A monothiophene unit incorporating both fluoro and ester substitution enabling high-performance donor polymers for non-fullerene solar cells with 16.4% efficiency

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Keywords: Thiophene derivative, Donor polymer, Fluorination, Esterification, Non-fullerene solar cells

1. Materials and Instruments

All reagents and chemicals were commercially available and used without further purification unless otherwise stated. Anhydrous toluene was obtained through distillation on Na/benzophenone under argon. Monomers of BDT and BDD were purchased from Solarmer Co., Ltd. (Beijing, China). Unless otherwise stated, all reactions were carried out under inert atmosphere using standard Schlenk-line techniques. The monomers E-T were synthesized following the reported procedures.^[1] NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer using CDCl₃ and Cl₂CDCDCl₂ as the solvent. Elemental analyses of compounds were performed at Changchun Institute of Applied Chemistry Chinese Academy of Science (Changchun, China). High-resolution mass spectrometry was carried out on Thermo ScientificTM Q-Exactive. The molecular weight of the polymers was determined by hightemperature gel permeation chromatography (GPC, Agilent PL-GPC220) at 150 °C with 1,2,4trichlorobenzene as the eluent and polystyrenes as the standards. UV-vis absorption spectra of the polymer solution and films were recorded on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Temperature-dependent UV-vis absorption spectra of polymer solutions at various temperatures were collected on a Perkin Elmer Lambda 950 UV/VIS/NIR spectrometer. Cyclic voltammetry of films was performed on a CHI760 Voltammetry Workstation at a scanning rate of 50 mV s⁻¹ under argon atmosphere using N₂-saturated solution of 0.1 M tetra(*n*butyl) ammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile (CH₃CN) as the supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and a silver wire reference electrode were employed, and the ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as the reference for all measurements. Thermogravimetric analysis was carried out with a METTLER TOLEDO (TGA 1 STAR^e System) apparatus at a heating ramp of 10 °C min⁻¹ under N₂. Differential scanning calorimetry was performed on Mettler, STAR^e with a heating rate of 10 °C min⁻¹ in nitrogen. Atomic force microscopy (AFM) of blend films was conducted using a Dimension Icon Scanning Probe Microscope (Asylum Research, MFP-3D-

Stand Alone) in the tapping mode. Transmission electron microscopy (TEM) specimens were prepared following conditions identical to those of the actual devices, but they were drop-cast onto a 40 nm PEDOT:PSS-covered substrate. After drying, the substrates were transferred to deionized water and the floated films were transferred onto TEM grids. TEM images were obtained on Tecnai Spirit (20 kV) TEM. GIWAXS measurement was carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2°. The samples for GIWAXS measurements are fabricated on silicon substrates using the same recipe for the devices.

2. Synthesis of monomers



(3,4-dibromothiophene-2,5-diyl)bis(trimethylsilane) 1. *n*-BuLi (2.4 M, 27.8 mL, 66.89 mmol, 2.2 eq) was added dropwise to diisopropylamine (11.4 mL, 55.9 mmol, 2.64 eq) in anhydrous Et₂O (30 mL) at 0 °C. After keeping at 0 °C for 0.5 h, the prepared LDA solution was transferred by syringe into a solution of 3,4-dibromothiophene (10 g, 30.4 mmoL) with anhydrous Et₂O. The reaction mixture was cooled to -78 °C, then trimethylchlorosilane (19.2 mL, 84.8 mmol, 4.0 equiv) was added. The reaction was warmed slowly to ambient temperature overnight. The reaction was then quenched by water and extracted with CHCl₃ three times. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether (PE) as the eluent to provide product 1 (11.4 g, 98%). ¹H NMR data is consistent with previous reports^[1] but the starting material 3,4-dibromothiophene is cheaper than tetrabromothiophene.



