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Supporting Information

for

Terrylene Diimide-Based Middle-Low Bandgap Electron Acceptors for Organic Photovoltaics

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1.	DFT results	S2
2.	Optical and electrochemical properties of T ₂ -TDI ₂ and <i>o</i> -F ₂ T ₂ -TDI ₂	S2
3.	OPV device fabrication and characterization	S3
4.	XRD results	S4
5.	SCLC measurement	S5
6.	Experiment details	S5
7.	NMR spectra of compounds	S7
8.	HRMS spectra	S10
9.	References	S11



Fig. S1. (a) The modify dihedral angles of T_2 -TDI₂ and o-F₂T₂-TDI₂. (A₁: atom 55, 54, 6, 10; A₂: atom 8, 9, 4, 5; A₃: atom 5, 1, 18, 17); (b) Pictorial representation of oneelectron wavefunctions of T_2 -TDI₂ and o-F₂T₂-TDI₂ molecules, using B3LYP functional and 6-31G(d) basis set. All values in eV.

	Dihedral angel				
	A ₁ (°)	A ₂ (°)	A ₃ (°)		
o-F ₂ T ₂ -TDI ₂	8.1	2.8	3.8		
T ₂ -TDI	13.5	4.4	11.3		

Table S1. Summary of dihedral angel for T₂-TDI₂ and *o*-F₂T₂-TDI₂ molecules.

2. Optical and electrochemical properties of T₂-TDI₂ and *o*-F₂T₂-TDI₂

Table S2. Summary of optical and electrochemical properties of T_2 -TDI₂ and *o*-F₂T₂-TDI₂.

	sol. λ _{max}	<i>E</i> r	$E_{\rm g}^{\rm opt}$	E _{LUMO}	E _{HOMO}	$E_{\rm g}^{\rm CV}$
	[nm]	[M ⁻¹ cm ⁻¹]	[eV]	[eV]	[eV]	[eV]
T ₂ -TDI ₂	668.5	1.23	1.62	-3.82	-5.42	1.60
o-F ₂ T ₂ -TDI ₂	668.8	1.23	1.64	-3.84	-5.45	1.61



Fig. S2. The T_2 -TDI₂ and o- F_2T_2 -TDI₂ reductive cyclic voltammetry in *o*-dichlorobenzene solution.

3. OPV device fabrication and characterization

The inverted OSC devices: Cleaning the ITO-coated glass (15 Ω/\Box) with deionized water, acetone, and isopropanol for 20 min in an ultrasonic bath, respectively. After oxygen plasma cleaning for 20 min, spin-casting a 40 nm thick ZnO cathode buffer layer onto the ITO substrate, then it was dried by baking in an oven at 200 °C for an hour. Herein, the polymeric donor PBDB-TF was chosen as the donor material. Different PBDB-TF:acceptor ratio and different solvent additive voltage of 1-CN and DIO were carefully optimized. Of which, the polymer concentration was 10 mg/mL in CB and the solution was stirred 40 °C for at least 4 hours. Then, the solution was spin-coated onto the ZnO buffer layer for 80-nm-thick active layers via spin-coating and the active layer was dried at 130 °C for 20 min. The device fabrication process was completed by thermally evaporating 10-nm-thick MoO₃ as the anode buffer layer under vacuum at a pressure of 3 × 10⁻⁴ Pa. Ultimately, 100-nm-thick Al layer was evaporated on top of the active layer.

The conventional OSC devices: The conventional device was prepared using the ITO/PEDOT:PSS/blend/PFN-Br/A1 architecture. A 20-nm-thick PEDOT:PSS anode buffer layer was spin-coated onto the plasma-treated ITO substrate and then was dried by baking in an oven at 150 °C for 15 mins. After then, the active layer solution was spin-coated onto the PEDOT:PSS buffer layer for 80-nm-thick active layers followed with 10-nm-thick PFN-Br. Ultimately, 100-nm-thick A1 layer was evaporated on top of

the active layer.

