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Supporting Information

Wide Band Gap Benzodithiophene-Benzothiadiazole Copolymers for Highly Efficient Multi-Junction Polymer Solar Cells

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1. Materials and methods

General Details: All synthetic procedures were performed under argon atmosphere. All reactants and reagents are commercially available and used as received, unless otherwise specified. Solvents were dried over 4 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotopes Laboratory and used as received. [60]PCBM (purity of 99%) and [70]PCBM (purity of 99%) were purchased from Solenne BV.

NMR: ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy spectra were recorded AT 400 MHz and 100 MHz, respectively, on a VARIAN mercury spectrometer at 25 °C unless otherwise noted. ^1H and ^{13}C NMR spectra are referenced to tetramethylsilane (TMS) using the residual solvent peak impurity of the given solvent. Chemical shifts are reported in ppm, multiplicity (s = singlet, d = doublet, dd = double doublet). The coupling constants in Hz were denoted as absolute values.

GPC: Molecular weights and polydispersity index (PDI) were determined with GPC at 140 °C on a PL-GPC 120 system using a PL-GEL 10 µm MIXED-B column and 1,2-dichlorobenzene (*o*-DCB) as the eluent against polystyrene standards. All the polymer samples were dissolved in *o*-DCB at 140 °C overnight and the solutions were filtered through PTFE filters (0.2 µm) prior to injection.

UV-vis: UV-visible spectroscopy were recorded on a PekinElmer Lambda 900 UV/vis/near IR spectrophotometer at room temperature unless otherwise noted. All solution UV-vis experiments were run in *o*-DCB with sample concentration of 0.05 mg/mL. Films were prepared by spin-coating *o*-DCB solutions on quartz substrates.

Electrochemistry: Cyclic voltammetry (CV) was conducted with a scan rate of 0.1 V/s under an inert atmosphere with 1 M tetrabutylammonium hexafluorophosphate in *o*-DCB as the electrolyte. The working electrode was indium tin oxide (ITO) bar and the counter electrode was a silver electrode. A silver wire coated with silver chloride (Ag/AgCl) was used as quasi-reference electrode in combination with Fc/Fc⁺ as an internal standard. The samples were spin-coated on top of ITO work electrode to form ~50 nm thickness films.

TEM: Transmission electron microscopy (TEM) was performed on a Tecnai G² Sphera transmission electron microscope (FEI) operated at 20 kV.

AFM: Atom force microscopy (AFM) was performed on an extended Veeco MultiMode AFM connected to a Nanoscope III controller in tapping mode using PPP-NCH-50 probes (Nanosensors).

2. Synthesis

The synthetic route of BDT-BT-2T, BDT-FBT-2T, BDT-BT-2Fu and BDT-FBT-2Fu was exhibited in **Figure S1**. 5,6-Dibromo-benzo[2,1,3]thiadiazole (**1**),^[1] 5,6-difluoro-4,7-diiodobenzo[2,1,3]thiadiazole (**2**),^[2] 4,7-di(thiophen-2-yl)benzo[2,1,3]thiadiazole (**5**),^[3] 4,7-di(thiophen-2-yl)-5,6-difluorobenzo[2,1,3]thiadiazole (**7**),^[2] 4,7-bis(5-bromothiophen-2-yl)benzo[2,1,3]thiadiazole (**9**),^[3] and 4,7-bis(5-bromothiophen-2-yl)-5,6-difluorobenzo[2,1,3]thiadiazole (**11**)^[2] were synthesized according to literature procedures. 2-(Tributylstannyl)thiophene (**3**) and 2-(tributylstannyl)furan (**4**) were purchased from Sigma

Aldrich. 2,6-Bis(trimethyltin)-4,8-di(2,3-didecylthiophen-5-yl)-benzo[1,2-*b*:4,5-*b'*]dithiophene (**13**) was purchased from SunaTech Inc.

Figure S1. The synthesis route of BDT-BT-2T, BDT-FBT-2T, BDT-BT-2Fu and BDT-FBT-2Fu.

