Supporting Information for

High-efficiency photovoltaic cells with wide optical band gap polymers based

on fluorinated phenylene-alkoxybenzothiadiazole

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Material Syntheses

5,6-Difluorobenzo[c][1,2,5]thiadiazole was purchased from *Newell* Company. All other chemicals were purchased from Aldrich, Alfa Aesar and TCI Chemical Co. A series of 1,4-Bis(5-trimethylstannylthiophen-2-yl)benzene derivatives were synthesized by modifying the previous literatures.¹

Syntheses of monomers



5,6-Bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole (11).

2-Hexyldecanol (7.0 g, 29 mmol) was added into 2-neck round bottom flask containing 200 mL anhydrous *N*,*N*-dimethylformamide (DMF) under argon. After cooling down to 0 °C, sodium hydride (1.16 g, 29 mmol, 60% dispersion in paraffin) was added as one portion and the reaction mixture was stirred for 1 h at 0 °C. 5,6-Difluorobenzo[c][1,2,5]thiadiazole (2.0 g, 11.6 mmol) was added and the reaction mixture was warmed up to room temperature. After stirring overnight, the mixture was quenched by addition of 100 mL water and extracted with diethyl ether. The organic extract was dried over anhydrous magnesium sulfate and concentrated by rotary evaporator. The crude product was purified by column chromatography on silica gel using dichloromethane:hexane (1:3, by volume) as eluent, yielding a colorless oil (7 g, 98% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.11 (s, 2H), 3.95 (d, J= 5.3 Hz, 4H), 1.89 (m, 2H), 1.28 (m, 48H), 0.87 (m, 12H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 154.52, 151.41, 97.96, 71.41, 37.81, 31.91, 31.87, 31.35, 30.06, 29.72, 29.63, 29.37, 26.88, 26.85, 22.68, 14.11. MS (EI): Calcd m/z = 616.5; found M⁺= 617.



4,7-dibromo-5,6-bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole (M21).

Bromine (1.7)mL, 34.0 mmol) added solution of 5,6-bis((2was into а hexyldecyl)oxy)benzo[c][1,2,5]thiadiazole (7.0 g, 11.3 mmol) in a mixture of dichloromethane:acetic acid (200 mL : 100 mL) at room temperature. After stirring overnight under dark, the mixture was quenched by addition of aq. sodium sulfite solution and then extracted with diethyl ether ($100 \text{ mL} \times 3 \text{ times}$). The organic phase was dried over anhydrous magnesium sulfate then concentrated. The crude product was purified by silica gel column chromatography using dichloromethane:hexane (1:4, by volume) as eluent. After evaporation of solvent, 7.1 g of colorless oil was obtained (81% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.02 (d, J= 6.1 Hz, 4H), 1.92 (m, 2H), 1.56 (m, 4H), 1.30 (m, 44H), 0.89 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.84, 150.39, 106.01, 78.43, 39.22, 31.94, 1.09, 30.12, 29.79, 29.68, 29.39, 26.92, 26.89, 22.71, 14.13. MS (EI): Calcd m/z = 774.3; found $(M+1)^+ = 775$.



1,4-Bis(thiophen-2-yl)benzene (31).

1,4-Dibromobenzene (3 g, 12.7 mmol) and 2-(tributylstannyl)thiophene (12.3 g, 33.0 mmol) were added into a 2-neck round bottom flask. The reaction mixture was purged with argon and anhydrous tetrahydrofuran (100 mL) and tetrakis(triphenylphosphine)palladium(0) (730 mg) were added. After purging for another 10 min, the reaction mixture was heated at 90 °C for 24 h under argon. After cooling down the reaction solution to room temperature, the mixture was concentrated and passed through a short silica gel column by eluting with hexane and then with dichloromethane. The residue was recrystallized from hexane to obtain 2.26 g of colorless crystal (79% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.61 (s, 4H), 7.33 (d, J= 3.3 Hz, 2H), 7.28 (d, J= 5.0 Hz, 2H), 7.08 (t, J= 4.2 Hz, 2H). MS (EI): Calcd m/z = 242.0; found M⁺ = 242.



1,4-Bis(5-(trimethylstannyl)thiophen-2-yl)benzene (M41).