(3-bromo-4-fluorothiophene-2,5-diyl)bis(trimethylsilane) 2: To a solution of 1 (10 g, 26 mmoL) in 100 mL anhydrous diethyl ether was added excess *t*-BuLi (1.6 M, 48 mL, 3.0 eq) dropwise at -78 °C. After stirring at -78 °C for 0.5 h. N- Fluorobenzenesulfonimide (NFSI) (4.9 g, 17.2 mmol, 3eq) in THF (50 mL) was slowly added, and then overnight with warming to room temperature. The reaction was then quenched by water (100 mL) and extracted with CHCl₃ three times. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether (PE) as the eluent to provide product **2** (9.4 g, 95%). ¹H NMR

(400 MHz, CDCl₃) δ 0.39 (s, 9H), 0.33 (s, 9H). This is consistent with the NMR data reported in the literature. It is worth noting that excess *t*-BuLi increases the yield from 50% to 95%.^[2]



4-Fluoro-2,5-bis(trimethylsilyl)thiophene-3-carboxylic acid 3. To a solution of **2** (5.0 g, 15.75 mmoL) in 100 mL anhydrous diethyl ether was added excess *t*-BuLi (1.6 M, 29.5 mL, 3.0 eq) dropwise at -78 °C. After stirring at -78 °C for 1 h, the reaction mixture was warmed to room temperature. Excess dry ice was added into the reaction mixture for 12 h and the solvent was then evaporated under reduced pressure. To the residue was added 100 mL H₂O, acidified with 2 M HCl (aq), and filtered to afford a white solid, which was dried overnight in vacuum at 70 °C to afford the product compound **3** (4.3 g, yield: 95%). The product was pure enough without any further purification for the next step reaction. ¹H NMR (400 MHz, CDCl₃) δ 13.21 (s, 1H), 0.31 (d, *J* = 2.8 Hz, 18H). ¹H NMR data is consistent with our previous reports.^[3]



Methyl 4-fluoro-2,5-bis(trimethylsilyl)thiophene-3-carboxylate 4. To a solution of 3 (4.0 g, 13.8 mmol) in 50 mL CH₃OH was added H₂SO₄ (2mL) dropwise at room temperature. And the reaction mixture was stirred at 90°C for 24 h. The reaction was then quenched by water and extracted with CHCl₃ three times. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using CHCl₃:PE (1:4) as the eluent to provide product 4 (3.98 g, 95%). ¹H NMR (400 MHz, CDCl₃) δ 3.90 (s, 3H), 0.36 (d, *J* = 6.3 Hz, 6H). ¹H NMR data is

consistent with our previous reports.^[3] It is worth noting that this new route is conducive to reducing costs and industrialization.



Propyl 4-fluorothiophene-3-carboxylate 5. 4 (3.5 g, 11.5 mmol) was dissolved in 200 mL THF, TBAF (13.8 mL, 13.8 mmol, 1.2 eq) was added dropwise. The mixture was stirred at room temperature for 1 h. Then the reaction mixture was quenched with 40 mL H₂O and extracted with CHCl₃ (3×50 mL). The combined organic layer was washed with saturated NaHCO₃ (aq, 20 mL) and H₂O (40 mL), then dried over anhydrous Na₂SO₄. After the solvent was removed under vacuum, the residue was purified by column chromatography on silica gel with PE:CHCl₃ = 3:1 as the eluent to yield compound **5** (1.80 g, 98%) as a colorless liquid. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.98 (t, *J* = 5.0 Hz, 1H), 6.78 (s, 1H), 1.01 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 160.92 (d, *J* = 5.0 Hz, C=O), 157.63 (d, *J* = 279.6 Hz, C-F), 132.40, 122.41, 105.36, 66.43. ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -126.41. HRMS (ESI) m/z calcd for [C₆H₅FO₂S] 159.9994, found 161.0005 (M+H).



