water.



Figure S7 Contact angle measurements from droplets of water and diiodomethane on pristine PNDI2OD-2T, 4 kDa PS, 400 kDa PS, 1000 kDa PS film and PNDI2OD-2T/4 kDa PS blended films.



Figure S8 X-ray photoelectron spectroscopy (XPS) S 2p peaks of PS polymer blends with (a) 4 kDa, (b) 400 kDa, and (c) 1000 kDa, obtained at various depths from the air surface (0 nm) to the substrate.



Figure S9 Cross-sectional scanning electron microscopy images of neat, 4 kDa and 1000 kDa PS blended films before and after one day of water immersion, illustrating the microstructural evolution of the active layer.



Figure S10 Mobility changes in 4 kDa PS-blended films with varying PNDI2OD-2T MWs.

			Subthreshold		
Sample	μ_e	V_{TH}	On Current	Swing	Trap density
	$(cm^2 V^{-1} s^{-1})$	(V)	(A)	(V dec ⁻¹)	$(\times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1})$
Neat	$(1.1 \pm 0.8) \times 10^{-3}$	15.6 ± 2.5	1.0×10^{-6}	5.1	2.3
4 kDa PS					
blend	$(2.5 \pm 0.5) \times 10^{-2}$	3.7 ± 0.5	2.2×10^{-5}	2.1	0.9
400 kDa PS					
blend	$(6.2 \pm 2.2) \times 10^{-3}$	7.8 ± 2.9	6.4 × 10 ⁻⁶	2.8	1.2
1000 kDa PS					
blend	$(1.5 \pm 0.7) \times 10^{-3}$	15.0 ± 5.3	7.0×10^{-7}	4.7	2.1

Table S1 Device parameters of neat PNDI2OD-2T and various blended OFETs. The data shown are the mean values of 8 devices on average. Trap density is estimated from the subthreshold swing.¹

Table S2 Device mobilities of blended OFETs with various representative n- and p-type

 organic semiconductors, along with the reported benchmark mobilities.

Optimized blend system		Mobility (cm ² V ⁻¹ s ⁻¹)	Reported Mobility (cm ² V ⁻¹ s ⁻¹)	Reference
	PNDI2OD-2T/PS (1:1)	2.5×10^{-2}	1 × 10 ⁻² -8 × 10 ⁻²	2-4
N-type	PDI2T/PS (3:7)	1.2×10^{-3}	1.3 × 10 ⁻³	4
	Y6/PS (4:1)	7.1 × 10 ⁻³	1 × 10 ⁻²	5
P-type	PM6/PS (1:1)	4.5 × 10 ⁻²	2.17 × 10 ⁻³	6

	Contact angle (°)		Surface energy [mJ m ⁻²]	Interfacial energy (SiO ₂) [mJ m ⁻²]
	H ₂ O	CH_2I_2		
PNDI2OD-2T	107.4	62.5	28.2	18.0
4 kDa PS	91.7	41.3	39.1	13.9
400 kDa PS	92.1	39.6	40.1	14.4
1000 kDa PS	91.7	39.1	40.3	14.2
PNDI2OD-2T/PS (4 kDa)	110.6	65.5	26.8	/

Table S3 Contact angles and surface energy values calculated using the Wu model (harmonic mean) for various films. Interfacial energy with SiO_2 is also provided. The contact angles are average values from 3 measurements. The contact angle can be found in Figure S7.

Calculation of surface energy and interfacial energy:

The contact angle, denoted as θ , was integrated into the Wu model (harmonic mean) to determine the polar (γ^p) and dispersive (γ^d) components of the overall surface energy (γ)

$$\gamma_W (1 + \cos \theta_W) = \frac{4\gamma_W^d \gamma^d}{\gamma_W^d + \gamma^d} + \frac{4\gamma_W^p \gamma^p}{\gamma_W^p + \gamma^p}$$
(1)

$$\gamma_D (1 + \cos \theta_D) = \frac{4\gamma_D^d \gamma^d}{\gamma_D^d + \gamma^d} + \frac{4\gamma_D^p \gamma^p}{\gamma_D^p + \gamma^p}$$
(2)

where W and D refer to the water and diiodomethane, respectively. The total surface energy is:

$$\gamma = \gamma^d + \gamma^p \tag{3}$$

The corresponding interfacial energy was calculated using the following equation:⁷

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p}$$
(4)

where 1 and 2 refer to two different solids, such as the substrate and the polymer. With this equation, the interfacial energy with the substrate can be calculated.

