Support Information

Solid additive-assisted morphology optimization enables efficient nonhalogen solvent-processed polymer solar cells

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Experimental details

Device fabrication and testing: The devices were fabricated with conventional architectures of glass/ITO/PDEOT:PSS/active layer/PDINO/Al. The ITO-coated glass was pre-cleaned and modified by a thin layer of PEDOT: PSS which was spin-cast from a PEDOT:PSS aqueous solution (Baytron P VP AI4083 from H. C. Stark) at 5000 rpm for 40 s, and then dried at 150 °C for 15 min in air. The thickness of the PEDOT: PSS layer is about 30 nm. After the active layer blend solution were spin-coated onto ITO glasses, the electron-transport layer of PDINO (about 5 nm) was spin-coated on top of active layer from the methanol solution with a concentration of 1.0 mg/mL at 3000 rpm for 40 s. After the deposition of active layer, about 100 nm of Al were deposited at a pressure of 2.0×10^{-5} Pa onto the PDINO layer with a shadow

mask.

The current density-voltage (*J-V*) measurement of the OSCs were measured under a illumination of AM 1.5G (100 mW cm^{-2}) using a SS-F5-3A solar simulator (AAA grade, 50 × 50 mm^2 photobeam size) of Enli Technology CO., Ltd.. The EQE was measured by using a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The light intensity at each wavelength was calibrated by a standard single-crystal Si solar cell. Masks were made using laser beamcutting technology and had well-defined areas of 0.056 cm^2 to define the effective areas for accurate measurement.

Fabrication details for the PM6:Y6 -based OSCs:

PM6:Y6-based devices: the PM6:Y6 ratio was kept at 1:1.2 (w/w) with the polymer concentration of 12 mg/mL in *o*-xylene solution, and the active layer was spin-coated from the *o*-xylene solution with 0.5 % (v/v) CN then annealed at 110 °C for 10 min, or with the dual additives treatment of 0.5% CN and various weight ratios of BTBT or DTBDT (weight ratio relative to PM6) followed by TA treatment at different temperature. The optimal thickness of active layer is 96~107 nm.

The hole and electron mobilities were calculated by using the space-charge-limited current method.

$$J \cong (9/8)\varepsilon\varepsilon_0\mu_0 V^2 \exp(0.89\sqrt{V/E_0 L})/L^3$$

Where ε is the dielectric constant of the polymers, ε_0 is the permittivity of the vacuum, μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, and L is the thickness of the film.