Monomer FE-T. To a solution of compound **5** (1.5 g, 9.37 mmol) in CHCl₃ was added Br_2 (2.0 mL, 37.5 mmol, 4.0 eq) and a catalytic amount of FeCl₃. The reaction mixture was then heated to 60 °C and stirred at this temperature for 3 h. After cooled to room temperature, the reaction mixture was poured into H₂O and extracted with CHCl₃ three times. The combined organic layer was dried over anhydrous Na_2SO_4 and then filtrated. The organic solution was concentrated under reduced pressure and the residue was purified by column chromatography

on silica gel using CHCl₃ as the eluent to give the monomer FE-T (2.9g, 97%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 3.94 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 159.98, (d, *J* = 5.0 Hz, C=O) 152.99 (d, *J* = 273.4 Hz, C-F), 121.92, 117.83, 92.09, 52.39. ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -117.08. HRMS (ESI) m/z calcd for [C₆H₃Br₂FO₂S] 315.8205, found 316.8278 (M+H).

3. Synthesis of polymers



0.1 mmol monomer of BDT and 0.05 mmol bromide monomer of BDD and FE-T at distinct content (0.1 BDD/0 FE-T, 0.08 BDD/0.02 FE-T or 0.02 E-T, 0.05 BDD/0.05 FE-T, 0.02 BDD/0.08 FE-T, 0 BDD/ 0.1 FE-T) or E-T (0.08BDD/0.02E-T) were dissolve in toluene (10 mL). Pd(PPh₃)₄ (7 mg) was added into the mixtures after being flushed with argon for five minutes. Then, the reaction mixtures were purged with argon for another 10 min. The reactions were stirred at 120 °C for 5 h. The polymers were precipitated in Hex (120 mL) and filtrated. The dried precipitates were purified by flash silica gel column chromatography by using CHCl₃ as eluent. The polymer was then precipitated in methanol (60 mL) and dried under vacuum for 12 h before use. The yields are around 50%.

Elemental analysis calcd (%) for S1 (C62.5H69F2.2O2S8.9): C = 66.02%, H = 6.09%. Found: C= 66.32%, H= 6.00%.

Elemental analysis calcd (%) for S2 (C54H58.5F2.5O2S6.5): C = 64.63%, H = 5.82%. Found: C= 64.20%, H= 5.80%.

Elemental analysis calcd (%) for S3 (C45.6H48F2.8O2S5.6): C = 63.24%, H = 5.54%. Found: C= 63.04%, H= 5.52%.

Elemental analysis calcd (%) for S4 (C41H43F3O2S5): C = 62.31%, H = 5.36%. Found: C= 62.23%, H= 5.30%.

Elemental analysis calcd (%) for ES1 (C62.4H69.2F2O2S7.4): C = 66.32%, H = 6.48%.

Found: C= 66.20%, H= 6.40%.

Polymers	[KDa]	PDI	$[eV]^{a)}$	HOMO [eV]	LUMO [eV]
PM6	32.3	1.9	1.82	-5.45	-3.63
S 1	34.8	2.1	1.80	-5.52	-3.72
S2	32.2	2.2	1.83	-5.56	-3.73
S3	43.9	2.0	1.86	-5.60	-3.74
S4	33.6	2.2	1.91	-5.65	-3.74
ES1	32.4	2.4	1.88	-5.50	-3.62

Table S1. Basic properties of the polymers.

^{a)}Calculated from the formula: $E_{g}^{opt} = 1240/\lambda_{onset}$.

4. TGA measurements



Figure S1. (a) TGA analysis (heating ramp: 10 °C min⁻¹) of polymers in nitrogen.



5. Theory calculations



Figure S2. (a) Molecular energy levels and wave function distributions of the frontier orbits for the polymer models; (b) Chemical geometry of the molecular models for PM6 and S4.



6. Cyclic voltammograms

Figure S3. Cyclic voltammograms of polymers.



Figure S4. a) Valance band spectra of the PM6 and S1; b) UPS spectra of PM6 and S1, measured under -10 V bias. The work function are calculated with equation $E_F=21.2$ eV-($E_0-E_{F(Au)}$), where the $E_{F(Au)}$ is the Fermi level of reference Au under -10 V bias.



