

Supporting Information for

**Conformationally Locked Polythiophene Processed by Room-
temperature Blade Coating Enables Breakthrough of Power
Factor**

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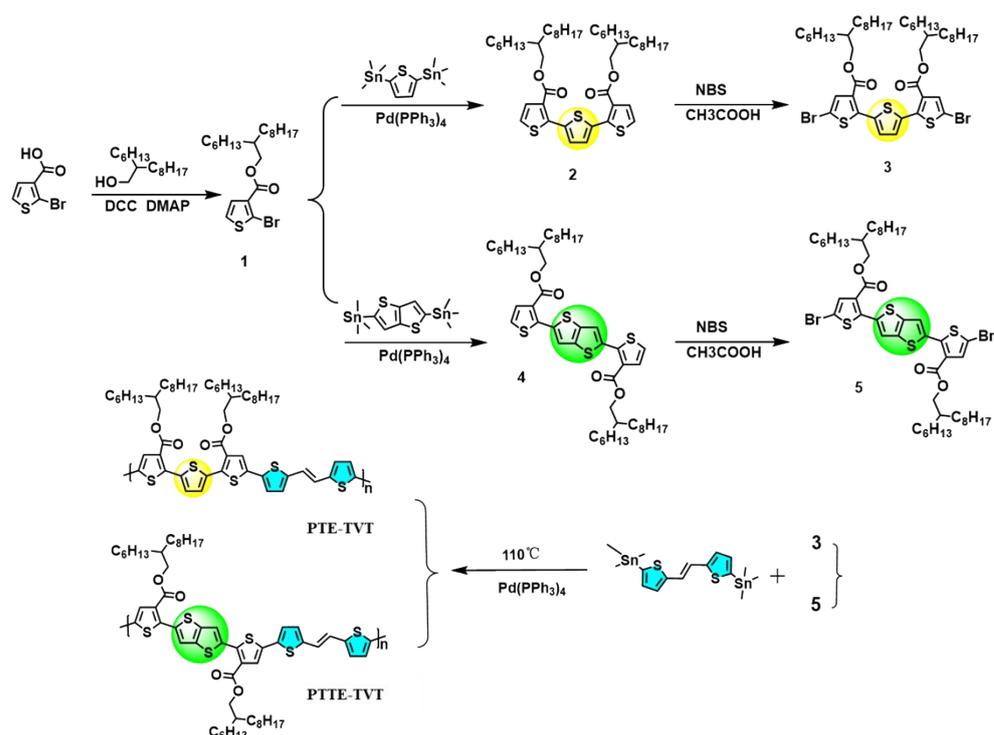
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Materials and Synthesis

All starting materials were purchased from commercial suppliers and used without further purification. 2-bromo-3-thiophenecarboxylic acid was purchased from the Shanghai Haohong Scientific Co., Ltd. 2-hexyl-1-decanol, 2,5-Bis(trimethyltin)-thieno[3,2-B]thiophene, 2,5-Bis(trimethyltinyl)thiophene and (E)-1,2-bis(5-(trimethyltinyl)thiophen-2-yl)ethane were purchased from the Suna Tech Inc. The synthetic routes are shown in Scheme S1 and their structures are consistent with molecular formulas characterized by ^1H NMR.



Scheme S1. The synthesis route of PTE-TVT and PTTE-TVT.

Synthesis compound 1

2-bromo-3-thiophenecarboxylic acid (5 g, 24 mmol), 2-hexyl-1-decanol (8.8 g, 36 mmol), DCC (4.9 g, 24 mmol) and DMAP (0.9 g, 7.2 mmol) were dissolved in 80 mL CH₂Cl₂ (DCM). The mixture was refluxed and stirred at 60 °C for 10 h under a nitrogen atmosphere. After the reaction, the mixture was quenched with water, extracted with DCM, and the combined organic layers were then dried over anhydrous MgSO₄. Subsequently, the organic solvents were evaporated under vacuum. The crude product was purified by chromatography on a silica gel column using hexane (Hex) as eluent to provide a colourless liquid, compound 1. ^1H NMR (400 MHz, CD₂Cl₂) δ (ppm): 1H NMR (400 MHz, CD₂Cl₂) δ 7.23 (d, 1H), 6.78 (d, 1H), 3.91 (d, 2H), 1.64 - 1.13 (m, 24H), 0.88 (t, 7H).

Synthesis Compound 2

To a two-neck round-bottom flask containing compound 1 (1 g, 2.3 mmol), 2,5-Bis(trimethyltinyl)thiophene (426.7 mg, 1.1 mmol) and Pd(PPh₃)₄ (126.7 mg, 0.1 mmol), 10 mL anhydrous toluene was added under nitrogen atmosphere, and the reaction was carried out at 110 °C for 24 hours. After eluting by 500 mL dichloromethane, all eluates were combined and dried, and then concentrated at reduced pressure to give crude compound 2. Then purified by flash column chromatography (hexane/dichloromethane = 4/1) to give a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.48 (d, 1H), 7.39 (s, 1H), 7.20 (d, 1H), 4.15 (d, 2H), 1.54 (s, 2H), 1.26 (d, 24H), 0.87 (dd, 7H).

