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Achieving 10% efficiency in non-fullerene all-small-molecules organic solar cells without extra treatments

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Table S1. The performances for the reported small molecules:Y6-based organic solar cells devices

No.	D : A	Treatments	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	References
1	BSFTR : Y6	**As-cast**	**0.94**	**0.97**	**23.78**	**0.22**	Adv. Mater., 2019, 31, 1904283
		TA (120°C/5min)	0.85	22.86	64.87	12.56	
		SVA (CF) +TA	0.85	23.16	69.66	13.69	
2	BTR : Y6	**As-cast**	--	--	--	--	Joule, 2019, 3, 3034-3047;
		TA (100°C/10min)	0.85	22.25	56.4	10.67	
	BTR : Y6	**As-cast**	**0.86**	**16.42**	**43.2**	**6.13**	Org. Electron., 2020, 105904.
		TA (110°C/10min)	0.85	20.18	70.5	12.12	
3	BTR-Cl : Y6	**As-cast**	--	--	--	--	Adv. Energy Mater. 2020, 10, 2001076.
		TA (120°C/10min)	0.86	24.17	65.5	13.61	
4	ZR1 : Y6	**As-cast**	**0.876**	**14.23**	**40.50**	**5.05**	Nat. Commun., 2019, 10, 5393
		TA (120°C/10min)	0.861	24.34	68.44	14.34	
5	BOHTR : Y6	**As-cast**	**0.85**	**8.3**	**28.3**	**2.1**	Sol. RRL, 2020, 4, 1900326
		TA (115°C/10min)	0.82	22.5	52.5	10.8	
6	BIHTR : Y6	**As-cast**	**0.72**	**2.2**	**23.0**	**0.5**	
		TA (115°C/10min)	0.84	21.5	66.9	12.3	
7	DCAO3TBDTT : Y6	**As-cast**	**0.917**	**2.74**	**21.38**	**0.54**	Angew. Chem. Int. Ed. 2020, 59, 2808-2815
		TA (105°C/10min)+CN	0.804	21.71	60.95	10.64	
8	BTEC-1F : Y6	**As-cast**	**0.941**	**4.92**	**22.59**	**1.05**	
		TA (105°C/10min)	0.870	21.21	61.35	11.33	
9	BTEC-2F : Y6	**As-cast**	**0.895**	**14.51**	**51.54**	**6.69**	
		TA (105°C/10min)+CN	0.854	21.55	72.35	13.34	
10	BT-2F : Y6	**As-cast**	**0.874**	**17.08**	**59.84**	**8.94**	J. Mater. Chem. A, 2020, 8, 7405–7411
		TA (100°C/10min)	0.853	22.38	72.27	13.80	
11	BDTT-TR : Y6	**As-cast**	**0.868**	**0.61**	**22.25**	**0.12**	Sci. China Chem., 2020, 63, 1246-1255
		TA (140°C/2min)	0.780	23.64	66.06	12.18	
12	TBFT-TR : Y6	**As-cast**	**0.879**	**0.95**	**22.18**	**0.19**	

		TA (140°C/2min)	0.784	24.59	72.78	14.03	
13	SM1 : Y6	**As-cast**	**0.897**	**2.70**	**21.9**	**0.53**	Adv. Mater. 2020, 32, 1908373
		TA (120°C/10min)	0.805	23.59	67.0	12.72	
14	SM1-S : Y6	**As-cast**	**0.921**	**1.26**	**20.2**	**0.23**	
		TA (120°C/10min)	0.825	23.23	37.7	12.94	
15	SM1-F : Y6	**As-cast**	**0.936**	**7.46**	**24.6**	**1.72**	
		TA (120°C/10min)	0.866	23.25	69.9	14.07	
16	FG3 : Y6	**As-cast**	**0.94**	**15.08**	**57.0**	**8.08**	Sol. RRL, 2020, 4, 2000460
		SVA (THF)	0.90	18.38	65.0	10.75	
17	FG4 : Y6	**As-cast**	**0.84**	**16.49**	**60.0**	**8.31**	
		SVA (THF)	0.79	20.92	67.0	11.07	
18	ZR2-C3: Y6	**As-cast**	**0.898**	**13.93**	**34.6**	**4.33**	Adv. Funct. Mater. 2020, 30, 2005426.
		TA (120°C/10min)	0.854	24.70	70.0	14.78	

