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Supporting Information

Green-solvent processable semiconducting polymers applicable in additives-free perovskite and polymer solar cells: molecular weights, photovoltaic performance, and thermal stability

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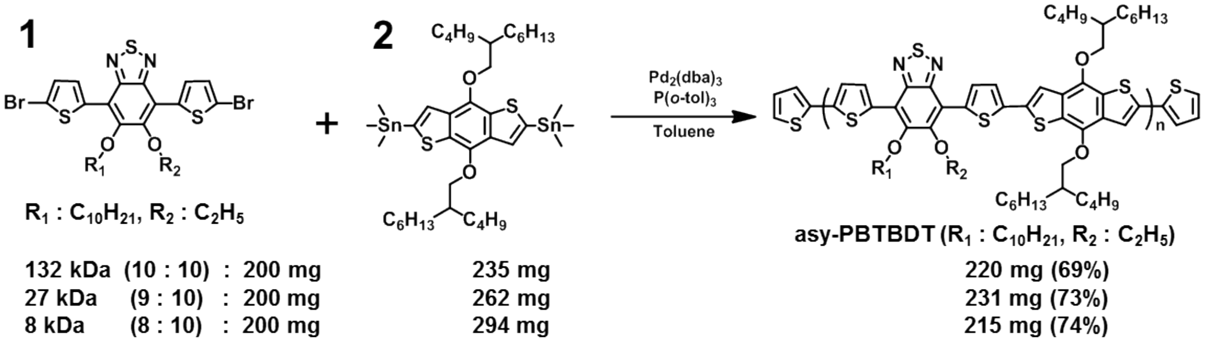
Experimental details

1. Synthesis details



Scheme S1. Synthesis scheme for the series of asy-PBTBDT.

1) Synthesis of the series of asy-PBTBDTs. Monomer 1 (4,7-bis(5-bromothiophen-2-yl)-5-(decyloxy)-6-ethoxybenzo[c][1,2,5]thiadiazole), Monomer 2 ((4,8-bis((2-butyloctyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane), Pd(dba) (1.8 mg, 0.002 mmol) and $P(o\text{-tol})_3$ (2.4 mg, 0.008mmol) are used for polymerization (at 170 ° C for 2 hours in microreactor).

132 kDa of asy-PBTBDT. Monomer 1 (200mg, 0.305 mmol), Monomer 2 (235 mg, 0.305 mmol) were used. GPC (CB, 40 °C): $M_n = 132.3$ K, $M_w = 310.9$ K, PDI = 2.35.

27 kDa of asy-PBTBDT. Monomer 1 (200mg, 0.305 mmol), Monomer 2 (262 mg, 0.344 mmol) were used. GPC (CB, 40 °C): $M_n = 27.4$ K, $M_w = 78.4$ K, PDI = 2.86.

8 kDa of asy-PBTBDT. Monomer 1 (200mg, 0.305 mmol), Monomer 2 (294 mg, 0.386 mmol) were used. GPC (CB, 40 °C): $M_n = 7.8$ K, $M_w = 18.8$ K, PDI = 2.41.

2) Solar cell fabrication. The FTO glass substrates were etched using zinc powder and HCl solution (2 M). Then, they were rinsed with detergent, DI water, Ace, and IPA, successively, the substrates were further cleaned with UV ozone treatment for 15 min. The spin-coated titanium oxide (S-TiO_2) compact layer was prepared by the following method. A solution of 0.5 mM TTIP in ethanol and 40 mM HCl solution in ethanol were slowly mixed together. The mixed solution was added dropwise onto the substrate and spin-coated at 2000 rpm for 1 min. The S-TiO_2 substrates were heated at 500 °C for 30 min. The mesoporous titanium oxide (m-TiO_2) layer was coated on S-TiO_2 substrates at 4000rpm for 20 s by using a diluted TiO_2 paste (150 mg ml-1 in EtOH) and annealed at 500°C for 30 min. Li ions doped on m-TiO_2 by spin coating of a 0.1 M solution of Li-TFSI in acetonitrile at 3000 rpm for 10 s followed by another sintering step at 450 °C for 30 min.. The precursor solution was prepared at ambient condition in a mixed solvent of DMF and DMSO; the volume ratio of DMF to DMSO was 4:1. The molar ratio for PbI2 /PbBr2 was fixed at 0.85:0.15, and the molar ratio for MABr /$PbBr_2$ was fixed at 1:1 and molar ratio for PbI_2/FAI was fixed at 1.1:1. CsI (1.5M in DMSO) was mixed 5 vol% in that solution. The spin-coating procedure was performed in a nitrogen flowing glovebox.

