All-Small Molecule Solar Cells Based on Donor Molecular Optimization with Highly Enhanced Efficiency and Stability

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1. Experimental Section



Scheme S1. Synthetic route of the BDT(TVT-SR)₂

Materials. IDIC was purchased from Solarmer Materials Inc. Solvents were dried and distilled from appropriate drying agents prior to use. Monomer 1^[1] and monomer 2^[2] were synthesized according to the procedures in the literatures, the synthetic route of the small molecule donor BDT(TVT-SR)₂ was shown in Scheme S1.

*Synthesis of BDT(TVT-SR)*₂: Compound 1 (237 mg, 0.20 mmol) and Compound 2 (365 mg, 0.44 mmol) were dissolved in toluene (15 mL); after being flushed with argon for 5min, Pd(PPh₃)₄ (46 mg, 0.04 mmol) was added. Then the mixture was purged with nitrogen for another 15 min, after which the reaction mixture was stirred at 110 °C in dark under an nitrogen atmosphere overnight. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane. The organic layer was further dried with anhydrous Mg₂SO₄ and filtered. The solevent was evaporated under reduced pressure. The crude product was purified by column

chromatography with hexane and dichloromethane (1:1) as eluent to afford a dark solid. BDT(TVT-SR)₂: (264 mg, 56% yield). ¹H NMR (400 MHz, CDCl3, δ): 8.41-8.42 (d, 2H), 8.34-8.35 (d, 2H), 8.31 (s, 2H), 7.97-7.98 (d, 2H), 7.75 (s, 4H), 7.54-7.55 (d, 2H), 7.40-7.41 (d, 2H) , 7.37 (m, 4H), 7.29-7.30 (d, 2H), 7.02-7.03 (d, 2H), 4.79-4.80 (d, 4H), 4.25-4.26 (d, 4H), 2.98-2.99 (d, 4H), 2.03-2.06(m, 4H), 1.60-1.63(m, 2H), 1.40-1.55(m, 8H), 1.26-1.38(m, 72H), 0.84-1.05 (m, 36H). MALDI-TOF MS: Calcd. for C130H158F4N8O4S12 m/z = 2355.90; Found 2351.0. Elemental analysis: Calcd for C130H158F4N8O4S12 (%): C, 66.23; H, 6.76; N, 4.75. Found (%):C, 66.35; H, 6.72;N, 4.76.

Material characterization. ¹H NMR spectra were measured on a Bruker DMX-400 spectrometer with *d*-chloroform as the solvent and trimethylsilane as the internal reference. Absorption profiles were recorded with a Perkin Elmer Lambda-35 absorption spectrometer from 350 nm to 1100 nm. Electrochemical properties were studied by cyclic voltammetry (CVA). CVA was performed on a CS350H electrochemcial workstation with a three-electrode system in a 0.1 M [Bu₄N]PF₆ acetonitrile solution at a scan rate of 20 mVs⁻¹. Glassy carbon disc coated with sample film was used as the working electrode. A Pt wire was used as the counter electrode and Ag/AgCl was used as the reference electrode. The HOMO and LUMO levels are calculated from the onset potentials of oxidation and reduction with respect to the energy level of ferrocene/ferrocenium couple, which was taken as -4.8 eV below the vacuum level.

Fabrication and characterization of the OSCs. All the devices were fabricated in the normal architecture. Photovoltaic devices were fabricated by doctor-blading on indium tin oxide (ITO)-covered glass substrates (from Osram). These substrates were cleaned