1. Experimental section

1.1 Instruments and characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker (AVANCE III 400MHz). High resolution time of flight mass spectrometer (TOF-MS) was obtained from AB Sciex (TripleTOF 4600). Thermogravimetric analysis (TGA) was under taken using a PerkinElmer (Diamond TG/DTA) under N_2 atmosphere at a heating rate of 10 °C min^{-1}. Absorption spectra of both solution and thin-film samples of the objective compounds were recorded using a Perkin Elmer (Lamdba 950) UV-Vis scanning spectrophotometer. The solution samples were prepared in chloroform solution at a concentration of 2.0×10^{-5} mol L^{-1}, while the film samples were obtained by spin-coating from chloroform solution (5 mg mL^{-1}, 2000 rpm) on quartz substrates.

The morphologies of the active layers were analyzed through atomic force microscopy (AFM) in tapping mode under ambient conditions using Bruker (Dimension ICON) instrument. GI-WAXS measurements were performed on a XEUSS SAXS/WAXS system (XENOCS, France) at the National Center for Nanoscience and Technology. The wavelength of the X-ray beam is 1.54 Å, and the incident angle was 0.18°. Scattered X-rays were detected by using a Dectris Pilatus 300 K photon counting detector. The blend films for GI-WAXS and AFM were made by the same method for device active layer except for the substrate as Si/PEDOT:PSS.

The Cyclic Voltammetry (CV) measurement was carried out in 2.0×10^{-4} mol L^{-1} anhydrous dichloromethane (DCM) with 0.1 mol L^{-1} tetrabutyl ammonium perchlorate (Bu_4NClO_4, as supporting electrolyte) under an argon atmosphere at a scan rate of 0.1 V s^{-1} using a PC controlled LK 2006A electrochemical workstation. The CV system was constructed using a Pt disk as the working electrode, a Pt wire as the counter electrode, and a Ag/$AgNO_3$ (0.1 mol L^{-1} in acetonitrile) electrode as the reference electrode. Ferrocene was used as an internal standard. The electrochemical potential was internally calibrated against the standard ferrocene/ ferrocenium redox couple (Fc/Fc^+), which has a known reduction potential of −4.80 eV relative to vacuum level. The HOMO and LUMO of the objective compounds are calculated according to the following equations:

$$\mathrm{HOMO} = -[E_{ox}^{onest} + 4.8\ ]$$

$$\mathrm{LUMO} = -[E_{red}^{onest} + 4.8\ ]$$

Where E_{ox}^{onset} and E_{red}^{onest} are the onset of oxidation potential and reduction potential *vs.* Fe/Fe^+, respectively.

1.2 SCLC measurement

Hole-only and electron-only devices were fabricated with the structure of ITO/MoO_3 /SM:Y6 (100 nm)/MoO_3/Ag and ITO/ZnO/SM:Y6 (100 nm)/PDINO/Al, respectively. Mobilities were extracted by fitting the current density-voltage curves using space charge limited current (SCLC), the *J-V* curves of the devices were plotted as $J^{0.5}$ versus V using Eq. 1:

$$J = \frac{9}{8}\frac{\varepsilon_r \times \varepsilon_o \times \mu \times V^2}{L^3}\exp\left(0.89\beta\sqrt{\frac{V}{L}}\right) \qquad (1)$$

where J is current density, L is film thickness of active layer, μ_h is hole mobility, μ_e is electron mobility, ε_r is relative dielectric constant of the transport medium, ε_0 is permittivity of free space (8.85×10^{-12} F m^{-1}), V (= V_{appl} - V_{bi}) is the internal voltage in the device, where V_{appl} is the applied voltage to the device and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