Perovskite precursor solution was spin-coated on the substrate at 1000 rpm for 10 s, 4000 rpm for 20s. CB was injected on the substrate 5 s prior to finish and then crystallized at 100 °C for 45 min in the glovebox. Polymer HTM in 2-MA was spin-coated on the perovskite layers in same method (15 mg/ml). Finally, a 100 nm gold electrode was vacuum-deposited on the HTM.

3) Device characterization. Using a Keithley 2400 SMU and an Oriel xenon lamp (450 W) with an AM1.5 filter, the solar cells were characterized in air under AM 1.5G illumination of 100 mW/cm^2 (Oriel 1 kW solar simulator), which was calibrated with a KG5 filter certified by National Renewable Energy Laboratory (NREL). The current density-voltage (J-V) curves of all devices (active area: 0.09 cm^2) were measured by 0.1 V/s of scan rate. The stabilized power output was measured under the maximum power point voltage.

4) SCLC measurement. Space charge limited current (SCLC) was measured to obtain hole mobility of asy-PBTBDT. Indium tin oxide (ITO)/PEDOT:PSS/asy-PBTBDTs/Au structure was constructed as a hole only device. ITO substrate was cleansed and UV-ozone treated. PEDOT:PSS was spin-coated on ITO substrate at 5000 rpm for 30 sec and then annealed at 140 °C. Previously prepared HTM solution was spin-coated to attain the 200 nm thickness layer. After drying, gold electrode (100 nm) was thermally evaporated in high vacuum condition. Obtained J-V curves were fitted to SCLC model to calculate the hole mobility using Child's law.

5) IPCE measurement. Constant 100 W Xenon lamp source with an automated monochromator filters and 0.76 mm x 1.0 mm rectangular spot size was used for incident-photon-to-current-efficiency (IPCE) spectra. The measurements were conducted in the wavelength range from 300 to 850 nm, chopped at 4 Hz (IQE-200B model).

6) PL measurement. Time-resolved and steady-state photoluminescence measurements were conducted using prepared samples: glass/perovskite or glass/perovskite/HTL. Time-resolved photoluminescence measurements were performed using time correlated single photon counting (TCSPC) system (HAMAMATSU/C11367-31). For TCSPC measurements, a pulsed laser source was laser diode with a wavelength of 474 nm, a repetition rate of 100 kHz, fluence of ~ 4 nJ/cm^2 and a pulse width of 70 ps. The samples were excited from the glass side under ambient conditions.

7) PSC fabrication and measurement. ITO coated glass substrates were cleaned with distilled water, acetone, and isopropanol by sonication sequentially. PEDOT:PSS (Baytron AI4083) was spin-coated onto the substrate and annealed at 140 °C for 10 min. The polymer (10 mg mL^{-1}) was blended with PC$_{71}$BM with a 1:1 weight ratio in 2-methylanisole. The blended solution was spin-cast on top of PEDOT:PSS in a N$_2$ filled glove box. The device was transferred to thermal evaporator, pumped down under vacuum (<10^{-6} Torr), and Al (100 nm) was deposited. The area of the Al electrode defines the active area of the device as 13.0 mm^2. Measurements were carried out inside the N$_2$ filled glove box by using a high quality optical fiber to guide the light from a solar simulator equipped with a Keithley 2635A source measurement unit. A mask (13.0 mm^2) made of a thin metal was attached for the photovoltaic characteristic measurements under AM 1.5 G illumination at 100 mW cm^{-2}. EQE measurements were performed using a PV measurement QE system using monochromatic light from a xenon lamp under ambient conditions. The monochromatic light was chopped at 100 Hz and the intensity was calibrated relative to a standard Si photodiode using a lock-in-amplifier.