Synthesis Compound 3

Compound 2 (500 mg, 0.64 mmol) and 3 mL of glacial acetic acid were dissolved in 20mL CH₂Cl₂, NBS were added gradually (283 mg, 1.59 mmol), and the mixture was stirred at 35 °C in the dark for 12 hours. After the reaction, the mixture was quenched with water, extracted with DCM, and the combined organic layers were then dried over anhydrous MgSO₄. Subsequently, the organic solvents were evaporated under vacuum. The crude product was purified by chromatography on a silica gel column using hexane (Hex) as eluent to provide a yellow solid, compound 3. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.42 (s, 1H), 7.33 (s, 1H), 4.13 (d, 2H), 1.53 (s, 2H), 1.25 (d, 24H), 0.87 (t, 8H).

Synthesis Compound 4

Compound 1 (1 g, 2.3 mmol) and 2,5-Bis(trimethyltin)-thieno[3,2-B]thiophene (512.4 mg, 1.1 mmol), Pd(PPh₃)₄ (126.7 mg, 0.1 mmol) were dissolved in 10 mL anhydrous toluene. After stirring for 24hours at 110 °C, the mixture the mixture was quenched with water, extracted with DCM, and the combined organic layers were then dried over anhydrous MgSO₄. Subsequently, the organic solvents were evaporated under vacuum. The crude product was purified by chromatography on a silica gel column using hexane (Hex) as eluent to provide a yellow solid, compound 4. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.66 (s, 1H), 7.50 (d, 1H), 7.24 (d, 1H), 4.15 (d, 2H), 1.56 (s, 1H), 1.25 (d, 24H), 0.86 (d, 7H).

Synthesis Compound 5

Compound 4 (500 mg, 0.59 mmol) and 3 mL of glacial acetic acid were dissolved in 20mL CH₂Cl₂, NBS (264.5 mg, 1.48mmol) were added gradually, and the mixture was stirred at 35 °C in the dark for 12 hours. After the reaction, the mixture was quenched with water, extracted with DCM, and the combined organic layers were

dried over anhydrous MgSO_4 . Subsequently, the organic solvents were evaporated under vacuum. The crude product was purified by chromatography on a silica gel column using hexane (Hex) as eluent to provide a yellow solid, compound 5. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.61 (d, 1H), 7.45 (d, 1H), 4.14 (d, 2H), 1.55 (s, 4H), 1.24 (s, 30H), 0.87 (t, 7H).

Synthesis of PTE-TVT

(E)-1,2-bis(5-(trimethyltinyl)thiophen-2-yl)ethene (TVT) (0.1 mmol, 51.8 mg), compound 3 (0.1 mmol, 94.2 mg) and $\text{Pd}(\text{PPh}_3)_4$ were added to a 25 mL clean two-neck round-bottomed flask. 8 mL of anhydrous toluene was added under nitrogen atmosphere, and the reaction was carried out at 110 °C for 12 hours. After cooling to room temperature, the solution was settled into methanol solution and filtered through a 0.45 μm Teflon filter. The polymer obtained by filtration was put into a Soxhlet extractor and washed with n-hexane, acetone and chloroform in sequence. The solution extracted with chloroform was subjected to rotary evaporation, and the polymer was separated and collected through a 100-200 mesh silica gel column, and then settled into methanol again to obtain a purple-red solid.

Synthesis of PTTE-TVT

(E)-1,2-bis(5-(trimethyltinyl)thiophen-2-yl)ethene (TVT) (0.1 mmol, 51.8 mg), compound 3 (0.1 mmol, 99.8 mg) and $\text{Pd}(\text{PPh}_3)_4$ was added to a 25 mL clean two-necked round-bottomed flask, 8 mL of anhydrous toluene was added under nitrogen atmosphere, and the reaction was carried out at 110 °C for 12 hours. After cooling to room temperature, the solution was settled into methanol solution and filtered through a 0.45 μm Teflon filter. The polymer obtained by filtration was put into a Soxhlet extractor and washed with n-hexane, acetone and chloroform in sequence. The solution extracted with chloroform was subjected to rotary evaporation, and the polymer was separated and collected through a 100-200 mesh silica gel column, and then settled into methanol again to obtain a purple-red solid.

Instruments

The ^1H NMR spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer. ^1H NMR chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Molecular weights of copolymers were determined with Agilent 1260 infinity II high temperature gel permeation chromatography (GPC) system with 10 μm of the column size by using 1,2,4-trichlorobenzene (TCB) as eluent at 150 °C.

Differential scanning calorimetry (DSC) analyses were performed on NETZSCH DSC200. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer TGA instrument for thermal analysis at a heating rate of 10 °C/min under nitrogen. Cyclic voltammetry (CV) was performed by a Zahner IM6e electrochemical work station, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. Polymers were drop-cast onto the electrode from CF solutions to form thin films. 0.1 mol/L⁻¹ 6tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte. The thickness of films was measured by Bruker DektakXT stylus profiler. The GIWAXS measurement was carried out at the PLS-II 6A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. The Ultraviolet Photoelectron Spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) were measured by using Kratos AXIS Ultra-DLD photoelectron spectroscopy with an ultra-high vacuum of 3×10⁻⁹ Torr. Polymers were drop-cast on the substrate from CF solutions to form thin films in the glove box. He-discharge lamp (21.22eV) and monochromatic Al K α source (1486.6 eV) as excitation source, respectively. The instrumental energy resolutions for UPS and XPS spectra were 0.1 and 0.5 eV, respectively.

