Supporting Information

Terthiophene based Low-Cost Fully Non-Fused Electron Acceptors for High-Efficiency As-Cast Organic Solar Cells

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1. Materials and General Procedures

All commercial chemicals were used without further purification. Column chromatography was carried out on silica gel (200-300 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF-254 with detection by UV. The ¹H and ¹³C NMR spectra were recorded on 400 MHz and 600 MHz spectrometer (Bruker) using CDCl₃ as solvent. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 1050+. Cyclic voltammogram (CV) measurements were carried out on Ivium-Vertex.C.EIS Electrochemical Analyzer. HRMS spectra (MALDI-TOF) were recorded on on a Bruker Autoflex III instrument. Atomic force microscopy (AFM) images of films were obtained on a Bruker Dimension Icon instrument. GIWAXS measurements were conducted on a Xenocs-SAXS/WAXS system with X-ray wavelength of 1.5418 Å. The film samples were irradiated at a fixed angle of 0.2° and all film samples were prepared from with o-xylene. The femtosecond transient absorption (fs-TA) spectrum was measured in the combined utilization of the Femtosecond Laser System (Coherent) and the Helios Pump-Probe System (Ultrafast Systems LLC).

2. Synthesis of Acceptors

Synthesis of 3a

To a Schlenk flask were added compound **1a** (1.07 g, 2.21 mmol, 2.3 eq), **2a** (450 mg, 0.96 mmol, 1 eq), Pd(PPh₃)₄(55 mg) and toluene (20 mL). The mixture was stirred

and refluxed under nitrogen for 12 h. After cooling to room temperature, the solvents were evaporated under vacuum. Then, the crude product was purified by silica gel column using hexane as an eluent to afford mixed compounds **3a** (593 mg) as a faint yellow oil, which was used directly without further purification.

Synthesis of **3b**

To a Schlenk flask were added compound **1b** (960 mg, 1.98 mmol, 2.3 eq), **2b** (400 mg, 0.86 mmol, 1 eq), Pd(PPh₃)₄ (50 mg) and toluene (20 mL). The mixture was stirred and refluxed under nitrogen for 12 h. After cooling to room temperature, the solvents were evaporated under vacuum. Then, the crude product was purified by silica gel column using hexane as an eluent to afford mixed compounds **3b** (542 mg) as a faint yellow oil, which was used directly without further purification.

Synthesis of 4a

A new-made Vislmeier reagent, which was prepared by POCl₃ (1.2 mL) stirred in DMF (5 mL) at 0 °C for 30 min, was dropped to a solution of compound **3a** (593 mg, 0.83 mmol) in 1,2-dichloroethane (30 mL) at 0 °C under nitrogen atmosphere. After refluxing at 85 °C overnight, the mixture was poured into ice water (50 mL), neutralized with saturated NaHCO₃ solution and stirred for 2 hours. Then the mixture was extracted twice with dichloromethane. The combined organic phases were washed with saturated pressure. The crude product was purified by column chromatography eluting with petroleum hexane/dichloromethane (v/v = 2:1) to afford **4a** as yellow solid (502 mg). ¹H NMR (400 MHz, CDCl₃) δ : 10.02 (s, 2H), 7.07 (s, 2H), 3.02-2.88 (m, 4H), 2.84-2.67 (m, 4H),

1.77-1.64 (m, 4H), 1.63-1.50 (m, 4H), 1.49-1.17 (m, 40H), 0.98-0.82 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ : 182.01, 153.46, 144.87, 143.19, 137.20, 131.17, 129.33, 32.21, 32.18, 31.73, 30.80, 30.23, 29.69, 29.67, 29.62, 29.59, 29.53, 28.86, 28.68, 23.02, 22.99, 14.43, 14.11. HRMS (MALDI-TOF) m/z Calcd for C₄₆H₇₃O₂S₃⁺ [M+H]⁺ 753.4767, Found 753.4751.