8) Determination of absolute solubility. Saturated solutions of the polymers was prepared by stirring overnight at room temperature and centrifugation at 15000 rpm for ten minutes was used. The centrifuged solutions were subsequently diluted to obtain an optical density. The absolute solubility was calculated by using beer-lambert law comparing its optical density with known concentrations.

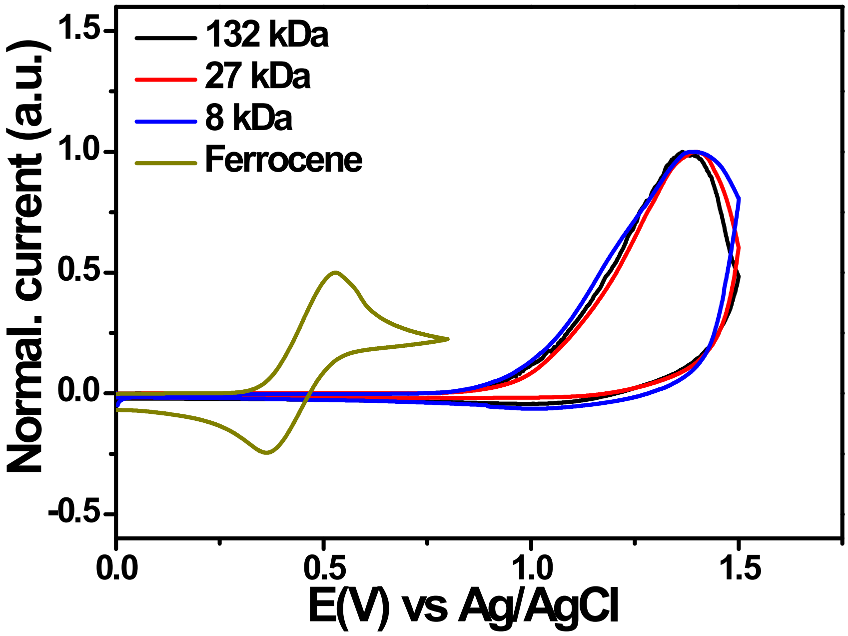


Fig. S1 Cyclic voltammogram (CV) of the series of asy-PBTBDTs

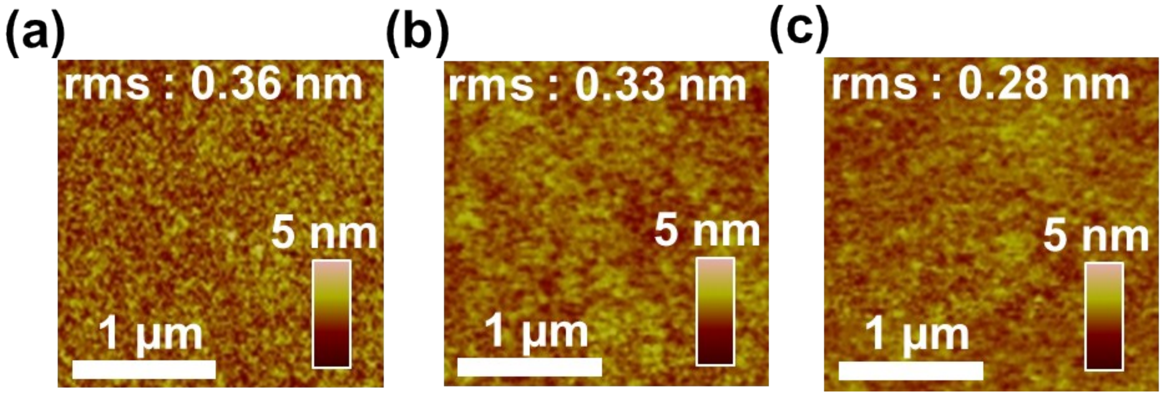


Fig. S2 Atomic force microscopy (AFM) images of asy-PBTBDTs on (a) 132 kDa, (b) 27 kDa, and (c) 8kDa