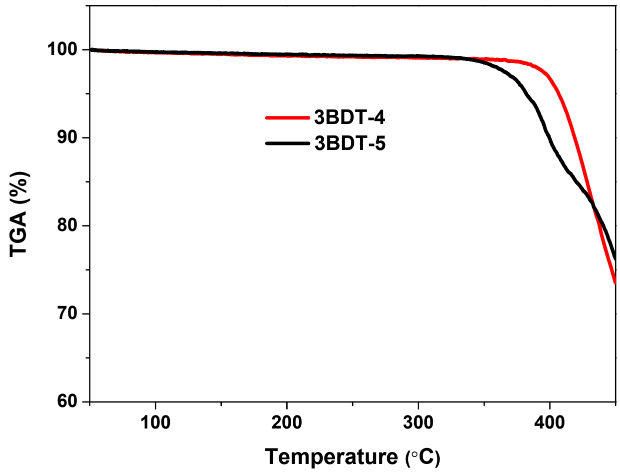

Figure S1. TGA curves of 3BDT-4 and 3BDT-5.

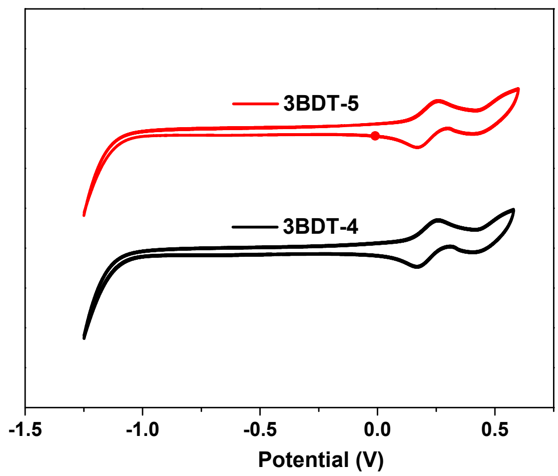

Figure S2. Cyclic voltammogram of 3BDT-4 and 3BDT-5.

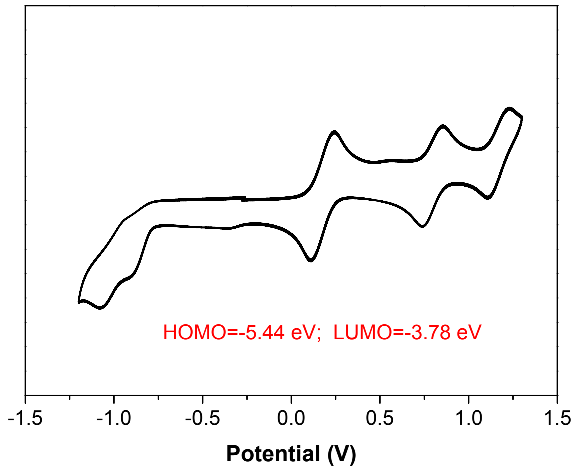

Figure S3. Cyclic voltammogram of the non-fullerene acceptor Y6.

Table S2. Photovoltaic performances of ASM-OSCs based on 3BDT-4:Y6 with different weight ratios without extra treatments.

Active layers	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [a] [%]
3BDT-4 : Y6 = 1 : 0.50	0.832	16.5	0.407	5.59 (5.48)
3BDT-4 : Y6 = 1 : 0.55	0.829	17.0	0.413	5.82 (5.68)
3BDT-4 : Y6 = 1 : 0.90	0.816	16.1	0.405	5.32 (5.21)

[a] Average values of 4 individual cells were given in parentheses.

Table S3. Photovoltaic performances of ASM-OSCs based on 3BDT-5:Y6 with different weight ratios without extra treatments.

Active layers	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [a] [%]
3BDT-5 : Y6 = 1 : 0.50	0.844	20.9	0.551	9.72 (9.40)
3BDT-5 : Y6 = 1 : 0.55	0.840	21.3	0.581	10.4 (10.0)
3BDT-5 : Y6 = 1 : 0.90	0.825	19.6	0.503	8.13 (7.86)

a) Average values of 4 individual cells were given in parentheses.

Table S4. Photovoltaic performances of ASM-OSCs based on 3BDT-5:Y6 (1:0.55, weight ratio) with different thermal annealing (TA) treatments.

Active layers	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [a)] [%]
As-cast	0.840	21.3	0.581	10.4 (10.0)
TA 80 °C/10min	0.832	21.6	0.590	10.6 (10.4)
TA 100 °C/10min	0.829	22.1	0.600	11.0 (10.7)
TA 120 °C/10min	0.815	19.5	0.635	10.1 (9.85)
TA 140 °C/10min	0.780	19.7	0.613	9.42 (9.20)

a) Average values of 4 individual cells were given in parentheses.