Organic Thermoelectric device fabrication

The glass substrate (1.2 cm×1.2 cm) was cleaned with detergent, deionized water, acetone and isopropyl alcohol in turn. The weighed polymer was dissolved in chloroform (10 mg/ mL) at 50 °C. Then the glass substrate was cleaned with ozone and the polymer was deposited by blade-coating YS 2019036. The film thickness was 1.5-2 μ m. The film was annealed at 120°C for 20 mins, and then soaked in FeCl₃/CH₃CN solution at a concentration of 3 mg/ml for different times, then annealed at 100 °C for 10 mins after washing away the excess dopant by CH₃CN. A four-probe method was used to determine the electrical resistivity with Seebeck coefficient by using the ZEM-3 TF Seebeck Coefficient/Electrical Resistance Measurement System (Advance Riko). The sample was performed three times at same condition. In addition, the substrate temperature (20 °C ~ 80 °C) and blading speed were regulated when preparing the films. Eventually, 25 ~ 30 °C was selected as the substrate temperature.

Fabrication of Organic Field-Effect Transistors

Top-gate/bottom-contact (TG/BC) organic field-effect transistors were fabricated to study charge transport properties of polymers. Interdigital electrodes (IDE) served as source/drain (S/D) electrodes were fabricated on glass substrates patterned by

photolithography, The channel length (L) is 10, 20, 50, and 100 μm and the channel width (W) is 5000 μm . Before film deposition, the substrates was cleaned with detergent, deionized water, acetone and isopropyl alcohol in turn. UV-ozone treatment to strengthen the surface tension for better adhesion. The polymers were spin-coated from chloroform solution (5 mg mL^{-1}) at 1500 rpm for 40 s, then annealed at 120 $^{\circ}\text{C}$ for 10 min. After that, Parylene C for PTE-TVT as the electrolyte layer was coated on top and annealed at 100 $^{\circ}\text{C}$ for 20 min. Finally, 50 nm Al was evaporated on top as the gate electrode to complete the device fabrication. The OTFT performance was characterized in a N₂-filled glove box using Keithley S4200 semiconductor analyzer. The saturated mobility was calculated based on the equation of $I_{\text{DS}} = \mu C_i (W/2L)(V_{\text{GS}} - V_{\text{th}})^2$, Where I_{DS} is the source-gate current, L is the channel length, W is the channel width, C_i is the capacitance per unit area of the insulating layer, and V_{th} is the threshold voltage.

Measurements of thermal conductivity

A differential 3ω method was utilized to determine the thermal conductivity of PTTE-TVT doping for 6 mins with FeCl_3 (3 $\text{mg} \star \text{ml}^{-1}$). The schematic diagram of the devices was shown in Figure S15. The uniform film was prepared on the Si/SiO₂ substrates. Then we evaporated 100 nm SiO and sputtering deposited 300 nm Si₃N₄ as encapsulation layer. After that, the gold heaters (50 $\mu\text{m} \times 0.71$ mm and 2 $\mu\text{m} \times 0.71$ mm) were patterned on the film by a photolithography technique for the measurement of thermal conductivity. The process of calculating data about thermal conductivity is similar to previous study [1].

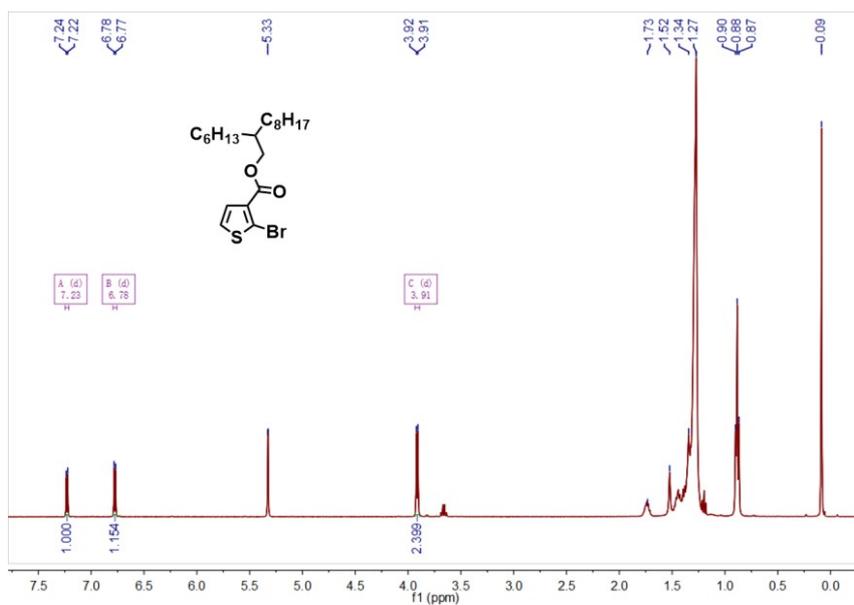


Figure S1. ¹H NMR spectrum of compound 1.

