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Supporting Information

Thenoyl-functionalized polythiophenes with deep HOMO levels as polymer donors for organic solar cells

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*Corresponding author: <u>wxp@ciac.ac.cn;</u> <u>chemtonghui@ciac.ac.cn;</u> <u>lixiang@ciac.ac.cn</u> **Materials and Synthesis.** 2,5-dibromothiophene-3-carboxylic acid (compound 1) and 3-chloro-2-(2-hexyldecyl)thiophene (compound 2) was synthesized according to the literature.¹⁻² Y6-BO, PDINO were purchased from Derthon Optoelectronic Materials Science Technology Co Ltd. The other chemicals and solvents were purchased from commercial sources (Sigma Aldrich, Energy Chemical, or Alfa Aesar).

(4-Chloro-5-(2-hexyldecyl)thiophen-2-yl)(2,5-dibromothiophen-3-yl)methanone

(compound 3): 2,5-dibromothiophene-3-carboxylic acid (5.7 g, 20 mmol) was dissolved in the solvent mixture of dichloromethane (50 mL) and N,Ndimethylformamide (1 mL). Oxalyl chloride (4.2 mL, 50 mmol) was added dropwise, and the mixture was stirred overnight at room temperature. The residue was dried under vacuum, and dichloromethane (50 mL) was added under argon protection. Aluminium chloride (5.3 g, 40 mmol) was added in portions at 0 °C, and then 3-chloro-2-(2hexyldecyl)thiophene (6.9 g, 20 mmol) was added. The reaction mixture was allowed to stir at 0 °C for 30 min and then at room temperature for 20 hours. The mixture was poured into ice with hydrochloric acid of 1 mol/L, and then extracted with dichloromethane. The organic layer was collected and the solvent was removed under vacuum. The crude product was purified by column chromatography with hexane/dichloromethane (3:1) as eluent. Yield: 67%. ¹H NMR (500 MHz, CDCl₃, δ/ppm): 7.38 (s, 1H), 7.18 (s, 1H), 2.78 (d, 2H), 1.75 (m, 1H), 1.26 (m, 24H), 0.87 (t, 6H). ¹³C NMR (500 MHz, CDCl₃, δ/ppm): 179.6, 149.5, 139.1, 135.0, 130.8, 124.2, 115.3, 112.5, 39.5, 31.8, 26.5, 22.7, 14.2. MS (MALDI-TOF): calcd for C₂₅H₃₅Br₂ClOS₂, m/z: 608.0; found: 609.0 [M+H]⁺.

P2T-TCI: Compound 2 (140 mg, 0.23 mmol), 2,5-bis(trimethylstannyl) thiophene (94 mg, 0.23 mmol), Pd₂(dba)₃ (4.2 mg) and P(o-tol)₃ were dissolved in 6 mL toluene and 0.75 mL DMF. The mixture was stirred at 110 °C for 24 hours. The crude polymer was precipitated in methanol and filtered. The precipitate was extracted with acetone, n-hexane and cyclohexane with a Soxhlet extractor, and then collected and dried under vacuum. Yield: 89%. ¹H NMR (500 MHz, CDCl₃, δ /ppm): 7.34 (br, aromatic protons),

7.12 (br, aromatic protons), 2.77 (br, methylene protons), 1.74 (br, methine protons),1.25 (br, methylene protons), 0.88 (br, methyl protons).

P3T-TCI: Compound 2 (116 mg, 0.20 mmol), 2,5-bis(trimethylstannyl)thiophene (94mg, 0.20mmol), Pd(PPh₃)₄ (8.8 mg) were dissolved in 6 mL toluene and 0.75 mL DMF. The mixture was stirred at 110 °C for 20 hours. The crude polymer was precipitated in methanol and filtered. The precipitate was extracted with acetone, n-hexane and cyclohexane with a Soxhlet extractor, and then collected and dried under vacuum. Yield: 90%. ¹H NMR (500 MHz, CDCl₃, δ /ppm): 7.33 (br, aromatic protons), 7.02 (br, aromatic protons), 2.78 (br, methylene protons), 1.75(br, methine protons), 1.27 (br, methylene protons), 0.88 (br, methyl protons).