in toluene, water, acetone, and isopropyl alcohol. After drying, the substrates were bladed with 40 nm PEDOT:PSS (HC Starck, PEDOT PH-4083). The photovoltaic layers was spin-coated in a glovebox from a solution of BDT(TVT-SR)₂:IDIC with 12 mg/mL in chloroform. After that, the layers were annealed at 110 °C for 10 min for the devices with thermal annealing treatment. A perylene diimide functionalized with amino N-oxide (PDINO) layer via a solution concentration of 1.0 mg/mL was deposited the top of active layer. Finally, top aluminum electrode of 100 nm thickness was evaporated in vacuum onto the cathode buffer layer at a pressure of 5×10^{-6} mbar. The typical active area of the investigated devices was 4 mm². The current-voltage characteristics of the solar cells were measured by a Keithley 2400 source meter unit under AM 1.5G irradiation from a solar simulator (Enlitech model SS-F5-3A). Solar simulator illumination intensity was determined at 100 mW cm⁻² using a monocrystal silicon reference cell with KG5 filter. Short circuit currents under AM 1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The external quantum efficiency was measured by a Solar Cell Spectral Response Measurement System QE-R3011(Enli Technology Co., Ltd.).

AFM measurements were performed with a Nanosurf Easy Scan 2 in contact mode. Single carrier devices were fabricated and the dark current-voltage characteristics measured and analyzed in the space charge limited (SCL) regime following the references. The structure of hole only devices was Glass/ITO/PEDOT:PSS/Active layer/MoO₃/Ag (100 nm). For the electron only devices, the structure was Glass/ITO/ZnO/Active layer/Ca (15 m)/Ag (80 nm), where both Ca and Ag were evaporated. The reported mobility data are average values over the two cells of each sample at a given film composition.



Fiugre S1. ¹H NMR spectrum of compound **1a** in CDCl₃.

Figure S2. TGA plots of BDT(TVT-SR)₂ with a heating rate of 10 °C min⁻¹ in air.

Figure S3. DSC thermograms of the BDT(TVT-SR)₂: 1st heating, 1st cooling, 2nd heating and 2nd cooling.

Table S1. Summary of optical properties and electronic energy levels of BDT(TVT-SR)₂.

Solution	Film	ε	$E_{\rm g}^{\rm opt,}$	HOMOd	LUMOd	F cv	LOMOe	
$\lambda_{max}{}^a$	$\lambda_{max}{}^{b}$	M ⁻¹	с			L_{g}		
(nm)	(nm)	cm ⁻¹	(eV)	(ev)	(ev)	(0)	(ev)	(ev)
510	558,	8.16 ×	1.00	5 1 1	2.02	2 10	5 22	2 1 0
519	602	104	1.82	-3.11	-3.02	2.10	-3.33	-3.18

^{*a*}Measured in chloroform solution. ^{*b*}Cast from chloroform solution. ^{*c*}Bandgap estimated from the onset wavelength (λ_{edge}) of the optical absorption: $E_g^{opt} = 1240/\lambda_{edge}$. ^{*d*}Measured by electrochemical cyclic voltammetry. ^{*e*}Obtained by DFT calculation.

Figure S4. UV-vis absorption spectra of H11 and BDT(TVT-SR)₂ in chloroform solutions (a) and in thin films (b).

Figure S5. Cyclic voltammogram of BDT(TVT-SR)₂ polymer film on a platinum electrode measured in 0.1 mol L^{-1} Bu₄NPF₆ acetonitrile solutions at a scan rate of 20 mV s⁻¹, the inser figure (black line) shows the ferrocene/ferrocenium (Fc/Fc⁺) couple used as an internal reference.

Figure S6. Molecular geometry of the small molecule donor materials calculated by DFT/B3LYP/6-31G(d, p) with methyl groups in replacing alkyl substituents to simplify the calculations.

Figure S7. LUMO and HOMO energy levels of the small molecules calculated by DFT/B3LYP/6-31G(d, p) with methyl groups in replacing alkyl substituents to simplify the calculations.

Figure S8. XRD patterns of BDT(TVT-SR) $_2$ and H11 films spin-coated from CHCl $_3$ on silicon wafer.

Figure S9. The dark J-V characteristics of pure BDT(TVT-SR)₂ and H11 films based hole-only devices, respectively. Solid lines are the fitting lines of the data.

Figure S10. *J-V* curves of the OSCs based on BDT(TVT-SR)₂:IDIC (2:1, wt%) under different annealing temperature conditions.