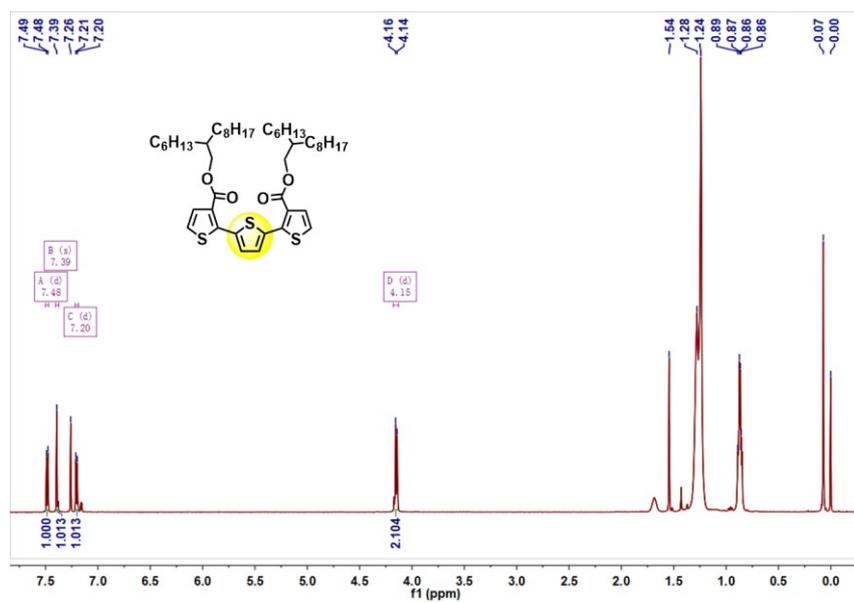


Figure S2. ¹H NMR spectrum of compound 2.

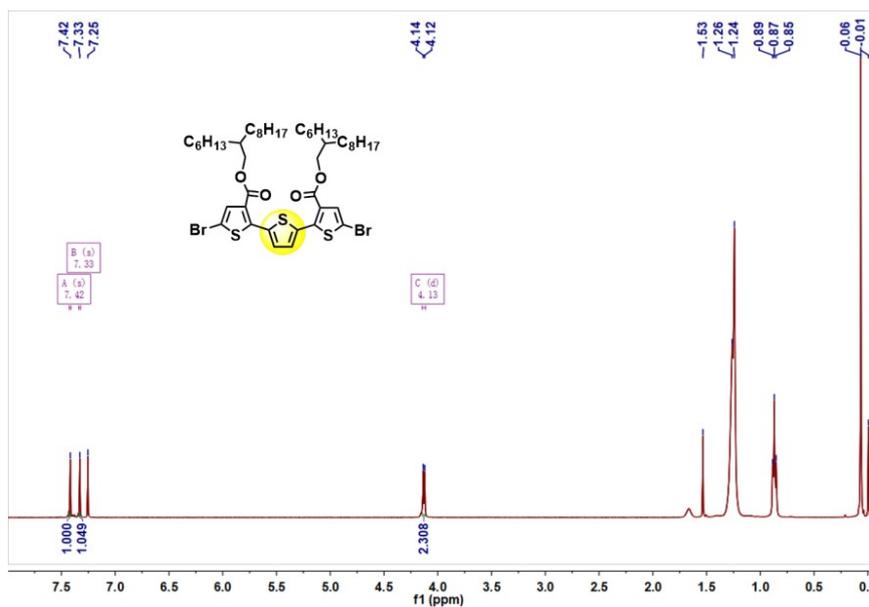


Figure S3. ¹H NMR spectrum of compound 3.

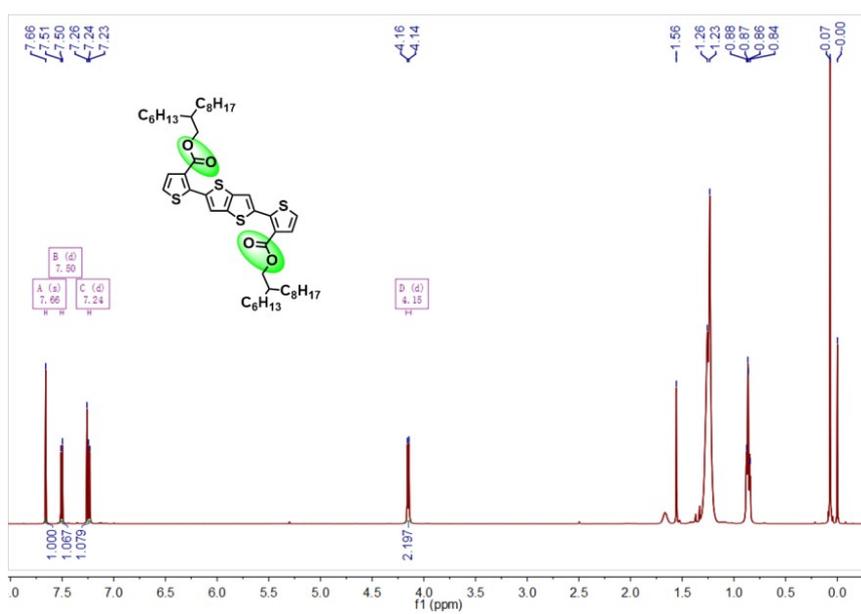


Figure S4. ¹H NMR spectrum of compound 4.