P4T-TCI: Compound 2 (201 mg, 0.33 mmol), 5,5"-Bis(trimethylstannyl)-2,2':5',2"terthiophene (189 mg, 0.33 mmol), and Pd(PPh₃)₄ (13.93 mg) were dissolved in 8mL toluene and 1mL DMF. The mixture was stirred at 110 °C for 40 hours. The crude polymer was precipitated in methanol and filtered. The precipitate was extracted with acetone, n-hexane and cyclohexane with a Soxhlet extractor, and then collected and dried under vacuum. Yield: 92%. ¹H NMR (500 MHz, CDCl₃, δ /ppm): 7.38 (br, aromatic protons), 7.11 (br, aromatic protons), 2.76 (br, methylene protons), 1.72(br, methine protons), 1.25 (br, methylene protons), 0.87 (br, methyl protons).



Scheme S1 The synthetic route of P3T-E.

2-hexyldecyl 2,5-dibromothiophene-3-carboxylate: 2,5-dibromothiophene-3-carboxylic acid (compound 1) (0.8g, 2.80mmol), N, N'-dicyclohexylcarbodiimide (DCC, 0.69g, 3.36mmol) and 4-dimethylaminopyridine (DMAP, 0.12g, 0.98mmol) were dissolved in 20mL DCM. 2-hexyldecyl 2,5-dibromothiophene-3-carboxylate was

added into the mixture after 20min. The reaction mixture was stirred at room temperature for 40h and then poured into water. The mixture was extracted with dichloromethane and filtered. The crude product was purified by column chromatography with hexane/dichloromethane (3:1) as eluent. Yield: 79%. ¹H NMR (500 MHz, CDCl₃, δ /ppm): 7.33 (s, 1H), 4.19 (d, 2H), 1.73 (m, 1H), 1.27 (m, 24H), 0.88 (t, 6H). ¹³C NMR (500 MHz, CDCl₃, δ /ppm): 161.1, 132.2, 131.8, 118.8, 111.3, 68.0, 37.3, 29.9, 26.7, 22.7, 14.1. MS (GC MS): calcd for C₂₁H₃₄Br₂O₂S, m/z: 510.0; found: 510.0.

P3T-E: The polymerization procedure for P3T-E was the same as that of P3T-TCl with 2-hexyldecyl 2,5-dibromothiophene-3-carboxylate(150mg, 0.29mmol), 2,5-bis(trimethylstannyl)thiophene (143mg, 0.29mmol) and Pd(PPh₃)₄ (11.8 mg). Yield: 81%. ¹H NMR (500 MHz, CDCl₃, δ /ppm): 7.13 (br, aromatic protons), 4.20 (br, methylene protons), 1.74(br, methine protons), 1.28 (br, methylene protons), 0.88 (br, methyl protons).

Measurements and characterization

General characterizations: ¹H and ¹³C NMR spectra were conducted with 400 MHz and 500 MHz Bruker Avance NMR spectrometer in CDCl₃ using tetramethylsilane (TMS; δ =0 ppm) as internal standard. Matrix-assisted laser desorption ionization timeof-flight mass spectra (MALDI-TOF MS) was recorded on a Bruker AutoflexIII smartbeam MALDI-TOF mass spectrometer. The high-temperature gel permeation chromatography (GPC) was measured by the Agilent PL-GPC220 high-temperature gel permeation chromatograph, with 1,2,4-trichlorobenzene (TCB) stabilized with 0.0125% BHT as the eluent and a narrow distribution of polystyrene as the standard sample, at the temperature of 150 °C. Thermogravimetric analysis (TGA) was performed by the TA-TGA55 thermogravimetric analyzer under N₂ atmosphere with a heating rate of 10 °C/min, ranging from room temperature to 800 °C. Differential scanning calorimetry (DSC) testing was performed by a Perkin-Elmer DSC-7 differential scanning