Table S2. Photovoltaic parameters of the OSCs based on BDTT-S-TR:IDIC (2:1, wt%	b)
under different annealing temperature conditions.	

Conditions	Annealing	V_{oc}	J_{sc}	FF	PCE
Conditions	[°C]	[V]	[mA/cm ²]	[%]	[%]
	0	1.01	10.22	54.63	5.64
	0	(1.01 ± 0.003)	(9.54 ± 0.377)	(53.03 ± 0.556)	(5.18 ± 0.231)
Temp.	70	1.01	11.32	58.57	6.70
(D:A; 2:1)	70	(1.00 ± 0.012)	(10.13 ± 1.004)	(56.32 ± 1.032)	(5.78 ± 0.539)
	00	0.99	13.91	64.37	8.86
	90	(0.99 ± 0.004)	(12.90 ± 0.432)	(65.31 ± 1.020)	(8.47 ± 0.218)

	0.98	15.92	71.15	11.10
110	(0.98 ± 0.004)	(15.56 ± 0.251)	(69.94 ± 1.104)	(10.60 ± 0.221)
120	0.96	14.81	65.81	9.36
120	(0.97 ± 0.004)	(14.52 ± 0.216)	(64.58 ± 1.362)	(9.07 ± 0.196)
140	0.95	14.66	60.42	8.41
140	(0.93 ± 0.015)	(14.46 ± 0.306)	(56.77 ± 2.383)	(7.63 ± 0.360)

Figure S11. *J-V* curves of the annealed OSCs based on BDT(TVT-SR)₂:IDIC with different blend D:A weight ratios. All of blends was treated by thermal annealing at 110 °C for 10 min.

Table S3. Photovoltaic parameters of the OSCs based on $BDT(TVT-SR)_2$:IDIC with	1
different blend D:A weight ratios, under the illumination of AM1.5G at 100 mW cm ⁻²	•

Conditions	D:A, w/w	V_{oc}	\mathbf{J}_{sc}	FF	PCE
Conditions		[V]	[mA/cm ²]	[%]	[%]
	1.1	0.96	14.02	60.36	8.12
	1:1	(0.95 ± 0.002)	(13.14 ± 0.475)	(58.83 ± 1.026)	(8.02 ± 0.254)
	15.1	0.98	15.03	67.57	9.95
Ratio	1.5:1	(0.97 ± 0.004)	(14.46 ± 0.229)	(66.15 ± 0.757)	(9.57 ± 0.485)
(Blends:	2:1	0.98	15.92	71.15	11.10
10min		(0.98 ± 0.004)	(15.56 ± 0.251)	(69.94 ± 1.104)	(10.60 ± 0.228)
@110 °C)	2.5:1	0.98	14.82	65.70	9.54
		(0.98 ± 0.008)	(14.05 ± 0.389)	(64.35 ± 1.327)	(9.34 ± 0.306)
	3:1	0.99	12.16	57.78	6.96
		(0.98 ± 0.006)	(11.51 ± 0.466)	(56.32 ± 1.063)	(6.53 ± 0.417)

Figure S12. *J-V* curves of the annealed OSCs based on BDT(TVT-SR)₂:IDIC with different photoactive layer thickness. The blends was treated by thermal annealing at 110 °C for 10 min.

Table S4. Photovoltaic parameters of the OSCs based on BDT(TVT-SR) ₂ :IDIC w	rith
different photoactive layer thickness, under one sun illumination.	

Conditions	Thickness	V_{oc}	\mathbf{J}_{sc}	FF	PCE
Conditions	[nm]	[V]	[mA/cm ²]	[%]	[%]
	75	0.98	15.27	66.63	9.97
	/5	(0.98 ± 0.002)	(14.95 ± 0.245)	(65.12 ± 1.214)	(9.52 ± 0.461)
	05	0.98	15.51	67.73	10.29
Thickness	93	(0.98 ± 0.002)	(15.46 ± 0.187)	(65.15 ± 1.489)	(9.88 ± 0.417)
(D:A: 2:1;	110 140	0.98	15.92	71.15	11.10
10min		(0.98 ± 0.004)	(15.56 ± 0.251)	(69.94 ± 1.104)	(10.60 ± 0.228)
@110 °C)		0.97	14.87	63.19	9.15
		(0.97 ± 0.006)	(14.12 ± 0.395)	(61.35 ± 1.319)	(8.54 ± 0.325)
	100	0.95	13.45	56.96	7.28
	180	(0.95 ± 0.006)	(12.68 ± 0.517)	(53.32 ± 1.798)	(6.71 ± 0.515)