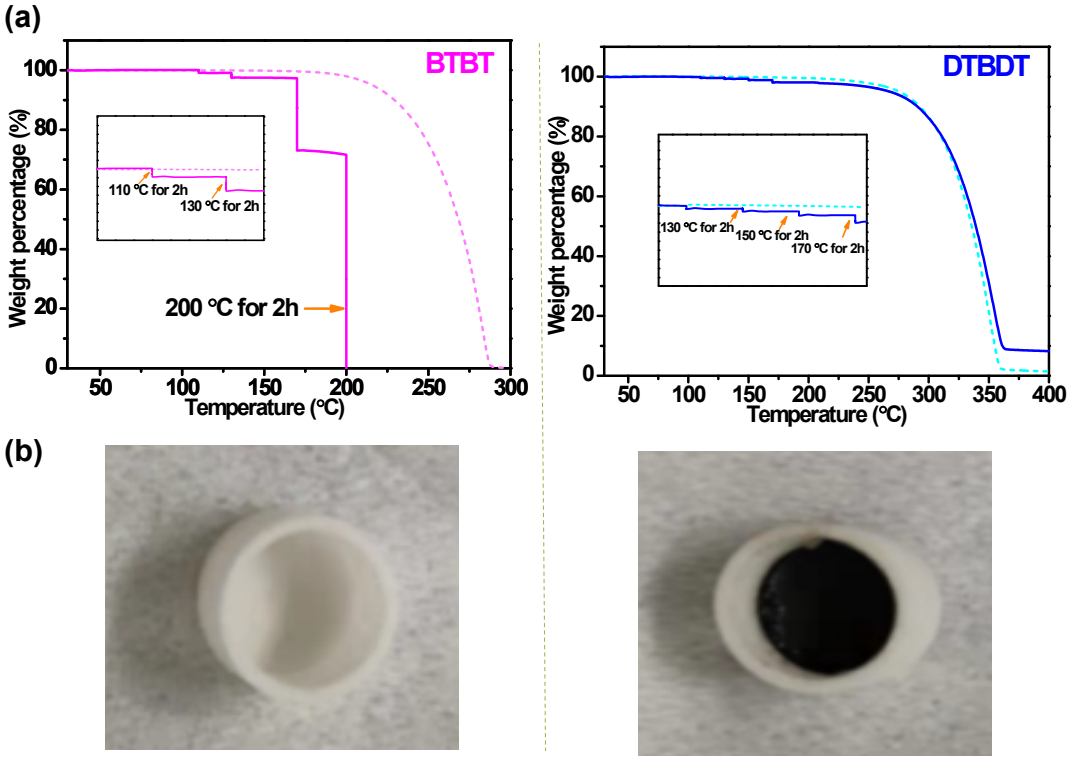

Figure S1 (a) TGA plot of BTBT and DTBDT at a scan rate of 10 °C min^{-1} under inert atmosphere. (b) Photos of crucibles with BTBT (left) and DTBDT (right) after the TGA measurements.

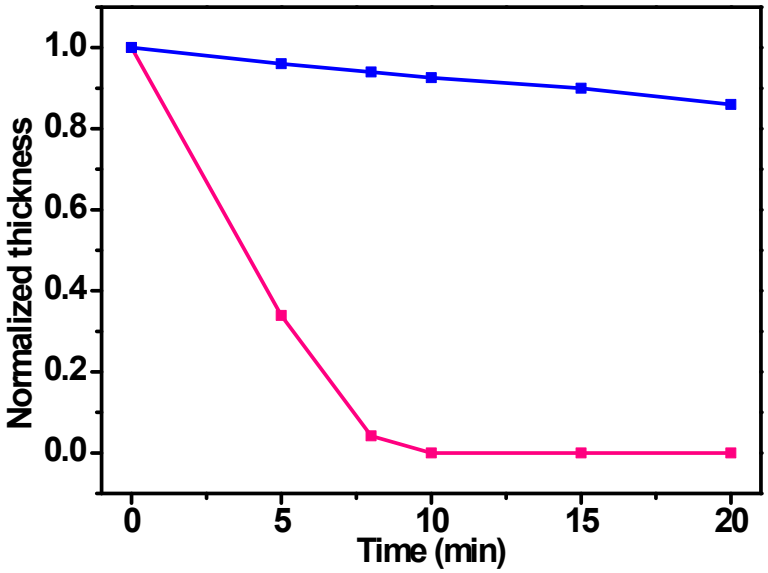

Figure S2 Normalized film thicknesses of pristine BTBT and DTBDT film spin-coated onto silicon wafer as a function of different duration time of TA under 110 °C and 130 °C, respectively.

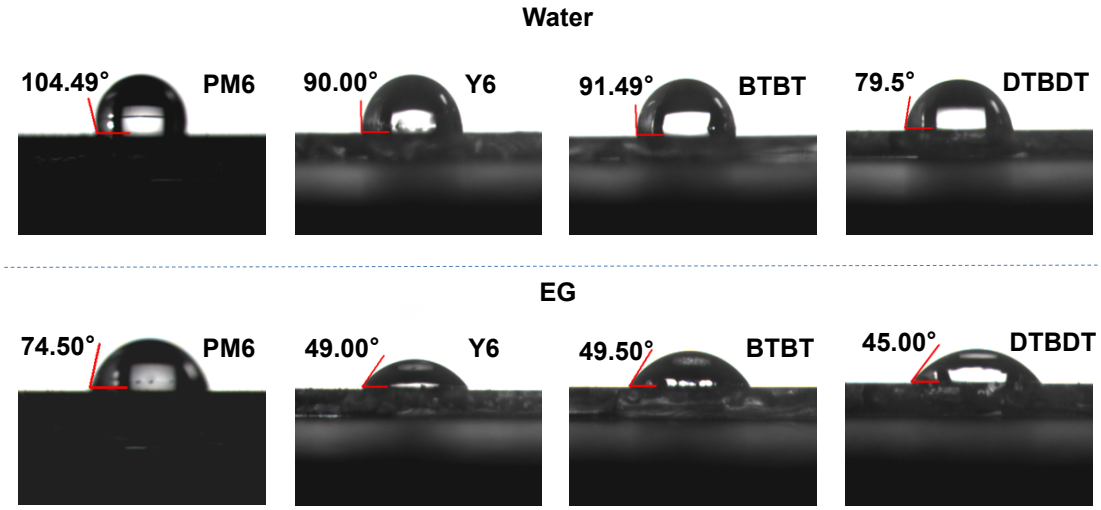

Figure S3 Contact angles of neat PM6Y6, BTBT,and DTBDT film.