calorimeter in a N2 atmosphere with a scanning rate of 10 °C/min and a ranging from room temperature to 280 °C or 300 °C, respectively. Ultraviolet-visible absorption (UV-vis) spectra of solution and films was measured on a PerkinElmer Lambda Model 35 spectrometer. Cyclic voltammetry (CV) measurements were performed on a CHI660a electrochemical workstation with a glassy carbon working electrode, a platinum counter electrode, and a saturated calomel reference electrode. Tetra-nbutylammonium perchlorate (n-Bu₄NClO₄) in acetonitrile solution with a concentration of 0.1 M was used as the supporting electrolyte. Ferrocene was used as the reference, and the potential of its redox couple (Fc/Fc^+) is assumed to be 4.8 eV below the vacuum level. The materials were casted on the working electrode for measurements, and all CV measurements were performed with a scan rate of 50 mV s⁻¹. The HOMO energy levels of the material were calculated according to the initial oxidation potential of ferrocene ($E_{\text{Fc/Fc+}}$) and the initial oxidation/reduction potential ($E_{\text{ox/red}}$) of the material by the following equation: $E_{\text{HOMO}} = -e (E_{\text{ox}} - E_{\text{Fc/Fc+}} + 4.8 \text{ V})$; the LUMO levels are calculated by E_{HOMO} and the optical band gaps. Atomic force microscope (AFM) images were obtained on the SPA300HV (Seiko Instruments, Inc., Japan) by tapping mode. Transmission electron microscope (TEM) images were obtained by a transmission electron microscope of JEOL JEM-1400 with an accelerating voltage of 120 kV.

Contact angle measurements and calculation method of interfacial tension: Contact angles of the materials were measured by a contact angle analyzer (Krüss, DSA 100), in which deionized water and ethylene glycol were chosen as liquids. Surface tension (γ) was calculate according to the equation: $\gamma = \gamma^d + \gamma^p$, in which γ^d and γ^p denote dispersion and polar component, respectively. γ^d and γ^p was calculated according to the Wu method which was shown below, using both the contact angle from water and ethylene glycol on pristine films:

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

$$\gamma_{EG}(\cos\theta_{EG}+1) = \frac{4\gamma_{EG}^d\gamma^d}{\gamma_{EG}^d+\gamma^d} + \frac{4\gamma_{EG}^p\gamma^p}{\gamma_{EG}^p+\gamma^p}$$

Where γ_{EG}^{d} is the dispersive component of ethylene glycol surface energy, γ_{EG}^{p} is the polar component of ethylene glycol surface energy, γ_{w} is the surface energy of water, γ_{w}^{d} is the dispersive component of water surface energy, γ_{w}^{p} is the polar component of water surface energy, θ_{EG} is the contact angle of ethylene glycol and θ_{w} is the contact angle of water.

Fabrication and Measurement of organic solar cell (OSC) devices: The OSCs devices were fabricated with the structure of Glass/ITO/PEDOT: PSS/active layer/PDINO/Al. The ITO glass substrates were ultrasonicated in isopropanol for 30 min, then in deionized water, and then acetone and isopropanol for 10 min, respectively. The cleaned ITO glass substrates were dried in oven at 120 °C for 1 h. After treated with UV-ozone for 30 min, PEDOT:PSS (Baytron PVP Al4083) was spin-coated on the surface of ITO glass at a spinning rate of 5000 r.p.m. for 40 s, and then baked in oven at 120 °C for 30 min. After that, the PEDOT:PSS-coated ITO substrates were transferred into a nitrogen-filled glovebox quickly. The PnT-TCl:Y6-BO blend solutions in chloroform were spin-coated onto PEDOT:PSS layer at 2500-3500 r.p.m. for 1 min. The PDINO of 1mg/mL in methanol was onto the active layer at a spinning rate of 3000 r.p.m. for 30 s. Al top electrode (100nm) was deposited on the top of the PDINO layer at a pressure of 2×10^{-4} Pa. The *J-V* curves were obtained by testing the device with a computer-controlled Keithley 2400 digital source meter under 100 mW cm⁻² AM 1.5G simulated sunlight radiation. The EQE curves were acquired by the QE-R3011 Spectral Response Tester, and the light intensity was calibrated by a standard silicon cell before each test.