4,7-Di(furan-2-yl)benzo[2,1,3]thiadiazole (6). In a 20 mL microwave reaction vessel, compound **1** (0.882 g, 3 mmol), excess of compound **4** (2.57 g, 7.2 mmol) and anhydrous THF (20 mL) were added. The mixture was then purged with argon for 15 minutes. Then, $\text{Pd(PPh}_3)_4$ (30 mg) was added and the vessel was sealed immediately. The vessel was put into a Biotage microwave reactor, and heated with the procedures: 60 °C for 1 minute, 90 °C for 1 minute, and 120 °C for 60 minutes. Upon cooling, the mixture was subjected to a silica gel column using a heptane/dichloromethane gradient. The product was further purified by recrystallization from methanol to afford compound **6** as orange needles (0.45 g, yield 56%). ^1H NMR (400 MHz, CDCl_3 , δ): 8.04 (s, 2H), 7.68-7.67 (dd, $J = 3.6, 0.6$ Hz, 2H), 7.59-7.58 (dd, $J = 1.8, 0.6$ Hz, 2H), 6.63-6.62 (dd, $J = 3.6, 1.8$ Hz, 2H); ^{13}C NMR (100 MHz,

CDCl_3 , δ): 151.30, 150.13, 142.81, 123.51, 121.76, 112.49, 112.15; MS (MALDI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_2\text{S}$, 268.29; found, 268.11.

4,7-Di(furan-2-yl)-5,6-difluorobenzo[2,1,3]thiadiazole (8). Compound **8** was synthesized as yellow solid with the yield of 86% according to the method of compound **6** described above using compound **2** instead of compound **1**. ^1H NMR (400 MHz, CDCl_3 , δ): 7.74 (dd, $J = 1.8$, 0.6 Hz, 2H), 7.58-7.57 (d, $J = 3.6$ Hz, 2H), 6.68-6.67 (dd, $J = 3.6$, 1.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 144.14, 130.37, 130.21, 120.58, 120.42, 115.20, 112.05; MS (MALDI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_6\text{F}_2\text{N}_2\text{O}_2\text{S}$, 304.27; found, 304.07.

4,7-Bis(2-bromo-5-furan-2-yl)benzo[2,1,3]thiadiazole (10). *N*-bromosuccinimide (NBS) (621 mg, 3.49 mmol) were portion-wisely added into compound **6** (425 mg, 1.59 mmol) in THF (20 mL) under stirring at 0 °C. The reaction mixture was stirred at room temperature for overnight, then the red-orange solid was filtered. Upon cooling, the mixture was subjected to a silica gel column using a heptane/dichloromethane gradient. The collected solid was recrystallized repeatedly from methanol to afford compound **10** as bright orange needles (297 mg, yield 44%). ^1H NMR (400 MHz, CDCl_3 , δ): 7.99 (s, 2H), 7.65-7.64 (d, $J = 3.60$ Hz, 2H), 6.55-6.54 (d, $J = 3.60$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 151.98, 150.76, 123.36, 120.90, 114.79, 114.37, 107.61; MS (MALDI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_6\text{Br}_2\text{N}_2\text{O}_2\text{S}$, 426.08; found, 425.86.

4,7-Bis(2-bromo-5-furan-2-yl)-5,6-difluorobenzo[2,1,3]thiadiazole (12). Compound **12** was synthesized as orange-brown needles with the yield of 74% according to the method of compound **10** described above using compound **8** instead of compound **6**. ^1H NMR (400 MHz, CDCl_3 , δ): 7.59-7.58 (d, $J = 3.60$ Hz, 2H), 6.59-6.58 (d, $J = 3.60$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 147.84, 147.64, 147.24, 147.13, 124.71, 117.71, 113.98; MS (MALDI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_4\text{Br}_2\text{F}_2\text{N}_2\text{O}_2\text{S}$, 462.06; found, 461.84.