1,4-Bis(thiophen-2-yl)benzene (1.0 g, 4.13 mmol) was dissolved in 100 mL anhydrous THF under argon. The solution was cooled down to -78 °C with a dry ice–acetone bath, and 1.6 M *n*-BuLi solution in hexane (6.5 mL, 10.3 mmol) was added dropwise for 10 min. After stirring at -78 °C for 1 h, trimethyltin chloride solution (10.3 mL, 10.3 mmol, 1 M in THF) was added rapidly. The mixture was allowed to warm up to room temperature and stirred overnight. The reaction was quenched by addition of 50 mL cold water and extracted with dichloromethane three times. The organic extract was washed with water twice and then dried by anhydrous magnesium sulfate. After removing the solvent under vacuum, recrystallization of the residue from hexane twice yielded the compound **M41** (1.75 g, 75%) as a pale green crystal. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.62 (s, 4H), 7.45 (d, J= 3.4 Hz, 2H), 7.18 (d, J= 3.4 Hz, 2H), 0.41 (t, J= 28.2 Hz, 18H). MS (EI): Calcd m/z = 568.0; found M⁺ = 568.



1,4-Bis(thiophen-2-yl)-2-fluorobenzene (32).

1,4-Dibromo-2-fluorobenzene (3 g, 11.8 mmol) and 2-(tributylstannyl)thiophene (11.5 g, 30.7 mmol) were added in a 2-neck round bottom flask. The mixture was purged with argon and anhydrous THF (100 mL) and tetrakis(triphenylphosphine)palladium(0) (680 mg) were added. The compound **32** was prepared similarly as described for **31**. The crude compound was recrystallized from methanol to obtain 1.85 g of colorless crystal (60% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.63 (t, J= 8.6 Hz, 1H), 7.50 (d, J= 3.8 Hz, 1H), 7.38 (m, 5H), 7.11 (m, 2H). MS (EI): Calcd m/z = 260.0; found M⁺ = 260.



1,4-Bis(5-(trimethylstannyl)thiophen-2-yl)-2-fluorobenzene (M42).

1,4-Bis(thiophen-2-yl)-2-fluorobenzene (1.0 g, 3.84 mmol) was dissolved in 100 mL anhydrous THF under argon. The solution was cooled down to -78 °C using a dry ice–acetone bath, and 1.6 M *n*-BuLi in hexane (6.0 mL, 9.6 mmol) was added dropwise for 10 min. After stirring at -78 °C for 1 h, trimethyltin chloride solution (9.6 mL, 9.6 mmol, 1 M in THF) was added rapidly. **M42** was prepared similarly as described for **M41**. Recrystallization from ethanol yielded the compound **M42** (1.65 g, 73%) as a pale yellow crystal. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.61 (m, 2H), 7.40 (m, 3H), 7.20 (m, 2H), 0.40 (t, J= 28.2 Hz, 18H). MS (EI): Calcd m/z = 586.0; found M⁺ = 586.



1,4-Bis(thiophen-2-yl)-2,3-difluorobenzene (33).

1,4-Dibromo-2,3-difluorobenzene (3 g, 11.0 mmol) and 2-(tributylstannyl)thiophene (10.7 g, 28.7 mmol) were added in a 2-neck round bottom flask. The mixture was purged with argon and anhydrous THF (100 mL) and tetrakis(triphenylphosphine)palladium(0) (640 mg) were added. The compound **33** was prepared similarly as described for **31**. The crude compound was recrystallized from ethanol to obtain 1.63 g of a colorless crystal (53% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.53 (d, J= 3.6 Hz, 2H), 7.40 (m, 4H), 7.14 (m, 2H). MS (EI): Calcd m/z = 278.0; found M⁺ = 278.



1,4-Bis(5-(trimethylstannyl)thiophen-2-yl)-2,3-difluorobenzene (M43).

1,4-Bis(thiophen-2-yl)-2,3-difluorobenzene (0.8 g, 2.87 mmol) was dissolved in 100 mL anhydrous THF under argon. **M43** was prepared similarly as described for **M41** as a pale yellow needle crystal (1.42 g, 82%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.61 (d, J= 3.3 Hz, 2H), 7.38 (d, J= 4.7 Hz, 2H), 7.22 (d, J= 3.6 Hz, 2H), 0.41 (t, J= 28 Hz, 18H). MS (EI): Calcd m/z = 604.0; found M⁺ = 604.