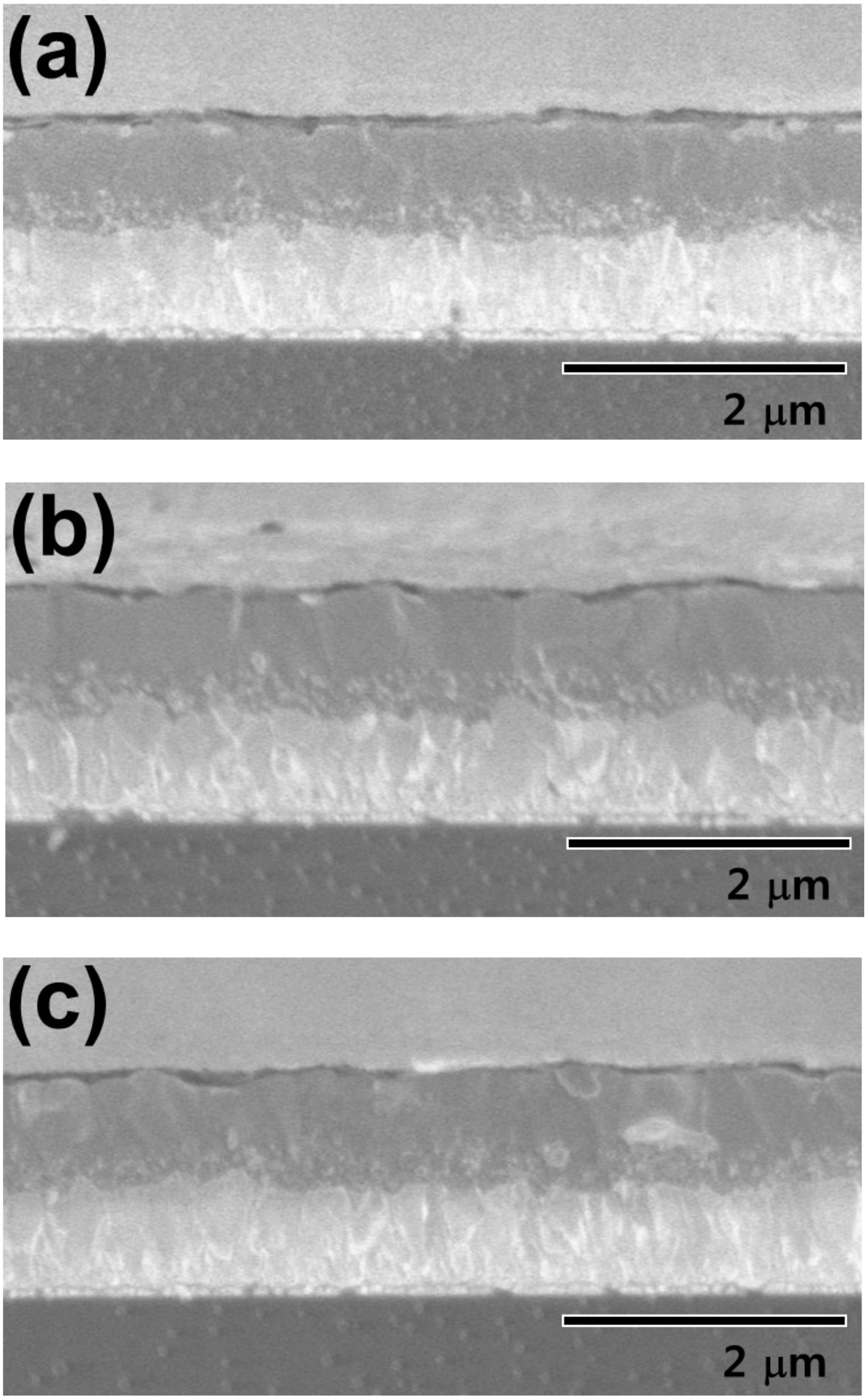


Fig. S3 Cross-sectional scanning electron microscopy (SEM) image of perovskite solar cells employing the asy-PBTBDT of (a) 132 kDa, (b) 27 kDa, and (c) 8 kDa MW