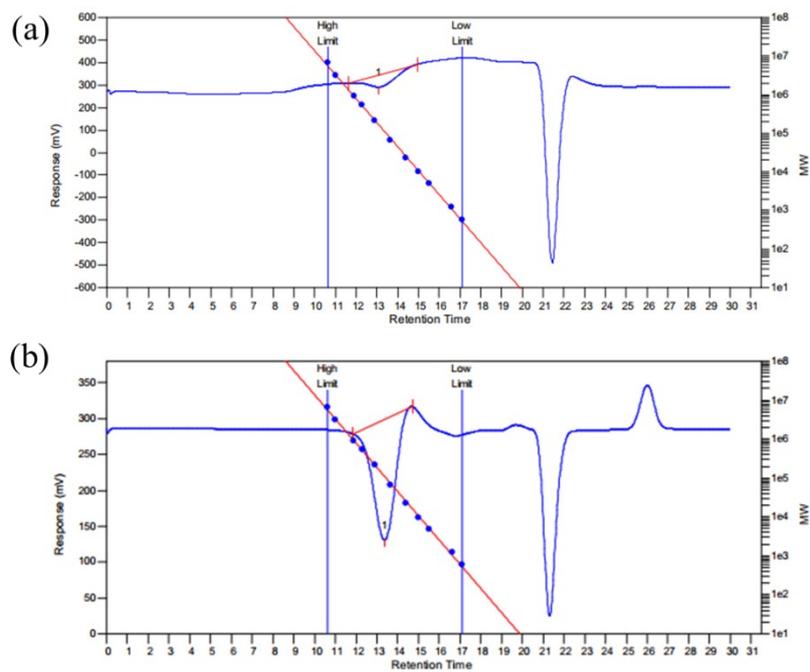


Figure S7. The molecular weight of polymers by HT-GPC (a) PTE-TVT; (b) PTTE-TVT.

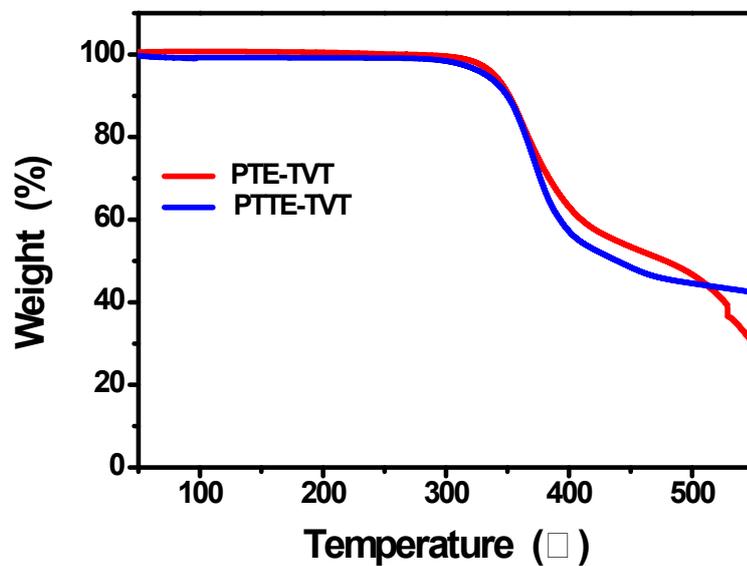


Figure S8. The thermogravimetric analysis (TGA) plot of PTE-TVT and PTTE-TVT.

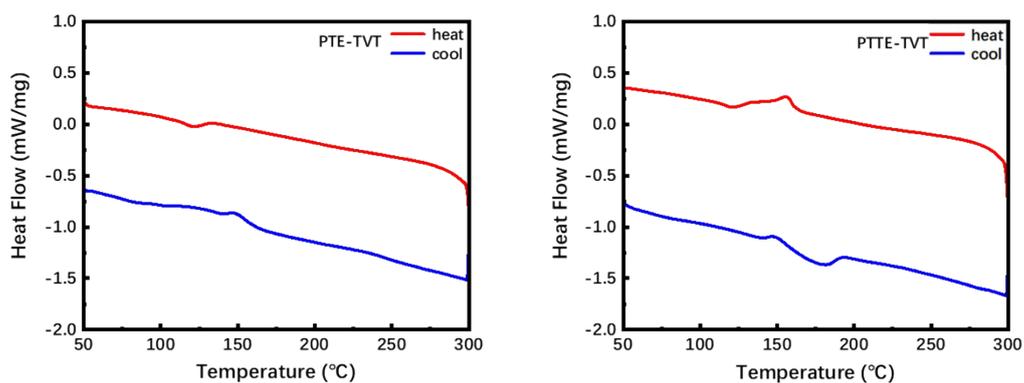


Figure S9. The differential scanning calorimetry (DSC) curves of polymers PTE-TVT (left) and PTTE-TVT (right).