Calculation of phase diagram:

The phase diagram describes the propensity and mechanism of L–L phase separation in a blend of organic and insulating polymers in a solvent. The diagram is derived from the ternary Flory–Huggins free energy (ΔG) of demixing, expressed as (subscripts 1, 2, and 3 denote the solvent, PS, and PNDI2OD-2T, respectively)

$$\frac{\Delta G}{RT} = n_1 \ln \varphi_1 + n_2 \ln \varphi_2 + n_3 \ln \varphi_3 + \chi_{12} n_1 \varphi_2 + \chi_{13} n_1 \varphi_3 + \chi_{23} N_2 n_2 \varphi_3$$
(5)

where R stands for the universal gas constant, T denotes the temperature, n_i is the number of

moles, φ_i represents the volume fraction, adhering to the incompressibility assumption $(i=1)^3 \varphi_i = 1$), N_i indicates the relative degrees of polymerization (site volume), and χ_{ij} is the interaction parameters between components, with no ternary interactions ($\chi_{123} = 0$). χ can be calculated by

Hildebrand solubility parameters (δ) ($\chi_{ij} = \frac{V_m}{RT} [\delta_i - \delta_j]^2 + \chi_s$, where V_m is the monomeric molar volume of solvent, χ_s is the entropic contribution, typically 0.34, and δ correlates with the square root of the surface energy (γ) for nonpolar materials as $\delta = K\sqrt{\gamma}$, where $K = 116 \times 10^3 \text{ m}^{-1/2}$).^{8,9}

The binodal line is established by equating the chemical potentials of liquid phases, determined iteratively, where the chemical potential $\Delta \mu_i$ is: $\Delta \mu_i = \frac{\partial \Delta G}{\partial n_i}$. The binodal can be computed from the equations below:

$$\frac{\Delta\mu_{1}}{RT} = \ln\varphi_{1} + (1-\varphi_{1}) - \frac{\varphi_{2}}{N_{2}} - \frac{\varphi_{3}}{N_{3}} + (\chi_{12}\varphi_{2} + \chi_{13}\varphi_{3})(\varphi_{2} + \varphi_{3}) - \chi_{23}\varphi_{2}\varphi_{3}$$
(6)
$$\frac{\Delta\mu_{2}}{RT} = \ln\varphi_{2} + (1-\varphi_{2}) - \varphi_{1}N_{2} - \frac{\varphi_{3}N_{2}}{N_{3}} + (\chi_{12}\varphi_{1}N_{2} + \chi_{23}N_{2}\varphi_{3})(\varphi_{1} + \varphi_{3}) - \chi_{13}\varphi_{1}\varphi_{3}N_{2}$$
(7)
$$\frac{\Delta\mu_{3}}{RT} = \ln\varphi_{3} + (1-\varphi_{3}) - \varphi_{1}N_{3} - \frac{\varphi_{2}N_{3}}{N_{2}} + (\chi_{13}\varphi_{1}N_{3} + \chi_{23}N_{3}\varphi_{2})(\varphi_{1} + \varphi_{2}) - \chi_{12}\varphi_{1}\varphi_{2}N_{3}$$
(8)
$$\Delta\mu_{i,A} = \Delta\mu_{i,B}$$
(9)

$$\varphi_{1,A} + \varphi_{2,A} + \varphi_{3,A} = \varphi_{1,B} + \varphi_{2,B} + \varphi_{3,B} = 1$$
(10)

Chemical List:

PNDI2OD-2T: poly{[N,N-9-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-

diyl]-alt-5,59-(2,29-bithiophene)}

PDI2T: poly[[1,2,3,8,9,10-hexahydro-2,9-bis(1-nonyldecyl)-1,3,8,10-tetraoxoanthra[2,1,9-

def:6,5,10-d'e'f']diisoquinoline-5,12-diyl][2,2'-bithiophene]-5,5'-diyl]

Y6: 2,2'-[[12,13-Bis(2-ethylhexyl)-12,13-dihydro-3,9-

diundecylbisthieno[2',3':4',5']thieno[2',3':4,5]pyrrolo[3,2-e:2',3'-g][2,1,3]benzothiadiazole-

2,10-diyl]bis[methylidyne(5,6-difluoro-3-oxo-1H-indene-2,1(3H)-

diylidene)]]bis[propanedinitrile]

PM6: poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-

b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-

c']dithiophene-4,8-dione)]

PDINO: 2,9-Bis[3-(dimethyloxidoamino)propyl]anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-

1,3,8,10(2H,9H)-tetrone

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