7. UV-Vis absorption spectra

Figure S5. (a-f) UV-vis spectra of polymers in chlorobenzene $(1 \times 10^{-6} \text{ mol } \text{L}^{-1})$ at various temperatures as indicated; (g) Normalized absorption spectra of polymers in chloroform $(1 \times 10^{-6} \text{ mol } \text{L}^{-1})$; (h) Normalized absorption spectra of all blend films.



Figure S6. UV-Vis absorption coefficients of (a) PM6 and S1 neat films and (b) PM6:Y6 and S1:Y6 blend films.



8. 2D GIWAXS patterns and packing parameter

Figure S7. 2D GIWAXS patterns of neat polymer films.

Polymer	d-spacing(100)	d-spacing(010)	FWHM (Å ⁻¹)	CCL(nm) (010)
PM6	19.62	3.54	0.26	21.73
S1	21.65	3.50	0.25	22.60
S4	20.93	3.54	0.31	18.32
ES1	22.42	3.54	0.27	20.93

Table S2. Summary of the crystal coherence length of neat polymer films

Table S3. Summary of the crystal coherence length of blend films

Polymer	Peak Location (Å ⁻¹)	FWHM (Å ⁻¹)	CCL(nm) (010)
PM6:Y6	1.77	0.24	23.55
S1:Y6	1.77	0.22	25.69
S4:Y6	1.78	0.29	19.48
ES1:Y6	1.76	0.25	22.61

9. SCLC Mobility measurement

The electron and hole mobilities were measured by using the method of space-charge limited current (SCLC) for electron-only devices with the structure of ITO/ZnO/active layer/Zracac/Al and hole-only devices with the structure of ITO/MoO_x/active layers/MoO_x/Al. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation: $J = 9\varepsilon_0\varepsilon_v\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, ε_r is the relative dielectric constant of the transport medium, and ε_0 is the permittivity of free space. $V = V_{app} - V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage. The carrier mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.



Figure S8. $J^{1/2}$ -V curves for the hole-only devices based on polymer neat films in dark.



Figure S9. $J^{1/2}$ -*V* curves for the electron-only (a) and hole-only (b) devices based on the blend films (in dark).

Table S4.	Hole	mobil	ities c	of pol	lymer	neat	films	1n 1	the o	dark

Device	$\mu_{\rm e} ({\rm cm}^2 {\rm V}^{-1}{\rm s}^{-1})$
PM6	8.29×10 ⁻⁴
S1	9.94×10 ⁻⁴
S4	7.04×10 ⁻⁴
ES1	9.12×10-4

Device ^{<i>a</i>}	$\mu_{\rm h} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$	$\mu_{\rm e}({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$	$\mu_{\rm h}\mu_{\rm e}$
PM6:Y6	5.80×10 ⁻⁴	3.47×10 ⁻⁴	1.67
S1:Y6	7.01×10 ⁻⁴	4.33×10 ⁻⁴	1.58
S4:Y6	4.38×10 ⁻⁴	1.82×10 ⁻⁴	2.40
ES1:Y6	6.37×10 ⁻⁴	3.16×10 ⁻⁴	2.01

Table S5. Hole and electron mobilities of S1, S2, S4 and ES1-based devices in the dark

Table S6. The parameters of exciton dissociation efficiency and charge collection efficiency.