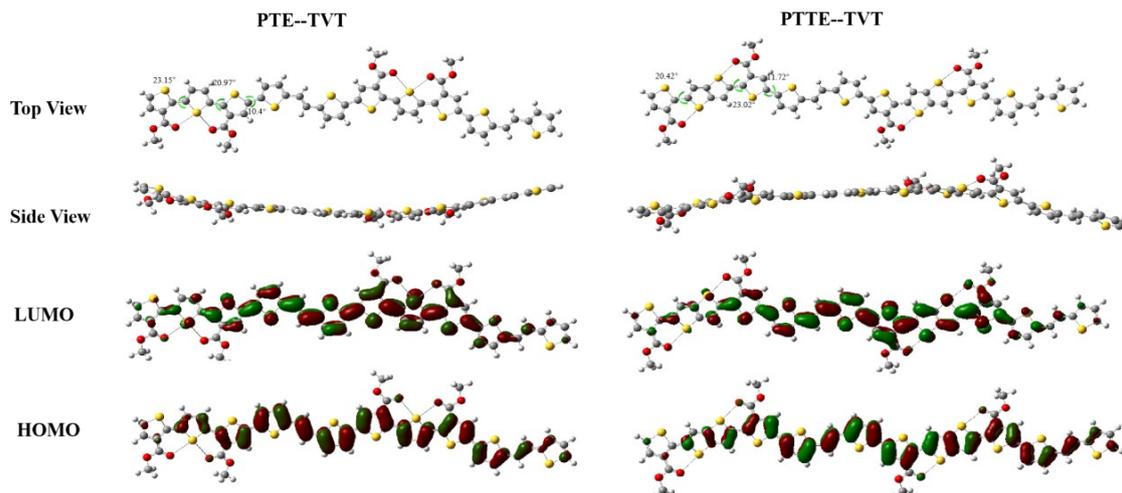


Figure S10. The calculated HOMO/LUMO molecular orbitals (B3LYP/6-31G* levels) of the polymers.

Table S1. Summary of optical, electrochemical, thermal, and photophysical properties of PTE-TVT and PTTE-TVT

Polymers	M_n (kDa)	PDI	λ_{\max} (nm)	T_d (°C)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{ele} (eV)
PTE-TVT	9.5	2.0	531	335	-5.30	-3.54	1.76
PTTE-TVT	9.6	1.5	554	330	-5.20	-3.62	1.58

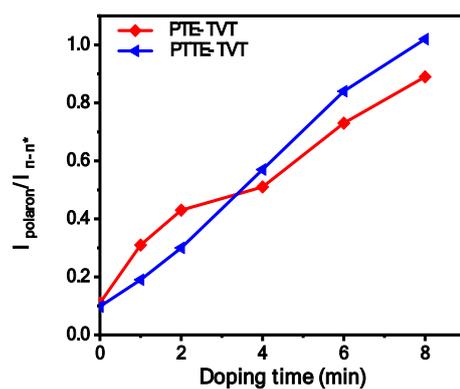


Figure S11. The ratios of polaron and $\pi-\pi^*$ absorbance peaks intensity of PTE-TVT and PTTE-TVT films with different dopant time.

Table S2. The related data of GIWAXS plots of pristine and the doped films for PTE-TVT and PTTE-TVT.

polymer	OOP				IP			
	FWHM (\AA^{-1})	$q_{(010)}$ (\AA^{-1})	π - π stacking distance (\AA)	CCL (\AA)	FWHM (\AA^{-1})	$q_{(100)}$ (\AA^{-1})	d-spacing (\AA)	CCL (\AA)
PTE-TVT	0.227	1.698	3.70	27.67	0.024	0.253	24.82	261.67
Doped PTE-TVT	0.133	1.715	3.66	47.22	0.022	0.275	22.84	285.45
PTTE-TVT	0.128	1.746	3.59	49.06	0.016	0.267	23.52	392.50
Doped PTTE-TVT	0.123	1.743	3.60	51.06	0.017	0.265	23.69	369.41

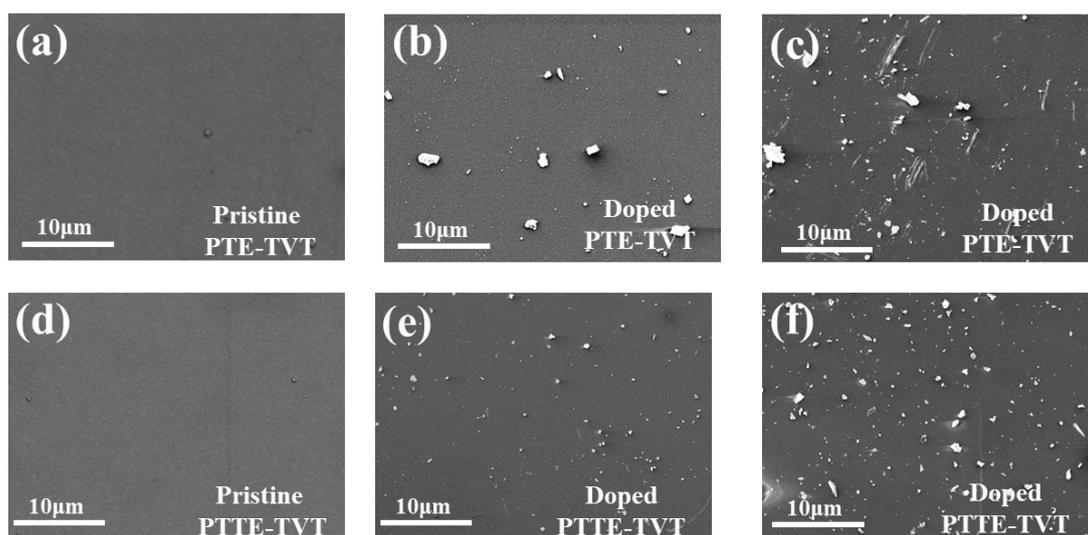


Figure S12. SEM images of PTE-TVT a) doped 0 min, b) doped 3 mins, c) doped 8 mins and the corresponding images for PTTE-TVT films(d)(e)(f).