Poly{(4,8-di(2,3-didecylthiophen-5-yl)-benzo[1,2-b:4,5-b']dithiophen-2,6-diyl)-alt-((4,7-di(thiophen-2-yl)benzo[2,1,3]thiadiazole)-5,5'-diyl)} (BDT-BT-2T). To a degassed solution of monomer 9 (36.66 mg, 0.080 mmol), 13 (99.30 mg, 0.080 mmol) in anhydrous toluene (2 mL) and anhydrous DMF (0.2 mL), tris(dibenzylideneacetone)-dipalladium(0) (2.19 mg, 0.0024 mmol) and tri(o-tolylphosphine) (5.84 mg, 0.0192 mmol) were added. The mixture was stirred at 120 °C for 18 hours, after which 2-(tributylstannyl)thiophene and 2-bromothiophene were sequentially added to the reaction with 2 hours interval. After another 2 hour, the reaction mixture was diluted with o-DCB, and refluxed with EDTA (100 mg) and water (2 mL) for 2 hours. Upon cooling, the reaction mixture was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was subjected to sequential Soxhlet extraction with acetone, hexane, dichloromethane, chloroform under argon protection. The residue in the thimble was dissolved in o-DCB at 140 °C for 2 hours, filtered hot, concentrated and precipitated in methanol to obtain BDT-BT-2T as a dark shiny solid (80 mg, yield 82%). $M_n = 47.6$ kg/mol, PDI = 2.7.

Poly{(4,8-di(2,3-didecylthiophen-5-yl)-benzo[1,2-b:4,5-b']dithiophen-2,6-diyl)-alt-((4,7-di(thiophen-2-yl)-5,6-difluorobenzo[2,1,3]thiadiazole)-5,5'-diyl)} (BDT-FBT-2T). BDT-FBT-2T was synthesized as a dark shiny solid with the yield of 80% according to the method of BDT-BT-2T described above using monomer 11 instead of compound 9. $M_n = 65.2$ kg/mol, PDI = 2.1.

The relative low molecular weight batch ($M_n = 45.5$ kg/mol, PDI = 2.4) was synthesized by control the stoichiometric ration of two relevant monomers, while extra-high molecular weight batch ($M_n = 108.8$ kg/mol, PDI = 4.2) was obtained by using the further purified catalyst of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ and 1,2,4-trimethylbenzene as solvent to delay the gelling point in the copolymerization.

Poly{(4,8-di(2,3-didecylthiophen-5-yl)-benzo[1,2-b:4,5-b']dithiophen-2,6-diyl)-alt-((4,7-di(furan-2-yl)benzo[2,1,3]thiadiazole)-5,5'-diyl)} (BDT-BT-2Fu). BDT-BT-2Fu was synthesized as a dark solid with the yield of 64% according to the method of BDT-BT-2T described above using monomer 10 instead of compound 9. The polymer can be totally washed away by chloroform during Soxhlet extraction, the chloroform fraction was thus collected. $M_n = 25.5$ kg/mol, PDI = 2.2.

Poly{(4,8-di(2,3-didecylthiophen-5-yl)-benzo[1,2-b:4,5-b']dithiophen-2,6-diyl)-alt-((4,7-di(furan-2-yl)-5,6-difluorobenzo[2,1,3]thiadiazole)-5,5'-diyl)} (BDT-FBT-2Fu). BDT-FBT-2Fu was synthesized as a dark shiny solid with the yield of 98% according to the method of BDT-BT-2T described above using monomer 12 instead of compound 9. $M_n = 34.5$ kg/mol, PDI = 2.3.

3. Device fabrication and characterization

Field-effect transistors (FETs): Field-effect transistors were prepared in a bottom-contact top-gate configuration on pre-cleaned glass substrates. Source and drain contacts were defined by evaporating chromium (2 nm) and gold (40 nm) through a shadow mask. Subsequently, the polymer was applied by spin coating in a nitrogen-filled glove-box from a 3 mg/mL solution in *o*-DCB, at room temperature, for 60 s at 1500 rpm. BDT-FBT-2T was spin coated from a solution at 120 °C. The polymer film was annealed at 200 °C for 20 min and cooled down to room temperature slowly. Next, a layer of Cytop was spin coated as gate dielectric. This spin coating step was performed at 1500 rpm for 60 s in a nitrogen-filled glove box. The Cytop was annealed at 80 °C for 10 min and at 200 °C for 15 min. The top gate electrode was applied by thermal evaporating gold (40 nm) through a shadow mask. The transistors were electrically characterized with a Keithley 2636 measuring unit. The length and the width of the transistor channel are 100 μ m and 1000 μ m, respectively.