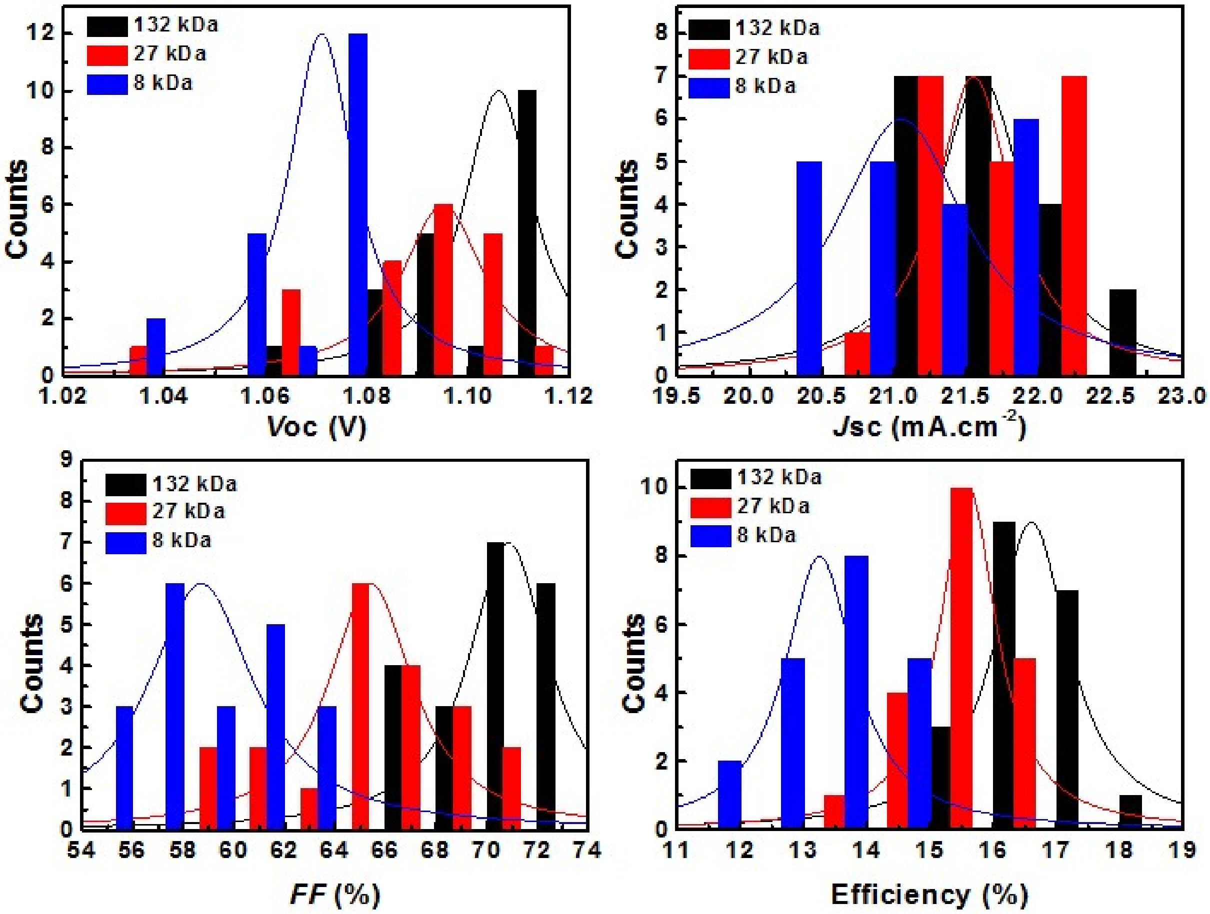


Fig. S4 Statics of perovskite solar cells devices for the series of dopant-free asy-PBTBDTs