Synthesis of **4b**

A new-made Vislmeier reagent, which was prepared by POCl₃ (1 mL) stirred in DMF (5 mL) at 0 °C for 30 min, was dropped to a solution of compound **3b** (542 mg, 0.76 mmol) in 1,2-dichloroethane (30 mL) at 0 °C under nitrogen atmosphere. After refluxing at 85 °C overnight, the mixture was poured into ice water (50 mL), neutralized with saturated NaHCO₃ solution and stirred for 2 hours. Then the mixture was extracted twice with dichloromethane. The combined organic phases were washed with saturated brine, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography eluting with petroleum hexane/dichloromethane (v/v = 2:1) to afford **4b** as yellow oil (428 mg).¹H NMR (600 MHz, CDCl₃) δ: 10.01 (s, 2H), 7.04 (s, 2H), 2.88-2.85 (m, 4H), 2.79-2.74 (m, 4H), 1.69-1.62 (m, 2H), 1.58-1.48 (m, 10H), 1.40-1.13 (m, 24H), 0.93-0.77 (m, 24H). ¹³C NMR (125 MHz, CDCl₃) δ: 182.03, 152.26, 144.98, 142.58, 137.96, 131.38, 130.39, 41.87, 40.31, 33.04, 32.92, 32.80, 32.71, 29.07, 29.02, 26.01, 23.29, 23.24, 14.34, 14.30, 11.23, 11.18, 11.07. HRMS (MALDI-TOF) m/z Calcd for C₄₆H₇₃O₂S₃⁺ [M+H]⁺ 753.4767, Found 753.4756.

Synthesis of **3T-1**

To a Schlenk flask were added compound **4a** (127 mg, 0.17 mmol, 1.0 eq), 2F-IC (157 mg, 0.68 mmol, 4 eq), pyridine (0.2 mL) and chloroform (20 mL). The mixture was stirred under nitrogen overnight. Then the solution was poured into 150 mL methanol. The precipitate was collected and further purified by silica gel column using hexane/dichloromethane (v/v = 1:1) as eluent yielding dark solids (173 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ : 9.02 (s, 2H), 8.57 (m, 2H), 7.68 (m, 2H), 7.32 (s, 2H), 3.07-2.90 (m, 8H), 1.80-1.58 (m, 12H), 1.57-1.26 (m, 36H), 0.97-0.84 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ : 186.04, 161.85, 159.26, 156.03 (m), 153.43 (m), 150.71, 145.78, 136.78 (m), 134.82 (m), 134.60, 133.53, 132.62, 129.26, 129.21, 120.94, 115.27 (m), 115.00, 114.75, 112.86 (m), 69.66, 32.29, 32.21, 32.08, 30.65, 30.44, 30.33, 29.76, 29.74, 29.56, 29.44, 23.10, 23.02, 14.48. HRMS (MALDI-TOF) m/z Calcd for C₇₀H₇₇F₄N₄O₂S₃⁺ [M+H]⁺ 1177.5139, Found 1177.5144.

Synthesis of **3T-2**

To a Schlenk flask were added compound **4b** (132 mg, 0.18 mmol, 1.0 eq), 2F-IC (166 mg, 0.72 mmol, 4 eq), pyridine (0.2 mL) and chloroform (20 mL). The mixture was stirred under nitrogen overnight. Then the solution was poured into 150 mL methanol. The precipitate was collected and further purified by silica gel column using dichloromethane as eluent yielding dark solids (187 mg, 91%). ¹H NMR (600 MHz, CDCl₃) δ : 9.01 (s, 2H), 8.57 (m, 2H), 7.70 (m, 2H), 7.32 (s, 2H), 2.98-2.9 (m, 8H), 1.77-1.69 (m, 2H), 1.68-1.61 (m, 2H), 1.58-1.46 (m, 4H), 1.42-1.24 (m, 28H), 0.94-0.83 (m, 24H). ¹³C NMR (150 MHz, CDCl₃) δ : 186.09, 161.30, 159.61, 156.10 (m), 153.50 (m), 150.98, 145.27, 136.83 (m), 135.20, 135.00 (m), 133.52, 133.25, 130.35,

121.21, 115.29 (m), 115.08, 114.74, 112.97 (m), 69.87, 42.35, 40.74, 34.86, 33.76, 32.83, 32.60, 29.15, 29.13, 29.08, 26.00, 25.86, 23.47, 23.37, 14.46, 11.37, 11.09. HRMS (MALDI-TOF) m/z Calcd for C₇₀H₇₇F₄N₄O₂S₃⁺ [M+H]⁺ 1177.5139, Found 1177.5131.



3. Optical and Electrochemical Properties

Figure S1. The UV-vis absorption spectra of 3T-1 and 3T-2.



Figure S2. The CV curves of two acceptors 3T-1 and 3T-2.

4. Quantum Calculations



Figure S3. Top and front view for the optimal conformations of **3T-1** and **3T-2** studied by DFT at B3LYP/6-31G (d, p) basis set.