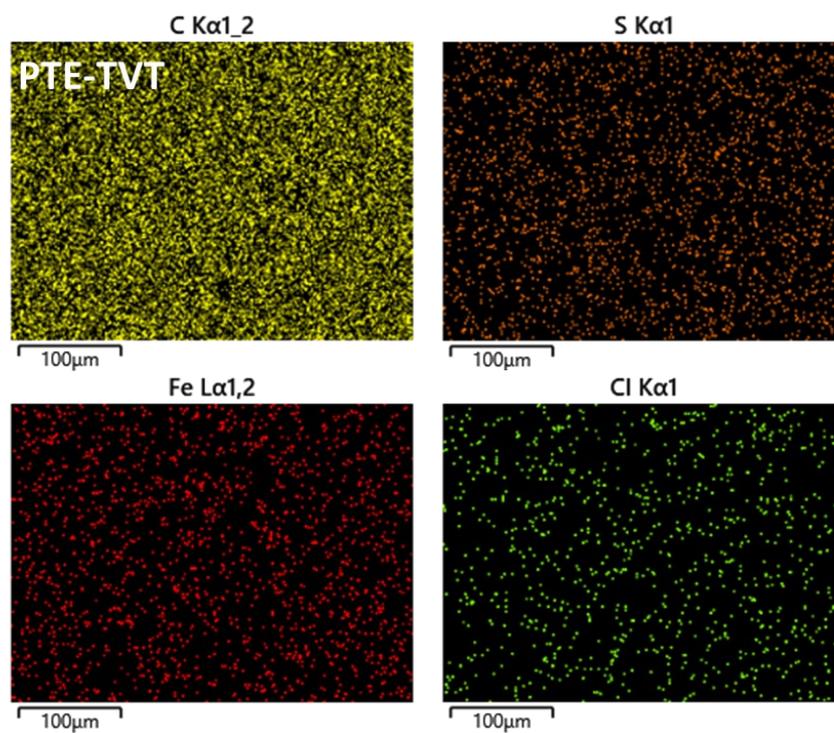


Figure S13. EDS images of PTE-TVT film with doping for 3 mins.

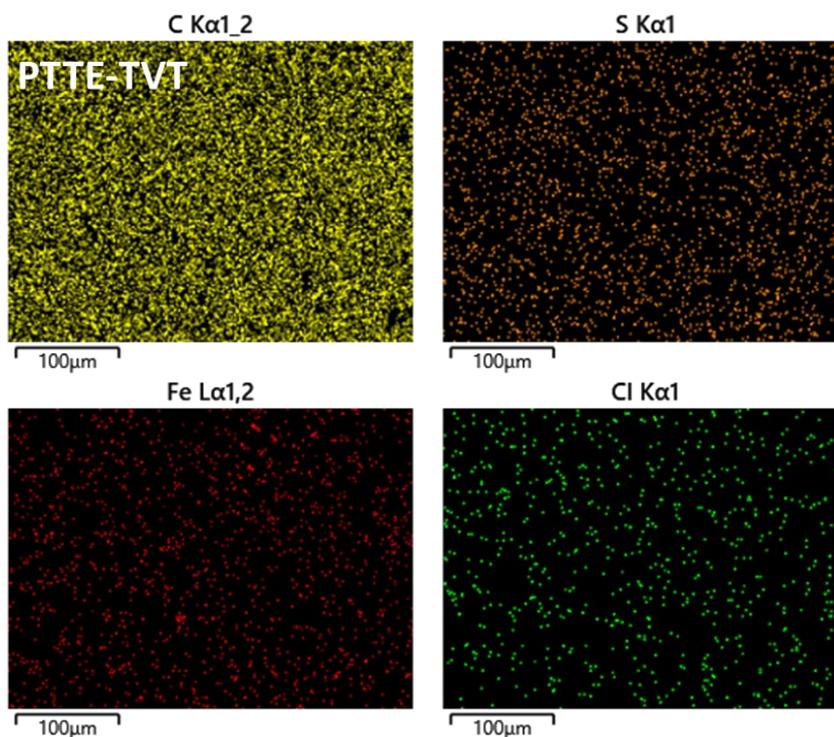


Figure S14. EDS images of the PTTE-TVT film with doping for 3 mins.

Table S3. The OTE performance of thiophen-based simple polymers with different room-temperature film treatments.

Material	Coating method	Dopant	σ (S cm ⁻¹)	S (μ V K ⁻¹)	PF (μ W m ⁻¹ K ⁻²)	Ref.
PTE-TVT	RT-Blade-Coating	FeCl ₃	247.6	73.6	134	This work
PTTE-TVT	RT-Blade Coating	FeCl ₃	302.6	79.2	189.9	This work
P3HT	Drop-Coating	FeCl ₃	7	74	3.9	26
P3HT	Drop-Coating	Fe(TFSI) ₃	320	39	62.4	26
P3RTe	Blade Coating	FeCl ₃	46	51	10	18
P3RSe	Blade Coating	FeCl ₃	29	89	13	18
P3POET	Spin-coating	FeCl ₃	193.5	34	19	3
PQT12	Drop-Coating	NOBF ₄	35	20.1	1.4	27
PQTS12	Drop-Coating	NOBF ₄	350	/	8	27
PBTTT	Spin-coating	EBSA	1300	14	25	1
PBTTT	Spin-coating	FTS	1000	33	~110	1
PBTTT	Spin-coating	F4TCNQ	670	42	120	2
C10-PBTTSe	Drop-Coating	Fe(TFSI) ₃	691	/	46.5	4
p(g42T-T)	Spin-coating	F4TCNQ	120	/	/	40
Pg ₃ 2T-OTz	Drop-Coating	F4TCNQ	550	~200	/	33
PQTC16-TT	Spin-coating	NOBF ₄	39	~38	/	28
PQTSC16-TT	Spin-coating	NOBF ₄	330	~20	/	28

Table S4. Repeatability measurement for 6-min-doped PTE-TVT and PTTE-TVT.