The overlapping area between the cathode and anode was defined a pixel size of 4 mm². The J-V measurement was performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mW cm⁻². The EQE data were obtained using a solar cell spectral response measurement system (QE-R3011, Enli Technology Co. Ltd). The film thickness data were obtained employing a surface profilometer (Dektak XT, Bruker).

Table S3. Photovoltaic parameters of the solar cells processed at different conditions under AM 1.5G illumination of 100 mW cm⁻²

Device Architecture	Active Layer	Condition	V _{oc} (V)	J _{SC} (mA cm ⁻²)	FF	PCE (%)
		1.25:1	0.804	10.63	0.404	3.48
		1:1	0.808	10.65	0.446	3.83
Conventional device	PBDB-TF: <i>o</i> - F2T2-TDI2	1:1.5	0.805	10.89	0.450	3.94
utilt		1% DIO	0.816	10.82	0.477	4.21
		1% CN	0.867	9.71	0.502	4.22
	PBDB-TF: <i>o</i> -F ₂ T ₂ - TDI ₂	W/O	0.814	11.16	0.476	4.33
		1% DIO	0.821	11.23	0.506	4.69
		1% CN	0.872	10.55	0.487	4.48
Inverted device		1% DIO +1% CN	0.850	10.83	0.575	5.29
		W/O	0.878	9.10	0.511	4.08
PBDB-TF:T ₂ -TDI ₂		1% DIO +1% CN	0.904	9.82	0.532	4.72

4. XRD results



Fig. S3. Powder XRD pattern of micro/nano-sized single crystals of T_2 -TDI₂ and *o*- F_2T_2 -TDI₂.

5. SCLC Measurement



Fig. S4. (a) Plots of $\ln(JL^3/V^2)$ VS $\ln(V/L)^{0.5}$ obtained from the hole-only devices and (b) plots of lnJ vs lnV obtained from the electron-only devices for the optimized solar cells based on T₂-TDI₂ and *o*-F₂T₂-TDI₂.

Table S4. Hole and electron mobilities of T_2 -TDI₂ and o-F₂T₂-TDI₂ blend films.

Active Layer	$\mu_{\rm h}$ (10 ⁻⁵ cm ² v ⁻¹ s ⁻¹)	μ _e (10 ⁻⁶ cm ² v ⁻¹ s ⁻¹)	μ_h/μ_e
PBDB-TF:T ₂ -TDI ₂	1.59	4.58	3.47
PBDB-TF: <i>o</i> -F ₂ T ₂ -TDI ₂	1.25	9.48	1.32

6. Experimental details

All chemicals were purchased from commercial suppliers and used without further

purification unless otherwise specified. TDI and TDI-Br were synthesized according to the literature.^{1,2}

Compound *o*-F₂T₂-TDI₂

A mixture of Br-TDI-C6 (150 mg, 0.167 mmol), (3,3'-Difluoro-2,2'-bithiene-5,5'diyl)bis(trimethylstannane) (39.8 mg, 0.075 mmol), and Pd(PPh₃)₄ (35 mg, 0.03 mmol) was dissolved in degassed toluene (15 ml). After refluxing the mixture overnight, it was poured into water and extracted with chloroform. The organic layer was washed three times with water and dried over magnesium sulfate. The crude product was purified by column chromatography on silica gel (Dichloromethane: petroleum, 1:3). The purified product was recrystallized with a large amount of chloroform and a small quantity of methanol to afford the pure product (87 mg, 62%)

¹H NMR (500 MHz, 373.2 K, CDCl₂CDCl₂, ppm) δ = 8.61-8.60 (m, 2H), 8.45-7.93 (m, 20H), 6.79 (s, 2H), 5.16 (m, 2H), 4.96 (m, 2H), 2.24-2.23 (m, 4H), 2.06 (m, 4H), 1.89-1.82 (m, 8H), 1.33-1.20 (m, 64H), 0.80-0.78 (m, 24H); ¹³C NMR (125 MHz, 373.2K, CDCl₂CDCl₂, ppm) δ = 163.71, 135.92, 135.54, 134.48, 134.20, 131.50 130.82, 130.69, 130.21, 129.94, 129.49, 129.33, 129.11, 127.65, 125.20, 123.61, 123.39, 122.42, 122.02, 121.36, 121.22, 117.24, 55.10, 54.80, 32.64, 31.79, 31.75, 29.21, 29.19, 27.14, 27.09, 22.54, 22.51, 13.91, 13.89. HRMS (MALDI, 100%) m/z calculated for C₁₂₈H₁₃₂F₂N₄O₈S₂: 1954.94695, found 1954.94601.