5. OSCs Fabrication

Organic solar cells (OSCs) were fabricated with a general configuration of ITO/PEDOT:PSS/active layer/PDINN/Ag. The conductivity of ITO was 15 Ω /sq. The ITO-coated glass substrates were thoroughly cleaned by deionized water, acetone, and isopropanol twice successively. The substrates were dried at 150 °C for 10 minutes, thin layers of PEDOT:PSS were spin-coated on them and then annealed at 100 °C for 10 min in the air. The blend of polymer **D18** and small molecules was dissolved in *o*-xylene with the polymer concentration of 4 mg mL⁻¹ and heated at 110°C at least 2 h to ensure a sufficient dissolution, and then spin-coated onto PEDOT:PSS modified glass substrates. PDINN was spin coated on the active layer with the concentration of 1 mg mL⁻¹ in a glove box. Followed 100 nm thick Ag layer were deposited sequentially to

complete the cell devices. Six cells were fabricated on one substrate with an effective area of 0.04 cm². Current-voltage characteristics were recorded using an Enli Technology Ltd., Taiwan (SS-F53A) AAA class solar simulator under AM 1.5G with an intensity of 100 mW cm⁻² as the white light source and the intensity was calibrated with a standard single crystal Si photovoltaic cell. The temperature while measuring the *J-V* curves was approximately 25 °C. The EQE measurements of OSCs were performed by the solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan), which was calibrated by monocrystalline silicon solar cell in advance.

 Table S1. The OSC devices optimization based on ITO/PEDOT:PSS/active

 layer/PDINN/Ag by different weight ratios of D18 to acceptors.

Activo lovor		$I_{(mA/am^2)}$	FF	PCE
Active layer		$J_{\rm sc}$ (IIIA/CIII ⁻)	(%)	(%)
D18:3T-1=1:0.8	0.86	5.46	40.10	1.87
D18:3T-1=1:1	0.84	7.11	40.80	2.43
D18:3T-1=1:1.2	0.83	6.85	38.54	2.18
D18:3T-2=1:0.8	0.87	17.90	65.82	10.27
D18:3T-2=1:1	0.87	17.85	71.21	11.12
D18:3T-2=1:1.2	0.87	17.78	67.40	10.46

Table S2. The OSC devices optimization based on ITO/PEDOT:PSS/active

layer/PDINN/Ag by different additives	5.
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Active layer	additive	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
D18:3T-2=1:1	0.2%1-CN	0.88	17.34	67.20	10.20
D18:3T-2=1:1	0.5%1-CN	0.88	16.29	65.56	9.40
D18:3T-2=1:1	0.2%DIO	0.87	17.26	65.41	9.86

Active layer	T (°C)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	РСЕ (%)
D18:3T-2=1:1	60°C	0.88	17.49	68.60	10.51
D18:3T-2=1:1	80°C	0.87	17.45	67.43	10.27
D18:3T-2=1:1	100°C	0.87	17.12	65.38	9.78
D18:3T-2=1:1	120°C	0.87	17.01	63.28	9.39

 Table S3.
 The OSC devices optimization based on ITO/PEDOT:PSS/active

 layer/PDINN/Ag with different annealing temperatures.

6. Space-Charge Limited Current Measurement

Hole/electron devices with a structure of ITO/PEDOT:PSS/active layer/Au and ITO/ZnO/active layer/PDINN/Ag were fabricated. Dark *J*–*V* curves of the hole/electron devices were measured by the space-charge limited current (SCLC) method. Hole and electron mobilities of devices were calculated according to the Mott-Gurney equation: $J = 9\varepsilon_o\varepsilon_r\mu V^2 / 8d^3$, where *J* is the space charge limited current, ε_o is the vacuum permittivity (ε_o =8.85×10⁻¹² F/m), ε_r is the permittivity of the active layer (ε_r = 3 F/m), μ is mobility, and *d* is the thickness of the active layer.



Figure S4. The curves of (a) hole and (b) electron mobility.



7. Femtosecond Transient Absorption Spectrum

Figure S5. (a) and (c) Contour plots of time-resolved absorption difference spectra of the 3T-1 and 3T-2 pure film; (b) and (d) TA spectra of the 3T-1 and 3T-2 pure film;
(e) the kinetic traces probing at 592 nm for the D18:3T-1 and D18:3T-2 blend film.
Table S4. The result of fitting recovery signals with double exponential of for the

D18:3T-1 and D18:3T-2 blend film at 592 nm.

Active layer	A_1	τ ₁ (ps)	A_2	τ ₂ (ps)
D18:3T-1	70.7%	13.53	29.3%	563.5
D18:3T-2	42.5%	2348	57.5%	2926