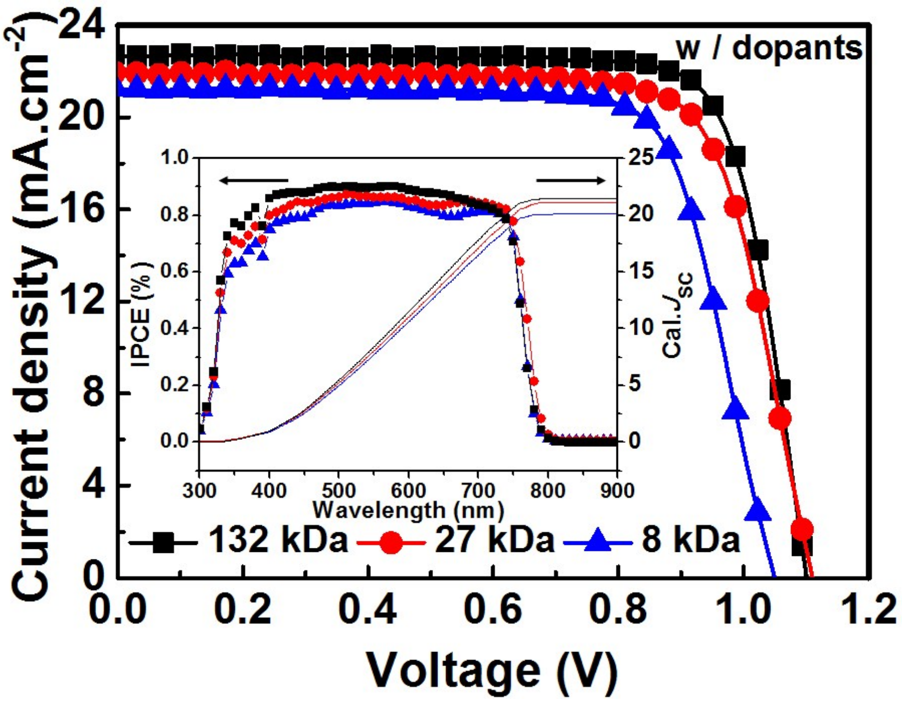


Fig. S5 J-V curve and IPCE of the perovskite solar cells with the series of doped asy-PBTBDTs

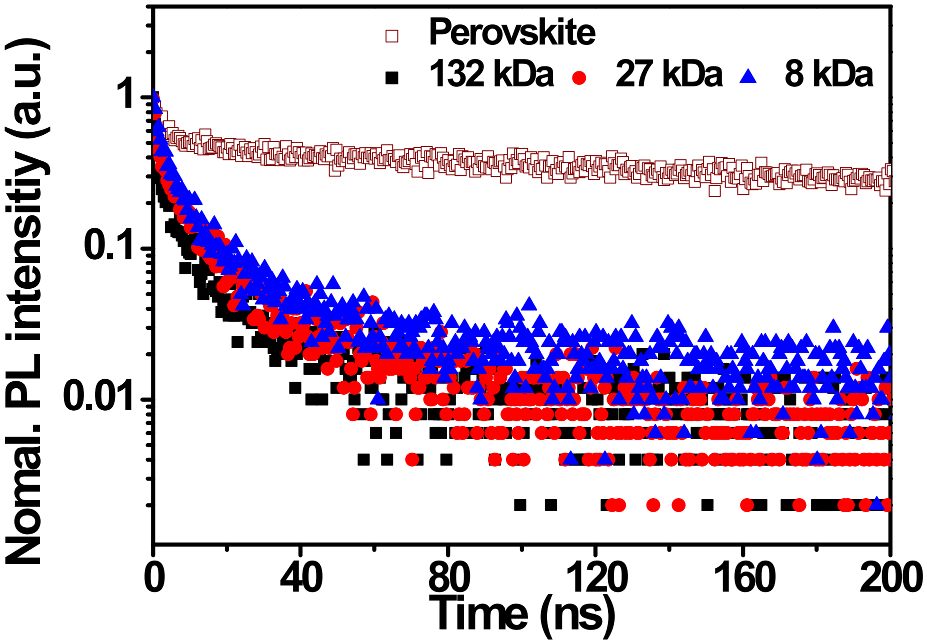


Fig. S6 Time-resolved photoluminescence (PL) of glass/perovskite and glass/perovskite/asy-PBTBDTs.