Fabrication of single-carrier devices: The single-carrier mobility was tested using the space-charge limiting current (SCLC) method, and the single-hole device structure was ITO/PEDOT: PSS/film/MoO₃/Al, and the single-electron device structure was ITO/ZnO/film /PDINO/Al. In the single hole devices, MoO₃ was evaporated at 15 nm

with a deposition rate of 0.8 Å/s, followed by evaporation of the Al electrode. In the single electronic devices, the ZnO interface layer was prepared by dissolving zinc acetate dihydrate (0.5 g) and ethanolamine (0.14 g) in 2-methoxyethanol (5 mL), stirring at room temperature for 12 h, filtering and applying directly, spin-coating on a cleaned and UVO-treated ITO substrate (spin coating speed of 3500 r.p.m., spin coating time of 1 min), then annealing at 200 °C for 1 h in air environment, and then quickly transferred to a glove box in a nitrogen atmosphere. The active layer was spin-coated as the same condition of the OSCs devices.

The *J-V* curve of the single carrier device was controlled by a computer-controlled Keithley 2400 digital source meter in the dark state. Mobility data were measured by the modified Mott-Gurney formula:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3} exp^{\text{ind}}(0.89\beta \frac{\sqrt{V}}{\sqrt{J}})$$

where *J* is the current density, ε_0 is the permittivity of free space (8.85 × 10⁻¹² F m⁻¹), ε_r is the relative permittivity (assumed to be 3F m⁻¹), μ is the mobility, *V* is the potential across the device ($V=V_{appl} - V_{bi}$, V_{appl} is the applied voltage, V_{bi} is the built-in voltage).

Mechanical Characterization

In the FOE test method, the image of the stretched polymer film on PDMS was obtained by Nikon ECLIPSE LV100N POL polarizing microscope (normal optical mode). The preparation for the films is as follows: The solution of poly(4-styrene sulfonic acid) (PSS) diluted in water at the concentration of 1 w% was spin-coated on glass at 5000 rpm for 40 s, and then the PSS film was placed in an oven and baked at 120 °C for 30 min. The donor solution was spin-coated on top of the PSS layer to form thin film of thickness ~60 nm. The PDMS (base:crosslinker = 10:1 w/w) was chosen as the elastomer substrate. The PDMS substrate was attached to the film and placed in water, and as PSS was dissolved in water, a thin film attached to the PDMS substrate was obtained.

The stress-strain curves of films were obtained from the pseudo free-standing tensile test. The films were spin-coated onto the water-soluble PSS coated glass substrate and plasma-etched into the shape of dog-bone with PDMS as a mask. The film floated on the surface of the water after the PSS layer was penetrated and dissolved. Subsequently, the thin films were pulled at a strain rate of 0.3 mm min⁻¹.



Fig. S1. (a) TGA curves of P2T-TCl, P3T-TCl and P4T-TCl. (b) DSC curves of P2T-TCl, P3T-TCl, P4T-TCl.



Fig. S2. (a) Optimized molecular geometries of tetra-3T-TCl and tetra-3T-E obtained by DFT calculations; (b) frontier molecular orbitals of tetra-3T-E.



Fig. S3. The temperature-dependent UV-vis absorption spectra of (a) P2T-TCl, (b) P3T-TCl, (c) P4T-TCl in chlorobenzene solutions.



Fig. S4. Cyclic voltammograms of P2T-TCl, P3T-TCl and P4T-TCl in thin film.



Fig. S5. OM images of the neat films of (a) P2T-TCl, (b) P3T-TCl and (c) P4T-TCl under 0~100% tensile strains.



Fig. S6. Chemical structure of P3T-E and the optical microscopy images of its films under $0 \sim 40\%$ strains.



Fig. S7. Stress-strain curves of P2T-TCl, P3T-TCl, P4T-TCl and P3T-E films.



Fig. S8. Space-charge-limited J-V plots from the electron-only device based on (a) P2T-TCI: Y6-BO, (b) P3T-TCI: Y6-BO and (c) P4T-TCI: Y6-BO films and the hole-only device based on (d) P2T-TCI: Y6-BO, (e) P3T-TCI: Y6-BO and (f) P4T-TCI: Y6-BO films.



Fig. S9. (a) 2D-GIWAXS patterns for Y6-BO neat films; (b) the corresponding GIWAXS line-cut profiles along OOP and IP directions.