Figure S13. *J-V* curves of the OSCs based on BDT(TVT-SR)₂:IDIC (2:1, wt%) using different solvents without and with TA treatments.

Conditions	ТА	V_{oc}	J_{sc}	FF	PCE
Conditions	treatment	[V]	[mA/cm ²]	[%]	[%]
	Without	1.01	10.22	54.63	5.64
Chloroform	without	(1.01 ± 0.003)	(9.54 ± 0.377)	(53.03 ± 0.556)	(5.18 ± 0.231)
(CF)	With	0.98	15.92	71.15	11.10
	With	(0.98 ± 0.004)	(15.56 ± 0.251)	(69.94 ± 1.104)	(10.60 ± 0.228)
	Without	1.00	9.65	52.71	5.09
Chlorobenz	without	(1.00 ± 0.005)	(9.10 ± 0.432)	(47.31 ± 2.120)	(4.39 ± 0.314)
ene (CB)	With	0.97	13.83	63.54	8.52
	vv Iuli	(0.96 ± 0.004)	(12.88 ± 0.313)	(57.85 ± 3.104)	(7.90 ± 0.312)
Dichlorobe	Without	1.01	8.95	49.32	4.46
		(1.00 ± 0.004)	(8.10 ± 0.356)	(44.39 ± 3.398)	(3.25 ± 0.413)
(ODCD)	With	0.97	12.87	57.58	7.19
(ODCB)	With	(0.96 ± 0.004)	(11.89 ± 0.417)	(52.63 ± 3.566)	(6.84 ± 0.376)

Table S5. Photovoltaic parameters of the OSCs based on BDT(TVT-SR)₂:IDIC (2:1, wt%) using different solvents without and with TA treatments (110 °C).

Figure S14. AFM top images (size: $5 \times 5 \ \mu m^2$) of BDT(TVT-SR)₂:IDIC (a) and H11:IDIC (b) blends.

Figure S15. The measured (a)FF and (b) V_{oc} of un-annealed and annealed devices as a function of light intensity (symbols), together with linear fits to the V_{oc} data (solid lines).

Figure S16. *J-V* characteristics in the dark for (a) hole-only devices and (b) electrononly devices of BDT(TVT-SR)₂:IDIC blends with and withtout TA treatment as well as the optimized H11:IDIC blends.

Figure S17. TEM image results of BDT(TVT-SR)₂:IDIC blend films (a) without and

(b) with TA treatment.

Figure S18. Specular XRD results for BDT(TVT-SR)₂:IDIC blend films without and with TA treatment.

Figure S19. Variation of normalized average device photovoltaic parameters over 200 h, one sun illumination for the encapsulated devices based on (a) BDT(TVT-SR)₂ blend and (b) H11 blend.

Figure S20. Changes of (a) normalized V_{oc} , (b) normalized J_{sc} , (c) normalized FF and (d) normalized PCE of BDT(TVT-SR)₂:IDIC, and H11:IDIC based devices as a function of annealing time at 80 °C.

Figure S21. UV-vis absorption of BDT(TVT-SR)₂:IDIC (a) and H11:IDIC (b) blends as a function of annealing time at $120 \text{ }^{\circ}\text{C}$.

Figure S22. AFM top images of morphological evolution of $BDT(TVT-SR)_2$:IDIC (top) and H11:IDIC (bottom) blends without (a, d) and with 2hours (b, e) and 24 hours (c, f) thermal annealing treatmetns. The scanning area is 5×5 mm2 for all images.

References

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