Single-junction solar cells: Single-junction photovoltaic devices were made by spin coating poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP AI 4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates in air ($14\ \Omega$ per square) (Naranjo Substrates). The polymer-fullerene photoactive layers were deposited by spin coating in air from the solutions containing corresponding polymers and [60]PCBM or [70]PCBM with different content ratio. The polymer/fullerene blends for BDT-BT-2T, BDT-BT-2Fu and BDT-FBT-2Fu were dissolved in *o*-DCB at $60\ ^\circ\text{C}$ for overnight and spin-coated at room temperature. BDT-FBT-2T:[70]PCBM blend was dissolved in chlorobenzene/1-chloronaphthalene (9/1, v/v) solvent mixture at $60\ ^\circ\text{C}$ for 2 hrs and spin-coated from hot solution. The thickness of active layer films was controlled by spin speed. LiF (1 nm) and Al (100 nm) were deposited by vacuum evaporation at $\sim 3 \times 10^{-7}$ mbar as the back electrode. The active area of the cells was 0.09 or $0.16\ \text{cm}^2$, which provided similar results. The fabrication of PMDPP3T:[60]PCBM single junction solar cells adopted the previously established procedures.^[4]

Optical and Electrical Modeling: Prediction of the performance of tandem and triple-junction cells was carried out as described earlier.^[5] In short: For a series of single-junction cells the performance as a function of photoactive layer thickness was determined. From these data the internal quantum efficiency and the shape of the $J-V$ as a function of layer thickness were extracted. Optical modeling using the transfer matrix formalism with a commercial software package SETFOS 3 (Fluxim) combined with the IQE data provides the current generation capacity in each subcell, depending on the exact layout of the optical stack. Combining these current generation capacities with the relevant $J-V$ shape with the subcell $J-V$'s according to Kirchhoff's law provides the $J-V$ characteristics for the tandem for any given thickness combination. The optical parameters of BDT-FBT-2T:[70]PCBM blends for these calculations were determined from reflection/transmission measurement on active layers

on quartz. The optical data for PMDPP3T:[60]PCBM were obtained from our previously published paper.^[4] The modeling results for the tandem cell are shown in Figure S12.

Tandem solar cells: Tandem solar cells were obtained by solution processing an intermediate contact consisting of ZnO nanoparticles^[6] and pH neutral PEDOT:PSS on the BDT-FBT-2T:PC₇₀BM active layer that was prepared as described above for single-junction cells. The ZnO layer was spun in nitrogen atmosphere from a solution of 10 mg mL⁻¹ ZnO nanoparticles in isopropanol. The pH neutral PEDOT:PSS (Orgacon, Agfa) was diluted 1:1 with ultrapure water after which 0.2 mL mL⁻¹ isopropanol was added to improve the wetting on the ZnO nanoparticles. Prior to spin casting in air the solution was filtered using a 5.0 µm Whatman Puradisc FP30 syringe filter. The PMDPP3T:[60]PCBM active layer was spun on top of the pH neutral PEDOT:PSS in air. Finally a back contact of 1 nm LiF and 100 nm Al was evaporated in vacuum for all devices. Device areas of 0.09 and 0.16 cm² were used, which provided similar results.