Compound T₂-TDI₂

A mixture of Br-TDI-C6 (150 mg, 0.167 mmol), 5,5-Ditrimethylstannyl-2,2'bithiophene (37.2 mg, 0.075 mmol), and Pd(PPh₃)₄ (35 mg, 0.03 mmol) was dissolved in degassed toluene (15 ml). After refluxing the mixture overnight, it was poured into water and extracted with chloroform. The organic layer was washed three times with water and dried over magnesium sulfate. The crude product was purified by column chromatography on silica gel (Dichloromethane: petroleum, 1:3). The purified product was recrystallized with a large amount of chloroform and a small quantity of methanol to afford the pure product (92 mg, 64%)

¹H NMR (500 MHz, 373.2 K, CDCl₂CDCl₂, ppm) $\delta = 8.63-6.79$ (m, 26H), 5.28-5.22 (m, 2H), 4.93 (m, 2H), 2.34-2.32 (m, 4H), 2.06-1.89 (m, 12H), 1.41-1.31 (m, 64H), 0.88-0.85(m, 24H); ¹³C NMR (125 MHz, 373.2 K, CDCl₂CDCl₂, ppm) $\delta = 164.00$, 163.76, 163.52, 163.23, 145.82, 137.30, 136.38, 135.38, 134.08, 133.77, 131.17, 130.73, 130.56, 130.45, 130.23, 130.07, 129.95, 129.64, 129.29, 129.11, 128.78, 128.27, 127.87, 127.56, 127.24, 124.71, 123.02, 122.91, 122.22, 122.07, 121.85, 121.72, 120.82, 55.05, 54.74, 32.68, 31.82, 31.78, 29.25, 29.23, 27.24, 27.15, 22.57, 22.54, 13.94. HRMS (MALDI, 100%) m/z calculated for C₁₂₈H₁₃₄N₄O₈S₂: 1918.96503, found 1918.96486.

7. NMR Spectra of compounds



Fig. S5. ¹H NMR spectrum of o-F₂T₂-TDI₂ in CDCl₂CDCl₂ at 373.2 K.



Fig. S6. ¹³C NMR spectrum of o-F₂T₂-TDI₂ in CDCl₂CDCl₂ at 373.2 K.



Fig. S7. ¹H NMR spectrum of T₂-TDI₂ in CDCl₂CDCl₂ at 373.2 K.



Fig. S8. 13 C NMR spectrum of T₂-TDI₂ in CDCl₂CDCl₂ at 373.2 K

8. HRMS spectra



 Meas. m/z
 # Ion Formula
 Score
 m/z
 err [ppm]
 Mean err [ppm]
 mSigma
 rdb
 e⁻ Conf
 N-Rule

 1954.946951
 1
 C128H132F2N4O8S2
 100.00
 1954.946014
 -0.5
 -0.1
 36.1
 64.0
 odd
 ok

Fig. S9. HRMS spectra of o- F_2T_2 - TDI_2 .



Fig. S10. HRMS spectra of T₂-TDI₂.

9. References:

- 1. L. Chen, C. Li and K. Mullen, J. Mater. Chem. C, 2014, 2, 1938-1956.
- 2. J. J. Feng, N. N. Liang, W. Jiang, D. Meng, R. Xin, B. W. Xu, J. Q. Zhang, Z. X. Wei, J. H. Hou and Z. H. Wang, *Org. Chem. Front.*, 2017, **4**, 811-816.