1,4-bis(thiophen-2-yl)-2,5-difluorobenzene (34).

1,4-Dibromo-2,5-difluorobenzene (3 g, 11.0 mmol) and 2-(tributylstannyl)thiophene (10.7 g, 28.7 mmol) were added in a 2-neck round bottom flask. The compound **34** was prepared similarly as described for **31**. The crude compound was recrystallized from hexane to obtain 1.95 g of a colorless crystal (64% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.51 (d, J= 3.7 Hz, 2H), 7.41 (m, 4H), 7.13 (m, 2H). MS (EI): Calcd m/z = 278.0; found M⁺ = 278.



1,4-Bis(5-(trimethylstannyl)thiophen-2-yl)-2,5-difluorobenzene (M44).

1,4-Bis(thiophen-2-yl)-2,5-difluorobenzene (1.0 g, 3.59 mmol) was dissolved in 100 mL anhydrous THF under argon. **M44** was prepared similarly as described for **M41** and recrystallized from hexane to yield a pale green needle crystal (1.53 g, 71%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.60 (d, J= 3.5 Hz, 2H), 7.40 (t, J= 9.2 Hz, 2H), 7.21 (d, J= 3.5 Hz, 2H), 0.41 (t, J= 28 Hz, 18H). MS (EI): Calcd m/z = 604.0; found M⁺ = 604.



1,4-Bis(thiophen-2-yl)-2,3,5,6-tetrafluorobenzene (35).

1,4-Dibromo-2,3,5,6-tetrafluorobenzene (3 g, 9.7 mmol) and 2-(tributylstannyl)thiophene (9.5 g, 25.3 mmol) were added in a 2-neck round bottom flask. The compound **35** was prepared similarly as described for **31**. The crude product was recrystallized from ethanol to obtain 1.80 g of a colorless crystal (59% yield).

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.68 (d, J= 3.7 Hz, 2H), 7.56 (dd, J¹= 5.2 Hz, J²= 1.0 Hz, 2H), 7.20 (t, J= 4.5 Hz, 2H). MS (EI): Calcd m/z = 314.0; found M⁺ = 314.



1,4-Bis(5-(trimethylstannyl)thiophen-2-yl)-2,3,5,6-tetrafluorobenzene (M45).

1,4-Bis(thiophen-2-yl)-2,3,5,6-tetrafluorobenzene (1.0 g, 3.18 mmol) was dissolved in 100 mL anhydrous THF under argon protection. **M45** was prepared similarly as described for **M41** and recrystallized from ethanol to yield a pale yellow needle crystal (1.46 g, 72%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.76 (d, J= 3.3 Hz, 2H), 7.27 (d, J= 3.6 Hz, 2H), 0.43 (t, J= 28.2 Hz, 18H). MS (EI): Calcd m/z = 639.9; found M⁺ = 640.

Syntheses of Polymers

Poly[(5,6-bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole-4,7-diyl)-alt-(5,5'-(1,4-phenylene)bis(thiophen-2-yl))] (PDTBTBz-0F).

4,7-Dibromo-5,6-bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole (M21) (155 mg, 0.20 mmol) and 1,4bis(5-(trimethylstannyl)thiophen-2-yl)benzene (M41) (114 mg, 0.20 mmol) was added into a 2 mL microwave tube. $Pd_2(dba)_3$ (3.7 mg) and $P(o-Tol)_3$ (4.8 mg) were added to the above reaction mixture in a glovebox. After capping the microwave tube, anhydrous chlorobenzene (1.5 mL) was added via a syringe. The polymerization was carried out in a microwave reactor at 150 °C for 90 min. The resulting polymer was precipitated into methanol and collected by filtration. The precipitate was dissolved in chlorobenzene and precipitated again into methanol. The precipitate was then subjected to Soxhlet extraction with methanol, hexanes, dichloromethane, and chloroform. The final polymer was obtained by precipitating into methanol and drying in vacuum for 12 h, yielding PDTBTBz-0F (134 mg, 78%). $M_n = 28,600$ Da and PDI = 1.53. The other polymers were similarly synthesized as described for PDTBTBz-0F.