Table S1 Contact angles and surface tensions of neat Y6, BTBT and DTBDT films.

Surface	γ (mN m^{-1})
PM6	29.64
Y6	48.37
BTBT	50.44
DTBDT	38.91

Table S2 Flory-Huggins interaction parameters of the blend films.

Blend film	χ
Y6:BTBT	0.022
Y6: DTBDT	0.514
PM6:BTBT	2.748
PM6:DTBDT	0.629

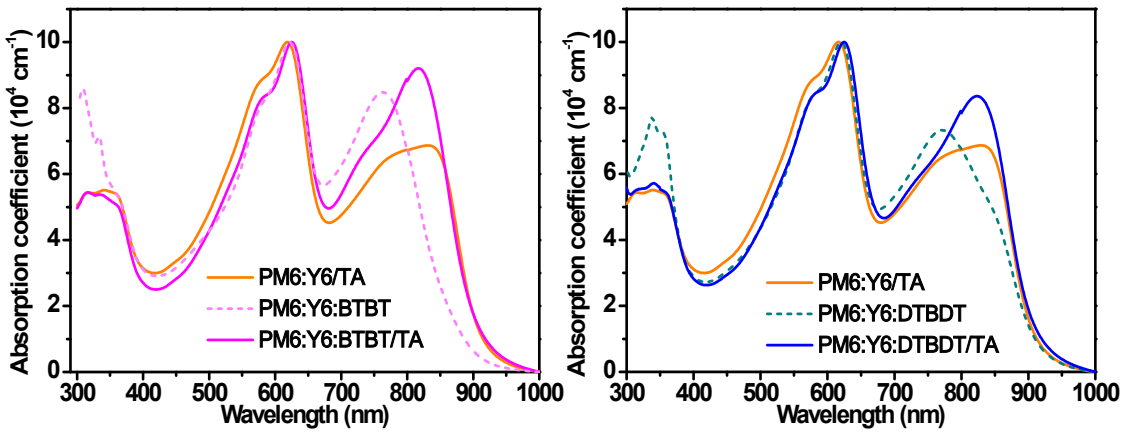

Figure S4 Absorbance of PM6:Y6 blend film under different treatment.

Table S3 Photovoltaic performances of the PM6:Y6-based OSCs processed by the solid additive of different weight ratio of BTBT and 0.5% (v/v) CN solvent additive with TA treatment at 110 °C for 10 min, under the illumination of AM 1.5 G, 100 mW cm^{-2}.

BTBT ratio (%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
0	0.789	19.62	66.3	10.25
20	0.792	25.56	74.7	15.06
25	0.791	25.81	75.5	15.42
30	0.811	26.14	77.3	16.37
40	0.791	25.87	73.9	15.13
50	0.787	25.54	73.6	14.80

Table S4 Photovoltaic performances of the PM6:Y6-based PSCs processed by 0.50% CN + 30% BTBT additives and TA at different temperature for 10 min under the illumination of AM 1.5 G, 100 mW cm^{-2}.

TA temperature (°C)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
/	0.814	22.36	63.3	11.53
90	0.813	24.69	73.6	14.77
110	0.811	26.14	77.3	16.37
130	0.807	26.28	74.3	15.76

Table S5 Photovoltaic performances of the PM6:Y6-based PSCs processed by different additive treatment under the illumination of AM 1.5 G, 100 mW cm^{-2}.[a]

additive	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
/	0.777	17.63	64.65	8.86
	(0.776 ± 0.002)	(17.32 ± 0.23)	(0.653 ± 0.007)	(8.90 ± 0.14)
CN	0.789	19.62	0.663	10.25
	(0.786 ± 0.004)	(18.52 ± 0.13)	(0.662 ± 0.006)	(10.25 ± 0.11)
BTBT	0.823	25.79	0.739	15.68
	(0.821 ± 0.003)	(25.98 ± 0.16)	(0.738 ± 0.004)	(15.70 ± 0.09)
CN+BTBT	0.811	26.14	0.773	16.37
	(0.813 ± 0.003)	(26.09 ± 0.22)	(0.772 ± 0.006)	(16.35 ± 0.13)

[a]The statistical values in brackets were calculated from 10 devices.

Table S6 Photovoltaic performances of the PM6:Y6-based OSCs processed by the solid additive of different weight ratio of DTBDT and 0.5% (v/v) CN solvent additive with TA treatment at 130 °C for 10 min, under the illumination of AM 1.5 G, 100 mW cm^{-2}.