Fig. S10. 2D-GIWAXS patterns for (a) P2T-TCl, (b) P3T-TCl and (c) P4T-TCl, and the corresponding GIWAXS line-cut profiles along (d) out-of-plane (OOP) and (e) in-plane (IP) directions.



Fig. S11. Views of surface contact angle measurements of P2T-TCl, P3T-TCl, P4T-TCl and Y6-BO.



Fig. S12. The AFM phase images of P2T-TCl: Y6-BO, P3T-TCl: Y6-BO and P4T-TCl: Y6-BO blend films.



Fig. S13. J-V curves of devices based on P2T-TCI:Y6, P3T-TCI:Y6 and P4T-TCI:Y6.



Fig. S14. J-V curves of devices based on P3T-E:Y6-BO.



Fig. S15. ¹H NMR spectrum of compound 2 in CDCl_{3.}



Fig. S16. ¹³C NMR spectrum of compound 2 in CDCl_{3.}



Fig. S17. Mass spectra of compound 2 in CDCl₃.



Fig. S18. ¹H NMR spectrum of P2T-TCl in CDCl₃.



Fig. S19. ¹H NMR spectrum of P3T-TCl in CDCl₃.



Fig. S20. ¹H NMR spectrum of P4T-TCl in CDCl₃.



Fig. S21. ¹H NMR spectrum of 2-hexyldecyl 2,5-dibromothiophene-3-carboxylate in CDCl₃.



Fig. S22. ¹³C NMR spectrum of 2-hexyldecyl 2,5-dibromothiophene-3-carboxylate in CDCl_{3.}



Fig. S23. ¹³H NMR spectrum of P3T-E in CDCl_{3.}



Scheme S2. The synthetic routes of PM6.



Scheme S3. The synthetic routes of D18.



Scheme S4. The synthetic routes of PTQ10.



Scheme S5. The synthetic routes of PDCBT.



Scheme S6. The synthetic routes of PDCBT-Cl.



Scheme S7. The synthetic routes of PTVT-T.



Scheme S8. The synthetic routes of P4T2F-HD.



Scheme S9. The synthetic routes of PTOBT-Z.



Scheme S10. The synthetic routes of P5TCN-2F.



Scheme S11. The synthetic routes of P2T-TCl, P3T-TCl and P4T-TCl.

	N	SS	R	Y	N	UO	N	CC	N	HC	SC^*	Def
polymer -	А	N	А	N	А	N	А	N	А	N	(%)	Kei
PM6	15	0.68	19.8	0.67	34	0.83	8	0.62	24	0.55	67.8	3
D18	18	0.82	22	0.69	41	1	10	0.77	30	0.68	79.3	4
PTQ10	7	0.32	2.93	0.25	13	0.33	1	0.08	14	0.32	26.2	5
PDCBT	6	0.27	8.03	0.47	9	0.22	3	0.23	13	0.30	30.9	6
PDCBT- Cl	7	0.32	4.98	0.35	11	0.22	3	0.23	16	0.36	31.0	7
PTVT-T	7	0.32	4.04	0.31	8	0.20	2	0.15	9	0.20	26.2	8
P4T2F- HD	9	0.41	5.39	0.38	17	0.41	5	0.38	25	0.57	41.4	9
PTOBT- Z	5	0.23	3.65	0.29	8	0.20	3	0.23	11	0.25	24.1	10
P5TCN- 2F	11	0.5	6.67	0.43	19	0.46	5	0.38	28	0.64	47.2	11
P2T-TCl	5	0.23	3.39	0.27	6	0.15	2	0.15	12	0.27	22.0	This work
P3T-TCl	6	0.27	3.51	0.28	8	0.20	3	0.23	13	0.30	25.9	This work
P4T-TCl	6	0.27	3.35	0.27	9	0.22	3	0.23	13	0.30	26.0	This work
$SC^* = 35N$ + 10NHC	SS/N	[SS _{max}	+ 25lo	og(RY))/log(for	RY _{max})	+ 15 rmali	NCC/N	NSS	hax + 15	NUO/N · RY	UO_{max}

 Table S1. SC calculation for the investigated systems.