Poly[(5,6-bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole-4,7-diyl)-alt-(5,5'-(2-fluoro-1,4-phenylene)bis(thiophen-2-yl))] (PDTBTBz-1F).

4,7-Dibromo-5,6-bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole (M21) (155 mg, 0.20 mmol) and 1,4bis(5-(trimethylstannyl)thiophen-2-yl)-2-fluorobenzene (M42) (117 mg, 0.20 mmol) was reacted using $Pd_2(dba)_3$ (3.7 mg) and $P(o-Tol)_3$ (4.8 mg) as a catalyst. Yield: 135 mg, 77%. GPC: $M_n = 46,200$ Da, PDI = 2.37.

Poly[(5,6-bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole-4,7-diyl)-alt-(5,5'-(2,3-difluoro-1,4-phenylene)bis (thiophen-2-yl))] (PDTBTBz-2F_{syn}).

4,7-Dibromo-5,6-bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole (M21) (155 mg, 0.20 mmol) and 1,4-bis(5-(trimethylstannyl)thiophen-2-yl)-2,3-difluorobenzene (M43) (121 mg, 0.20 mmol) was reacted using Pd₂(dba)₃ (3.7 mg) and P(*o*-Tol)₃ (4.8 mg) as a catalyst. Yield: 138 mg, 77%. $M_n = 111,900$ Da, PDI = 3.10.

Poly[(5,6-bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole-4,7-diyl)-alt-(5,5'-(2,5-difluoro-1,4-phenylene)bis(thiophen-2-yl))] (PDTBTBz-2F_{anti}).

4,7-Dibromo-5,6-bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole (M21) (155 mg, 0.20 mmol) and 1,4-bis(5-(trimethylstannyl)thiophen-2-yl)-2,5-difluorobenzene (M44) (121 mg, 0.20 mmol) was reacted. Yield: 144 mg, 81%. $M_n = 182,600$ Da, PDI = 2.09.

Poly[(5,6-bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole-4,7-diyl)-alt-(5,5'-(2,3,5,6-tetrafluoro-1,4-phenylene)bis(thiophen-2-yl))] (PDTBTBz-4F).

4,7-Dibromo-5,6-bis(2-hexyldecyloxy)benzo[c][1,2,5]thiadiazole (M21) (155 mg, 0.20 mmol) and 1,4-bis(5-(trimethylstannyl)thiophen-2-yl)-2,3,5,6-tetrafluorobenzene (M45) (128 mg, 0.20 mmol) was polymerized. Yield: 142 mg, 78%. $M_n = 182,300$ Da, PDI = 3.06.



Fig. S1 Reported wide band gap polymers with high PCEs.

Polymer	$E_{\rm g}^{\rm opt}$ (eV)	$V_{\rm OC}({ m V})$	$J_{\rm SC}$ (mA cm ⁻²)	FF (%)	PCE (%)	Reference
РЗНТ	1.90	0.85	10.6	74	6.7	2
PCDTBT	1.88	0.88	10.6	66	6.1	3
PBDFTPD	1.97	0.97	11.2	68	7.4	4
PDCBT	1.90	0.91	11.0	72	7.2	5
PBDTFBZS	1.81	0.88	12.4	71	7.7	6
PBDT[2F]T	2.10	0.90	10.7	72	7.0	7
PDBT-T1	1.85	0.92	14.1	75	9.7	8
PM6	1.80	0.98	12.7	74	9.2	9
PffT2-FTAZ	1.88	0.80	13.3	69	7.8	10

Table S1 Summary of previously reported high PCE wide band gap polymers.



Fig. S2 TGA thermograms of polymers.



Fig. S3 DSC thermograms of polymers.



Fig. S4 Calculated HOMO and LUMO electronic structures of polymers (B3LYP/6-31G** level).

 Table S2 Summary of torsional profiles of energy minimum conformations.