Davias	$J_{ m ph}$	$J_{ m ph}{}^{ m a}$	$J_{ m ph}{}^{ m b}$	$\eta_{ m diss}$	$\eta_{ m coll}$
Device	(mA/cm ²)	(mA/cm^2)	(mA/cm ²)	(%)	(%)
PM6:Y6	26.279	25.011	21.984	95.2	83.7
S1:Y6	26.529	25.402	22.807	95.8	86.0
S4:Y6	18.362	12.777	7.985	69.6	43.5
ES1:Y6	27.537	24.866	21.567	90.3	78.3

^{a)}Under short circuit condition; ^{b)}Under the maximal power output condition

10. Solar cell fabrication and characterization

Solar cells were fabricated in a conventional device configuration of ITO/PEDOT:PSS/active layers/Zracac/Al. The ITO substrates were first scrubbed by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried overnight in an oven. The glass substrates were treated by UV-Ozone for 30 min before use. PEDOT:PSS (Heraeus Clevios P VP AI 4083) was spin-cast onto the ITO substrates at 3000 rpm for 30 s, and then dried at 150 °C for 15 min in air. The polymer:Y6 blends (1:1.2 weight ratio) were dissolved in chloroform (the concentration of polymers were 8.5 mg mL⁻¹), with the addition of 0.5% 1-CN

as an additive, and stirred on a hotplate in a nitrogen-filled glove box. The blends solution were spin-cast on the top of the PEDOT:PSS layer. The thermal annealing step at 90 °C for 5 min was performed to optimize the blend morphology. The interlayer of Zracac (1-2 mg/mL, in ethanol) was generally deposited on the active layer via spin-coating at 2000-4000 rpm for 30s. In our case, Zracac was prepared in ethanol at a concentration of 1.4 mg/mL, and was spincoated at a rate of 3000rpm for 30s. which was followed by the deposition of Al (100 nm) (evaporated under 5×10^{-5} Pa through a shadow mask). The optimal active layer thickness measured by a Bruker Dektak XT stylus profilometer was about 105 nm. The current densityvoltage (*J-V*) curves of all encapsulated devices were measured using a Keithley 2400 Source Meter in the air under AM 1.5G (100 mW cm⁻²) using a Newport solar simulator. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement to bring spectral mismatch to unity). Optical microscope (Olympus BX51) was used to define the device area (5.9 mm²). EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.



Figure S10. (a) The *J-V* characteristics of NF-PSCs with various FE-T contents in the blend films; (b) The EQE spectra of the NF-PSCs.

Polymer	$V_{\rm OC}$	$J_{ m SC}{}^{ m b)}$	FF	PCE ^{a)}
donor	[V]	$[mA cm^{-2}]$	[%]	[%] [ave.]
S1	0.877	25.402 (24.899)	0.737	16.421
				(15.753±0.337)
S2	0.896	22.954 (22.891)	0.636	13.077
				(12.778±0.202)
S3	0.911	19.915 (19.689)	0.502	9.111
				(8.706±0.302)
S4	0.929	12.777 (12.475)	0.485	5.764
				(5.554±0.246)

Table S7. The photovoltaic parameters of NF-PCSs with different compositions.

^{a)}Average PCEs are based on 20 cells; ^{b)}Values in brackets are calculated from EQE.



Figure S11. The *J-V* characteristics of NF-PSCs with different electron transporting layers.

Fable S8. The photovoltaic parameters of NF-PCSs with different interlayers.

Interlayer	V _{OC} [V]	$J_{\rm SC}$ [mA cm ⁻²]	FF [%]	PCE [%]
Zracac	0.877	25.402	0.737	16.421
PDINO	0.874	25.753	0.726	16.351
PNDI-F3N	0.880	25.925	0.712	16.257



Figure S12. The *J-V* characteristics of NF-PSCs with differnet thickness.

Table S9. The photovoltaic parameters of NF-PCSs using active layer (S1:Y6) with different thickness.

Thickness(nm)	V _{OC} [V]	$J_{\rm SC}$ [mA cm ⁻²]	FF [%]	PCE [%]
83	0.877	23.483	0.733	15.097
105	0.877	25.402	0.737	16.421
156	0.871	25.885	0.695	15.641
204	0.874	25.552	0.610	13.621



Figure S13. (a) FTPS-EQE curves of the blend films and neat film; (b) Electroluminescence (EL) spectra.









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