External quantum efficiency: EQE measurements were done in a homebuilt set-up, with the devices kept in a nitrogen filled box with a quartz window and illuminated through an aperture of 2 mm. Mechanically modulated (Stanford Research, SR 540) monochromatic (Oriel, Cornerstone 130) light from a 50 W tungsten halogen lamp (Osram 64610) was used as probe light, in combination with continuous bias light from a solid state laser (B&W Tek Inc. 532 nm, 30 mW and 780 nm, 21 mW). The intensity of the bias laser light was adjusted using a variable-neutral density filter. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford Research Systems SR 830). For all the single junction devices and the PMDPP3T:[60]PCBM subcell, the measurement was carried out under representative illumination intensity (AM1.5G equivalent, provided by the 532 nm laser). For the BDT-FBT-2T:[70]PCBM subcell, the measured EQE was mathematically corrected for the intensity difference between the monochromatic light and AM1.5G. For the

tandem subcells, a compensating electrical bias was applied by the lock-in amplifier to ensure short-circuit conditions in the respective subcells during the spectral response measurements. More details can be found in literatures.^[7]

Current-density – voltage characteristics: J – V curves were measured under simulated solar light (100 mW cm^{-2}) from a tungsten–halogen lamp filtered by a Hoya LB100 daylight using a Keithley 2400 source meter. No mismatch correction was done. For single-junction cells the accurate short-circuit current density (J_{sc}) was determined from the EQE by convolution with the AM 1.5G solar spectrum. For the tandem solar cell measurements, the simulated solar light spectrum was tuned to provide appropriate illumination to each subcell. This was achieved by adjusting the voltage over the tungsten halogen lamp and the distance to the sample in such a way that both the wide band-gap and the narrow band-gap single-junction reference cell gave the exact J_{sc} as determined from the EQE measurement. The J – V curves of the tandem solar cells were measured under illumination through a mask of identical dimensions to the device area determined by the overlap of the ITO and Al electrodes, to avoid extra current generation due to the high lateral conductivity of the pH neutral PEDOT:PSS.^[8]

4. Additional Figures and Tables

Table S1. Electrochemical properties of BDT-BT-2T, BDT-FBT-2T, BDT-BT-2Fu, and BDT-FBT-2Fu.

Polymer	E_{ox}^a (V)	HOMO ^b (eV)	E_{red}^a (V)	LUMO ^b (eV)	E_{g}^{CV} (eV)
BDT-BT-2T	-0.05	-5.18	-1.68	-3.55	1.63
BDT-FBT-2T	0.10	-5.33	-1.60	-3.63	1.70
BDT-BT-2Fu	0.13	-5.36	-1.64	-3.59	1.77
BDT-FBT-2Fu	0.05	-5.28	-1.63	-3.60	1.68

^a Versus Fc/Fc⁺. ^b Determined using a work function value of -5.23 eV for Fc/Fc⁺.

Figure S2. Cyclic voltammograms of BDT-BT-2T, BDT-FBT-2T, BDT-BT-2Fu, BDT-FBT-2Fu, and ferrocene in *o*-DCB.

Figure S3. Transfer characteristics of FETs of BDT-BT-2T (a), BDT-FBT-2T (b), BDT-BT-2Fu (c), and BDT-FBT-2Fu (d).

Figure S4. Bright field TEM images of the optimized blend films for BDT-BT-2T:[70]PCBM (a, e), BDT-FBT-2T:[70]PCBM (b, f), BDT-BT-2Fu:[70]PCBM (c, g), and BDT-FBT-2Fu:[60]PCBM (d, h). (a, b, c, d) Image size: $1.5 \times 1.5 \mu\text{m}^2$; scale bar: 200 nm. (e, f, g, h) Image size: $350 \times 350 \text{ nm}^2$; scale bar: 50 nm.

Figure S5. AFM height images ($5 \times 5 \mu\text{m}^2$, vertical scale 20 nm) of the optimized blend films for BDT-BT-2T:[70]PCBM (a), BDT-FBT-2T:[70]PCBM (b), BDT-BT-2Fu:[70]PCBM (c), and BDT-FBT-2Fu:[60]PCBM (d). The root mean square roughness (R_q) of these films is 1.17, 1.06, 1.75, and 1.33 nm from (a) to (d).

Table S2. Solar cell performances of BDT-FBT-2T:[70]PCBM single-junction solar cells fabricated from different conditions under illumination of simulated AM1.5G (100 mW cm⁻²).