+ 10NHC/NHC_{max}; Values used for the normalization: NSS_{max}=22; RY_{max}=86.9; NUO_{max}=41; NCC_{max}=13; NHC_{max}=44. ¹²

Material	<i>M</i> n [kDa]	Ð	<i>T</i> _d [°C]	Δ _{H_m} [J g ⁻¹]	Δ _{H_c} [J g ⁻¹]	<i>T</i> _m [°C]	<i>T</i> _c [°C]	Elastic modulus (MPa)	COS
P2T-TC1	23	2.4	367	3.9	3.7	172	148	80	53%
P3T-TC1	25	2.4	372	6.7	4.6	214	185	120	29%
P4T-TC1	21	4.3	398	9.2	8.8	262	257	197	23%

Table S2. The Molecular weights, thermal and mechanical parameters of the polymers.

Table S3. The hole and electron mobilities of the blend films.

Active layer	$\mu_{\rm e} [{\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1}]$	$\mu_{\rm h} [{\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1}]$	$\mu_{ m e}/\mu_{ m h}$
P2T-TC1:Y6-BO	4.05×10 ⁻⁴	2.16×10-4	1.88
P3T-TCl:Y6-BO	5.12×10 ⁻⁴	2.56×10-4	2.00
P4T-TC1:Y6-BO	8.57 ×10 ⁻⁴	5.33×10 ⁻⁴	1.61

 Table S4. GIWAXS parameters of the neat films.

Materials	(OOP (01	.0)	IP (100)			
	q (Å-1)	d (Å)	CCL (Å)	q (Å-1)	d (Å)	CCL (Å)	
Y6-BO	1.77	3.55	18.0	0.31; 0.40	20.1; 15.9	85.7; 56.0	
P2T-TC1	-	-	-	0.23	27.3	69.8	
P3T-TC1	-	-	-	0.22	28.5	93.6	
P4T-TC1	1.47	4.26	10.0	0.21	29.9	99.0	

Mataria1-	OOP (010)			IP (100)			
Materials	q (Å-1)	d (Å)	CCL (Å)	q (Å-1)	d (Å)	CCL (Å)	
P2T-TCl:Y6-BO	1.74	3.61	21.9	0.24; 0.38	25.6;16.6	80.8; 22.1	
P3T-TCl:Y6-BO	1.76	3.57	23.5	0.29; 0.39	20.9;16.0	52.4; 35.3	
P4T-TCl:Y6-BO	1.78	3.53	23.7	0.21; 0.31; 0.39	29.6; 20.3; 15.9	122.9; 75.4; 58.3	

 Table S5. GIWAXS parameters of the blend films.

Table S6. The contact angles, surface tension of individual materials, and $(\sqrt{\gamma_{donor}} - \sqrt{\gamma_{acceptor}})^2$ values.

Organic layer	Contact angle [water] (deg)	Contact angle [EG] (deg)	γ ^d (mN/m)	γ ^p (mN/m)	γ ^{a)} (mN/m)	$(\sqrt{\gamma_{donor}}_2 - \sqrt{\gamma_a})$
Y6-BO	96.9	69.5	16.99	7.40	24.39	
P2T-TCl	104.8	80.7	14.15	5.51	19.65	0.256
P3T-TCl	102.4	74.8	17.52	5.03	22.55	0.036
P4T-TCl	101.5	73.5	17.85	5.25	23.10	0.018

a) surface tension (γ) was calculated according to the equation: $\gamma = \gamma^d + \gamma^p$, in which γ^d and γ^p denote dispersion and polar component, respectively. Here, γ^d and γ^p was calculated according to the Wu method.

D/A	V _{OC} [V]	$J_{ m SC}$ [mA cm ⁻²]	FF [%]	PCE [%]
1:1.2	0.88	9.62	40.8	3.45
1:1.4	0.87	9.40	40.0	3.27
1:1.6	0.88	9.72	38.8	3.32
1:1.8	0.86	9.02	37.9	2.94

Table S7. The photovoltaic performance of the devices based on P2T-TCI:Y6-BO with different donor/acceptor (D/A) ratio (The solvent is CF).