DTBDT ratio (%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
0	0.789	19.62	66.3	10.25
20	0.793	23.99	66.1	12.57
25	0.794	25.69	69.3	14.14
30	0.798	25.28	71.4	14.40
40	0.787	23.44	66.6	12.18
50	0.774	22.57	61.6	10.75

Table S7 Photovoltaic performances of the PM6:Y6-based OSCs processed by 0.50% CN + 30% DTBDT additives and TA at different temperature for 10 min under the illumination of AM 1.5 G, 100 mW cm^{-2}.

TA temperature (°C)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
/	0.812	20.07	47.2	7.66

110	0.783	25.13	70.7	13.87
130	0.798	25.28	71.4	14.40
150	0.753	25.62	67.9	12.92

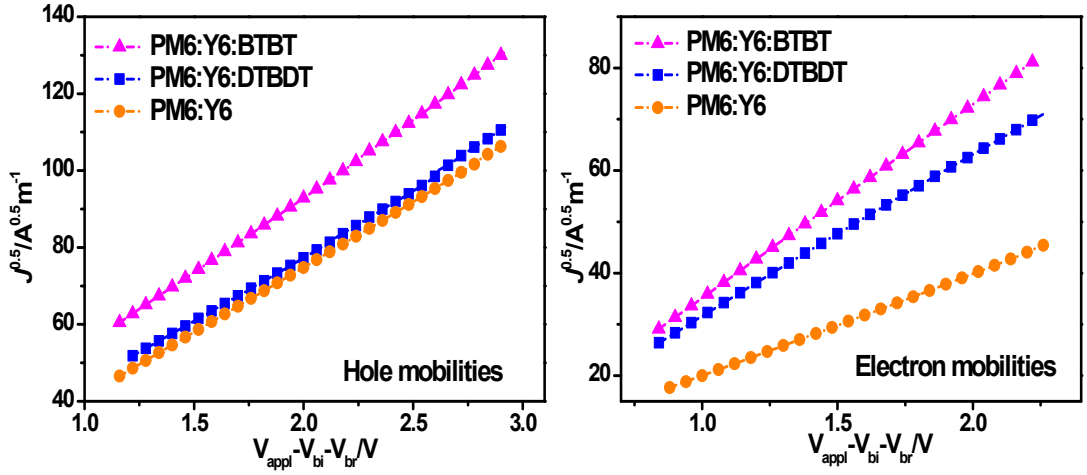

Figure S5 $J^{0.5}$ *vs* (V_{appl}-V_{bi}-V_{br}) plots of hole-only and electron-only devices of PM6:Y6 (1:1.2, w/w) processed with different additive treatment.

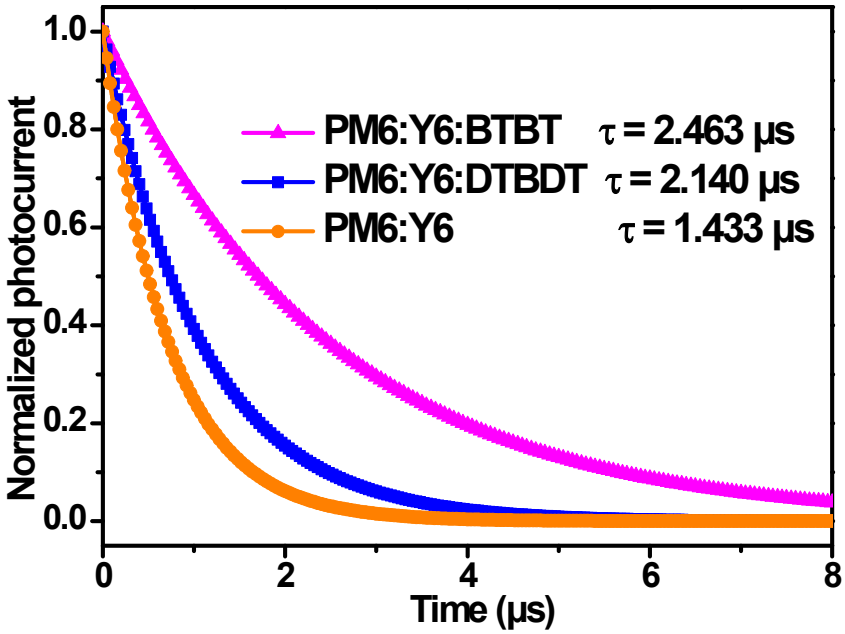

Figure S6 TPV measurements of the PM6:Y6-based PSCs processed with different additive treatment.