Solvent	Thickness (nm)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
CB	116	10.2	0.83	0.65	5.5
CB/CN (95/5)	88	9.4	0.84	0.66	5.2
CB/CN (90/10)	127	10.6	0.85	0.7	6.3
CB/CN (85/15)	125	10.5	0.84	0.67	5.9
CB/CN (80/20)	143	10.5	0.84	0.65	5.7
CB/CN (75/25)	156	10.4	0.84	0.70	6.2
CB/CN (70/30)	140	10.4	0.83	0.67	5.8
<i>o</i> -DCB/CN (95/5)	130	10.5	0.85	0.70	6.2
<i>o</i> -DCB/CN (90/10)	140	10.5	0.85	0.66	5.8
<i>o</i> -DCB/CN (85/15)	125	10.6	0.85	0.70	6.3
<i>o</i> -DCB/CN (80/20)	101	10.2	0.85	0.70	6.0
<i>o</i> -DCB/CN (75/25)	120	10.7	0.85	0.67	6.1
<i>o</i> -DCB/CN (70/30)	98	9.8	0.84	0.68	5.6

Table S3. Performance parameters of single-junction PSCs based on BDT-BT-2T, BDT-FBT-2T, BDT-BT-2Fu and BDT-FBT-2Fu.^a

Polymer	J_{sc} (mA cm ⁻²) ^a	J_{sc} (mA cm ⁻²) ^b	V_{oc} (V) ^c	FF (-) ^c	PCE (%) ^d
BDT-BT-2T	11.2	10.6	0.75 (0.75)	0.64 (0.64)	5.4 (5.0)
BDT-FBT-2T	13.3	12.4	0.85 (0.85)	0.68 (0.67)	7.7 (7.0)
BDT-BT-2Fu	7.9	8.6	0.86 (0.85)	0.55 (0.55)	3.7 (4.1)
BDT-FBT-2Fu	8.7	8.1	0.86 (0.86)	0.59 (0.59)	4.4 (4.1)

^aDetermined from the integration of the EQE. ^bAverage value from $J - V$ characteristic for 4 devices. ^cAverage values from 4 devices in parenthesis. ^dDetermined using J_{sc} based on EQE, numbers in parenthesis are average values for 4 devices based on J_{sc} from $J - V$. It should be noted that the deviation of the data from $J - V$ measurement and EQE integration are different for different polymers due to the intensity and spectral variations of illuminated light during $J - V$ measurements.

Table S4. Solar cell performances and external quantum efficiency (EQE) maxima of BDT-FBT-2T:[70]PCBM single-junction solar cells with various active layer thicknesses under illumination of simulated AM1.5G (100 mW cm^{-2}).

Thickness (nm)	J_{sc}^a (mA cm^{-2})	J_{sc}^b (mA cm^{-2})	V_{oc}^c (V)	FF ^c	PCE ^d (%)	EQE _{max}
89	11.9	11.7	0.85 (0.85)	0.66 (0.64)	6.6 (6.4)	0.67
100	13.3	12.4	0.85 (0.85)	0.68 (0.67)	7.7 (7.0)	0.72
121	12.8	12.9	0.86 (0.86)	0.69 (0.69)	7.6 (7.6)	0.70
144	12.3	12.2	0.84 (0.84)	0.67 (0.66)	6.9 (6.8)	0.64
165	11.9	12.3	0.85 (0.85)	0.68 (0.66)	6.8 (6.8)	0.63
191	13.3	13.0	0.84 (0.84)	0.65 (0.65)	7.1 (7.1)	0.73
218	14.0	14.4	0.84 (0.84)	0.63 (0.63)	7.4 (7.6)	0.74
246	14.9	14.7	0.84 (0.84)	0.61 (0.61)	7.7 (7.5)	0.76

^aDetermined from the integration of the EQE. ^bAverage value from $J - V$ characteristic for 4 devices. ^cAverage values from 4 devices in parenthesis. ^dDetermined using J_{sc} based on EQE, numbers in parenthesis are average values for 4 devices based on J_{sc} from $J - V$. It should be noted that the deviation of the data from $J - V$ measurement and EQE integration are different for different polymers due to the intensity and spectral variations of illuminated light during $J - V$ measurements.