Polymer	Doping time (FeCl ₃ : 3mg/ml)	σ (S cm ⁻¹)	S (μ V K ⁻¹)	PF (μ W m ⁻¹ K ⁻²)
PTE-TVT	6 mins	251.5	75.08	141.8
PTE-TVT	6 mins	213.7	76.16	124
PTE-TVT	6 mins	247.6	73.56	134
PTE-TVT	6 mins	232.6	78.72	144.1
PTE-TVT	6 mins	281.1	70.24	138
PTTE-TVT	6 mins	337	75.39	191.6
PTTE-TVT	6 mins	224.5	87.7	172.6
PTTE-TVT	6 mins	217.1	94.96	195.8
PTTE-TVT	6 mins	302.6	79.2	189.9
PTTE-TVT	6 mins	312.9	78.2	191.4

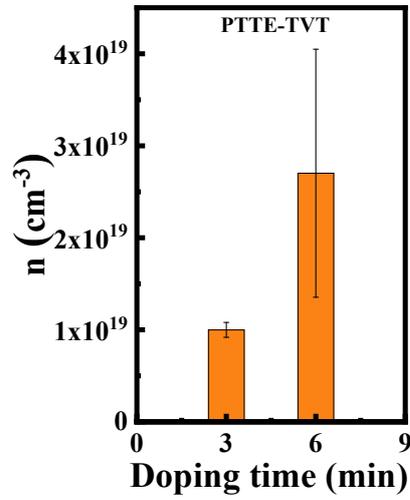


Figure S15. n_{Hall} of 3 and 6-min-doped PTTE-TVT with FeCl_3 ($3\text{mg} \star \text{ml}^{-1}$).

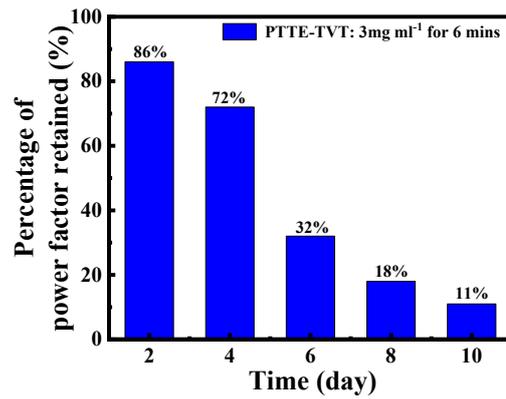


Figure S16. The retained Power factor of 6-min-doped PTTE-TVT with FeCl_3 ($3\text{mg} \text{ml}^{-1}$) after 10 days.

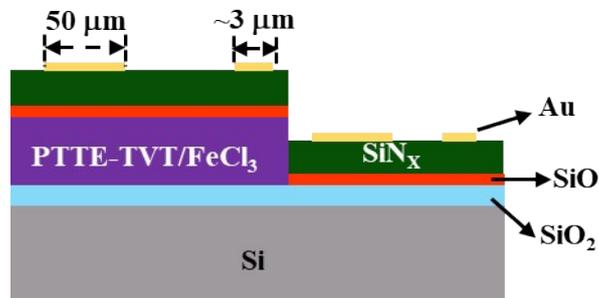


Figure S17. Device diagram for the measurement of the thermal conductivity.

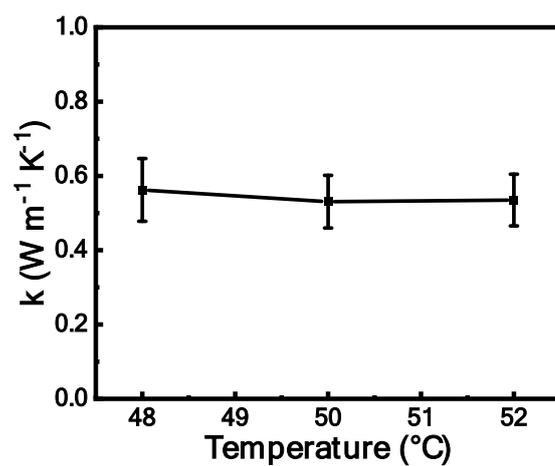


Figure S18. Thermal conductivity of 6-min-doped PTTE-TVT film with FeCl₃ (3mg★ml⁻¹) at 48°C, 50 °C and 52 °C.

References

1. D. Huang, H. Yao, Y. Cui, Y. Zou, F. Zhang, C. Wang, H. Shen, W. Jin, J. Zhu, Y. Diao, W. Xu, C. a, Di and D. Zhu, *J. Am. Chem. Soc.*, 2017, **139**, 13013-13023.