Dalamaa	Θ_1	θ_2	θ_3	Θ_4	θ_5	θ_6	Θ_7
Polymer	(degree)						
PDTBTBz-0F	-173	20	-159	-178	-174	20	-26
PDTBTBz-1F	-172	163	-161	-172	-168	168	-156
$PDTBTBz-2F_{syn}$	-171	168	170	-170	-170	-164	165
PDTBTBz-2F _{anti}	-171	179	-1	-173	-174	-179	1
PDTBTBz-4F	-172	0	-1	-175	-173	2	0

Table S3 Calculated frontier orbital levels based on two repeating units by DFT.

Dalumar	НОМО	LUMO	Band gap
	(eV)	(eV)	(eV)
PDTBTBz-0F	-4.87	-2.55	2.32
PDTBTBz-1F	-4.95	-2.63	2.32
PDTBTBz-2F _{syn}	-5.03	-2.69	2.34
PDTBTBz-2F _{anti}	-4.97	-2.67	2.30
PDTBTBz-4F	-5.11	-2.75	2.36



Fig. S5 Cyclic voltammograms of polymers and ferrocene as a reference.



Fig. S6 (a) J-V curves and (b) EQE spectra of optimum polymer: PC₇₁BM devices prepared from CB solvent without DPE.

Donor:PC71BM	$J_{ m SC}$	$[Cal.]J_{SC}^{a)}$	V _{oc}	EE	PCE (%)
	$(mA cm^{-2})$	(mA cm ⁻²)	(V)	ГГ	Best (Ave.) ^{b)}
PDTBTBz-0F	6.0	6.1	1.00	0.37	2.2 (2.1)
PDTBTBz-1F	6.4	6.9	1.02	0.40	2.6 (2.6)
PDTBTBz-2F _{syn}	8.4	8.3	0.94	0.66	5.2 (5.0)
PDTBTBz-2Fanti	10.6	10.1	0.93	0.55	5.4 (5.2)
PDTBTBz-4F	4.2	3.7	0.89	0.66	2.5 (2.2)

Table S4 Summary of device parameters (CB solvent without DPE).

 $a^{-1}[Cal.] J_{SC}$, calculated J_{SC} from a EQE curve. b^{-1} Average PCE values obtained from 15 devices.



Fig. S7. Tapping-mode AFM topography images of polymer:PC₇₁BM blend films (solvent: CB without and with DPE, DIO and CN (from left to right).



Fig. S8 (a) J-V curves and (b) EQE spectra for PDTBTBz-2F_{anti}:PC₇₁BM prepared from CB solvent without and with DPE, DIO and CN.

Solvent	$J_{\rm SC}$ (mA cm ⁻²)	$[Cal.] J_{SC}^{a)}$ (mA cm ⁻²)	V _{OC} (V)	FF	Best PCE (%)
СВ	10.6	10.1	0.93	0.55	5.4
CB : 3% DPE	14.0	13.8	0.97	0.72	9.8
CB : 3% DIO	13.1	12.9	0.98	0.66	8.5
CB : 3% CN	12.0	11.8	0.97	0.65	7.5

^{*a*)}[*Cal*.] J_{SC} , calculated J_{SC} from a EQE curve



Fig. S9 In-plane (a) and out-of-plane (b) GIWAXS line-cut data for pristine polymers (left panel), polymer: $PC_{71}BM$ (middle), and polymer: $PC_{71}BM$ films with DPE (right panel).