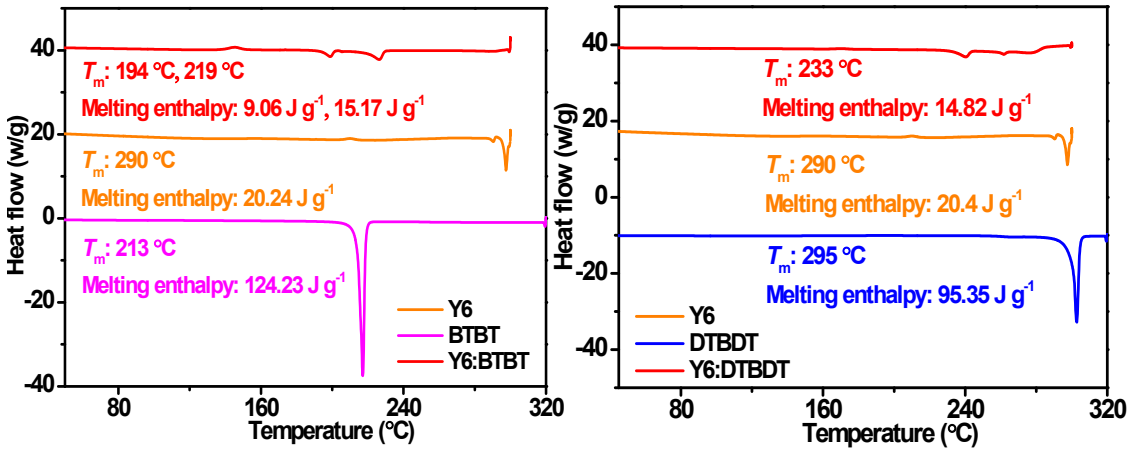

Figure **S7** (a) DSC thermograms (the first heating cycle) of BTBT, Y6, and Y6:BTBT (4:1, w/w), the mixtures were prepared by solution-cast method (dissolving the mixture of DIB and Y6 in *o*-XY and then removing the solvent). (b) DSC thermograms (the first heating cycle) of DTBDT, Y6, and Y6:DTBDT (4:1, w/w) by solution-cast method.

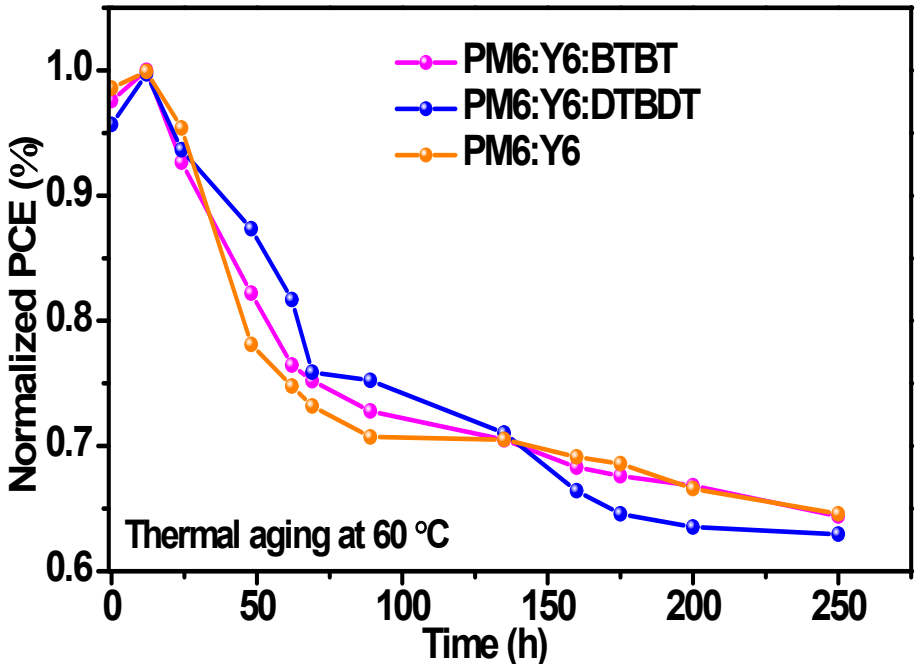

Figure S8 Normalized PCEs of PM6:Y6-based PSCs processed with different additive treatment over the 60 °C thermal aging time in a nitrogen-filled glovebox.