Table S8. The photovoltaic performance of the devices based on P2T-TCI:Y6-BO at different concentration (The solvent is CF, D/A = 1:1.2).

Concentration	V _{OC}	$J_{ m SC}$	FF	PCE
[mg/ml]	[V]	$[mA cm^{-2}]$	[%]	[%]
10	0.88	9.62	40.8	3.45
12	0.88	12.90	37.0	4.30
14	0.87	12.12	37.9	3.99
16	0.89	12.45	35.8	3.96
18	0.85	12.83	34.9	3.81

ТА	V _{OC} [V]	$J_{ m SC}$ [mA cm ⁻²]	FF [%]	PCE [%]
w/o	0.88	12.90	37.0	4.30
80°C	0.87	11.01	46.1	4.41
100°C	0.86	13.33	45.8	5.25
120°C	0.86	13.20	44.6	5.06
140°C	0.84	14.44	41.3	5.01
160°C	0.86	10.73	41.5	3.83

Table S9. The photovoltaic performance of the devices based on P2T-TCI:Y6-BO at different annealing temperature (The solvent is CF, D/A = 1:1.2).

Table S10. The photovoltaic performance of the devices based on P3T-TCI: Y6-BO at different concentration (The solvent is CF, D/A = 1:1.6).

Concentration	V _{OC}	$J_{ m SC}$	FF	PCE
[mg/ml]	[V]	[mA cm ⁻²]	[%]	[%]
10	0.77	9.67	37.7	2.80
12	0.79	11.98	36.7	3.48
14	0.79	10.79	36.3	3.09
16	0.79	11.84	35.2	3.29
18	0.80	9.62	35.2	2.71

TA	V _{OC} [V]	$J_{ m SC}$ [mA cm ⁻²]	FF [%]	PCE [%]
w/o	0.81	15.17	40.8	5.01
80°C	0.78	16.52	41.9	5.40
100°C	0.77	16.40	41.7	5.27
120°C	0.77	16.31	41.9	5.26
140°C	0.75	15.28	42.5	4.87

Table S11. The photovoltaic performance of the devices based on P3T-TCI:Y6-BO at different annealing temperature (The solvent is CF, D/A = 1:1.6).

Table S12. The photovoltaic performance of the devices based on P4T-TCl:Y6-BO with different donor/acceptor (D/A) ratio (The solvent is CF).

D/A	V _{OC} [V]	$J_{ m SC}$ [mA cm ⁻²]	FF [%]	PCE [%]
1:1.2	0.72	15.14	44.8	4.88
1:1.4	0.78	19.18	43.7	6.53
1:1.6	0.72	14.58	46.8	4.84

Concentration [mg/ml]	V _{OC} [V]	$J_{ m SC}$ [mA cm ⁻²]	FF [%]	PCE [%]
8	0.78	19.18	43.7	6.53
10	0.74	18.73	42.5	5.89
12	0.74	19.08	42.0	5.94
14	0.71	15.23	46.8	5.06
16	0.71	14.58	46.8	4.84

Table S13. The photovoltaic performance of the devices based on P4T-TCI:Y6-BO at different concentration (The solvent is CF, D/A = 1:1.4).

Table S14. The photovoltaic performance of the devices based on P4T-TCl:Y6-BO at different annealing temperature (The solvent is CF, D/A = 1:1.4).

ТА	V _{OC} [V]	J _{SC} [mA cm ⁻²]	FF [%]	PCE [%]
r.t.	0.78	19.18	43.7	6.53
80°C	0.75	19.93	50.0	7.47
110°C	0.73	20.13	55.6	8.17
140°C	0.73	20.30	59.3	8.79
160°C	0.73	19.61	63.9	9.15
180°C	0.73	19.75	57.7	8.32

optimized conditions.							
polymer	V _{OC} [V]	J _{SC} [mA cm ⁻²]	FF [%]	PCE [%]			
P2T-TC1	0.86	14.64	43.9	5.53			
P3T-TC1	0.82	18.66	47.7	7.30			
P4T-TC1	0.69	20.23	64.9	9.02			

Table S15. The photovoltaic performance of the devices based on polymer:Y6 under optimized conditions.

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