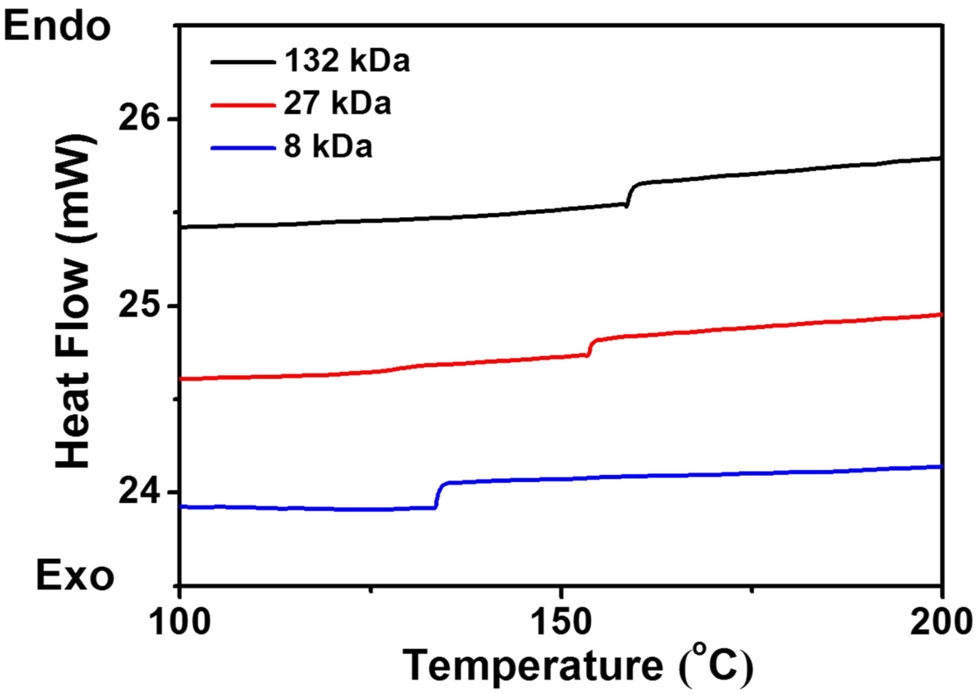


Fig. S7 Differential scanning calorimeter (DSC) profiles

Table S1 Summary of the polymeric, photoelectric, and electric properties for the series of asy-PBTBDTs

Polymer	Mn (g/mol)	PDI	Absorption in film		CV in film	In film		μ_h (w/ dopants) (10^3 cm^2/Vs)
			λ_{max} (nm)	ΔE_{gap} (eV)	E_{ox} (V)	HOMO (eV)	LUMO (eV)	
asy-PBTBDT	132.3k	2.35	610	1.81	1.00	-5.36	-3.55	4.91 (5.77)
	27.4k	2.86	603	1.81	1.01	-5.37	-3.56	3.12 (3.98)
	7.8k	2.41	572	1.81	0.97	-5.33	-3.52	1.64 (2.27)

Table S2 Summary of the photovoltaic parameters obtained from best devices using the doped asy-PBTBDTs. The average PCE (PCE$_{avg}$) of 20 devices is shown.

Device conditions	***PSC J-V curves***			
M.W. (Da)	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF* (%)	PCE (PCE$_{avg}$) (%)
132 k	22.7	1.10	79.7	20.0 (19.2)
27 k	22.0	1.13	75.6	18.4 (13.3)
8 k	21.3	1.05	74.6	16.8 (9.4)