Table S5. Photovoltaic performances of ASM-OSCs based on 3BDT-5:Y6 (1:0.55, weight ratio) with different solvent vapor annealing (SVA) treatments using Chloroform as solvent.

Active layers Treatments	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [a)] [%]
As-cast	0.840	21.3	0.581	10.4 (10.0)
SVA 60s	0.841	20.7	0.542	9.44 (9.23)
SVA 90s	0.834	22.1	0.571	10.5 (10.2)
SVA 120s	0.831	20.0	0.509	8.46 (8.30)

a) Average values of 4 individual cells were given in parentheses.

Table S6. Photovoltaic performances of ASM-OSCs based on 3BDT-4:Y6 (1:0.55, weight ratio) with different thermal annealing treatments.

Active layers	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [a] [%]
As-cast	0.829	17.0	0.413	5.82 (5.68)
TA 80 °C/10min	0.820	18.2	0.428	6.39 (6.30)
TA 100 °C/10min	0.815	17.3	0.447	6.30 (6.22)
TA 120 °C/10min	0.803	16.5	0.459	6.08 (5.96)

a) Average values of 4 individual cells were given in parentheses.

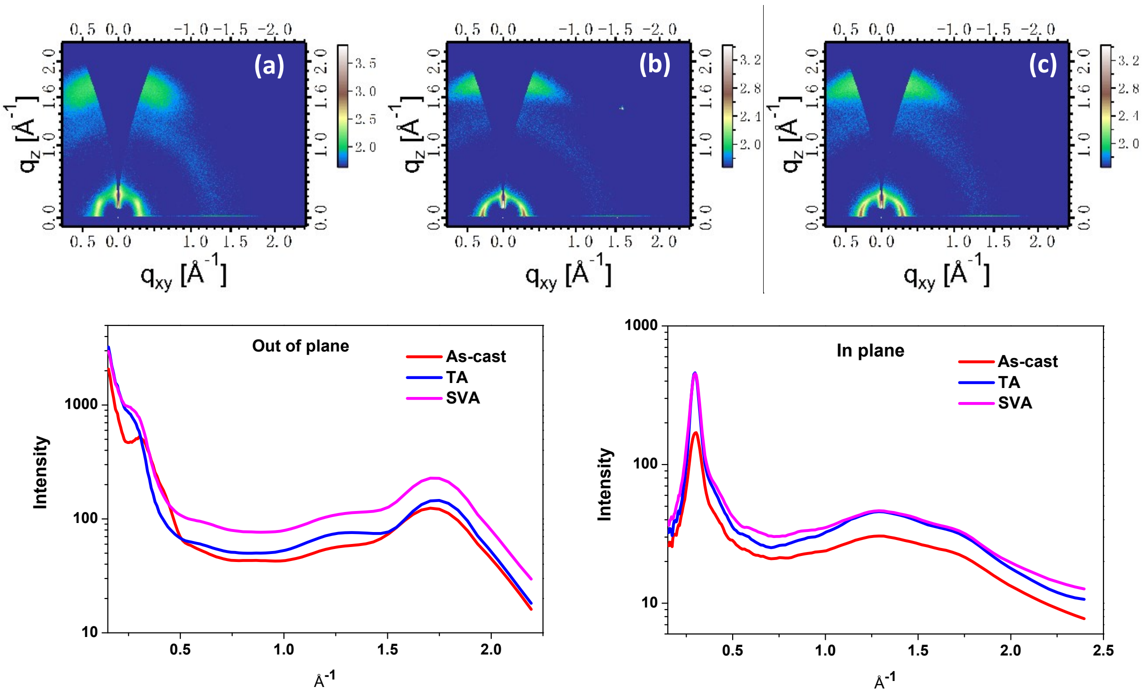

Figure S4. 2D GIWAXS patterns of the as-cast 3BDT-5:Y6 blend films (a), with TA (b), with SVA (c), and the corresponding out-of-plane and in-plane line cuts of the blend films.