Figure S6. Current density – voltage characteristics of BDT-FBT-2T:[70]PCBM single-junction solar cells with various active layer thickness under illumination of simulated AM1.5G (100 mW cm^{-2}).

Figure S7. $J-V$ characteristics under illumination of simulated AM1.5G (100 mW cm^{-2}) and corresponding EQE spectra of single-junction solar cells upon active layer thickness variation of BDT-BT-2T (a, b), BDT-BT-2Fu (c, d), and BDT-FBT-2Fu (e, f). [70]PCBM was used as acceptor for all devices.

Figure S8. Refractive index (n) and extinction coefficient (k) of BDT-FBT-2T:[70]PCBM (1:1.5) blend film vs. wavelength

Figure S9. $J - V$ characteristics under illumination of simulated AM1.5G (100 mW cm^{-2}) (a) and EQE spectra (b) of BDT-FBT-2T:[70]PCBM single-junction solar cells with different molecular weight batches of BDT-FBT-2T.

Table S5. Solar cell performances and EQE maxima of BDT-FBT-2T:[70]PCBM single-junction solar cells with different molecular weight batches of BDT-FBT-2T.

M_n (kDa)	PDI	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)	EQE _{max}	Thickness (nm)
45.5	2.4	12.2	0.84	0.67	6.9	0.64	129
65.2	2.1	13.3	0.85	0.68	7.7	0.72	100
108.8	4.2	12.0	0.84	0.66	6.7	0.63	92

Figure S10. Thickness dependences of $J - V$ characteristics (recorded with simulated AM1.5G (100 mW cm⁻²)) and EQE response of single-junction solar cells of BDT-FBT-2T:[70]PCBM with low molecular weight (a, b) and extra-high molecular weight (c, d) of BDT-FBT-2T.

Table S6. Thickness dependences of solar cell performances and EQE response of single-junction solar cells of BDT-FBT-2T:[70]PCBM with low molecular weight and extra-high molecular weight of BDT-FBT-2T.

M_n (kg/mol)	Thickness (nm)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)	EQE _{max}
45.5	107	11.6	0.84	0.66	6.3	0.65
	129	12.2	0.84	0.67	6.9	0.64
	174	11.2	0.84	0.63	5.9	0.62
	194	12.2	0.84	0.64	6.5	0.70
	234	13.5	0.84	0.59	6.7	0.70
	347	12.2	0.83	0.50	5.1	0.62
108.8	92	12.0	0.84	0.66	6.7	0.63
	105	12.3	0.84	0.64	6.6	0.63
	119	12.4	0.84	0.63	6.6	0.63
	137	11.9	0.84	0.65	6.5	0.62
	175	12.1	0.84	0.61	6.2	0.68
	209	13.2	0.84	0.59	6.5	0.72
	299	12.8	0.83	0.52	5.4	0.61

Figure S11. (a) Chemical structure of PMDPP3T; (b) Device structure of tandem solar cells.

Figure S12. Predicted photovoltaic parameters for tandem cells as a function of the thickness of the BDT-FBT-2T:[70]PCBM front subcell and the PMDPP3T:[60]PCBM back subcell.

Table S7. Solar cell performances of tandem PSCs with different subcell thickness.^a

d_{front} (nm) ^b	d_{back} (nm) ^c	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
123	121	8.9 (8.8)	1.42 (1.42)	0.63 (0.63)	7.9 (7.9)
144	121	9.5 (9.3)	1.42 (1.42)	0.64 (0.64)	8.7 (8.4)
153	121	10.1 (9.9)	1.42 (1.42)	0.62 (0.62)	8.9 (8.7)
153	133	9.9 (9.9)	1.39 (1.39)	0.60 (0.58)	8.3 (7.9)

^aAverage values from 6 devices are given in parentheses. ^bThickness of front subcell (WBG cell). ^cThickness of back subcell (NBG cell).

5. References

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