		Packing parameters						
Films	Polymers	Axis	<i>π-π</i> stack [Å ⁻¹]	d-spacing [Å]	Lamella stack [Å ⁻¹]	d-spacing [Å]		
	ΡΓΤΡΤΡ 7 ΔΕ	$q_{_{xy}}$	-	-	0.22	28.55		
	FDIBIB2-0F	$q_{vertical}$	1.69	3.72	-	-		
	PDTRTR7-1F	$q_{_{xy}}$	1.66	3.79	0.31	20.20		
_		$q_{vertical}$	1.68	3.74	0.33	18.48		
Dristing polymor	PDTBTBz-2F	$q_{_{XY}}$	1.67	3.76	0.31	20.27		
Fristine polymer	syn	$q_{vertical}$	1.69	3.72	0.34	18.48		
	PDTBTBz-2F	$q_{_{XY}}$	1.68	3.74	0.32	19.63		
	anti	$q_{vertical}$	1.69	3.72	0.35	17.95		
	PDTRTR7.4F	$q_{_{XY}}$	1.70	3.70	0.30	20.94		
	I DI DI DZ-41	$q_{vertical}$	1.72	3.65	0.34	18.48		
	PDTBTBz-0F	$q_{_{XY}}$	-	-	-	-		
		$q_{vertical}$	-	-	-	-		
	PDTBTBz-1F	$q_{_{XY}}$	-	-	-	-		
_		$q_{vertical}$	-	-	-	-		
Polymer:PC ₇₁ BM	PDTBTBz-2F _{syn}	$q_{_{XY}}$	-	-	0.32	19.63		
blend		$q_{vertical}$	1.72	3.65	0.36	17.45		
	PDTBTBz-2F _{anti}	$q_{_{XY}}$	-	-	0.32	19.63		
		$q_{_{vertical}}$	1.73	3.63	0.35	17.95		
	DDTDTD ₇ 4F	$q_{_{XY}}$	1.69	3.72	0.31	20.27		
		$q_{vertical}$	1.75	3.59	0.34	18.48		
	PDTBTB7-0F	$q_{_{XY}}$	-	-	0.24	26.17		
	TDTDTD2-01	$q_{_{vertical}}$	-	-	-	-		
	PDTRTR7-1F	$q_{_{XY}}$	-	-	0.31	20.20		
		$q_{vertical}$	1.72	3.65	0.32	19.63		
Polymer:PC ₇₁ BM	PDTBTBz-2F	$q_{_{XY}}$	-	-	0.32	19.63		
blend with DPE	syn	$q_{vertical}$	1.72	3.65	0.35	17.95		
	PDTBTBz-2F	$q_{_{XY}}$	-	-	0.32	19.63		
-	anti	<i>q</i> _{vertical}	1.72	3.65	0.35	17.95		
		$q_{_{xy}}$	1.70	3.70	0.31	20.27		
		$q_{vertical}$	1.75	3.59	0.34	18.48		

Table S6 Packing parameters derived from GIWAXS measurements. ($q_{vertical}$ was taken near the vertical direction, but not exactly at $q_{xy}=0$ because of the inaccessible region of reciprocal space.)



Fig. S10 Resonant soft X-ray scattering (RSoXS) profiles of PDTBTBz-based polymer: $PC_{71}BM$ blends spin cast from a CB solvent with DPE additive. The Lorentz corrected curves were fit with log-normal distributions (solid black traces). The length scales based on the peak positions are 43, 51, 44, 38, and 60 nm for PDTBTBz-0F, PDTBTBz-1F, PDTBTBz-2F_{syn}, PDTBTBz-2F_{anti}, and PDTBTBz-4F, respectively.



Fig. S11 Transfer characteristic of PFET devices at $V_{\text{DS}} = -80 \text{ V} (W/L = 1000/20 \text{ }\mu\text{m}).$



Fig. S12 Output curves of PFET devices. (a) PDTBTBz-0F, (b) PDTBTBz-1F, (c) PDTBTBz-2 F_{syn} , (d) PDTBTBz-2 F_{anti} , and (e) PDTBTBz-4F.



Fig. S13 *J*–*V* characteristics of (a) hole- and (b) electron-only devices based on polymer: $PC_{71}BM$ blend films (CB:DPE = 97 : 3 vol%). Blue lines represent the best fit based on the Mott–Gurney relationship.

Sample	$\mu_{\rm h}({\rm cm}^2~{\rm V}^{-1}{\rm s}^{-1})$	$V_{\mathrm{T}}\left(\mathbf{V} ight)$
PDTBTBz-0F	2.4×10^{-2}	-8.1
PDTBTBz-1F	4.1×10^{-2}	-3.4
PDTBTBz- $2F_{syn}$	5.2×10^{-2}	-2.0
PDTBTBz-2Fanti	5.6×10^{-2}	-7.7
PDTBTBz-4F	9.0 × 10 ⁻³	-4.5

 Table S7 Field effect hole mobilities for polymers.

Table S8 SCLC charge mobilities for polymer:PC71BM blend films.

Polymer:PC ₇₁ BM with DPE	Hole mobility (μ_h) (cm ² V ⁻¹ s ⁻¹)	Electron Mobility (µ _e) (cm ² V ⁻¹ s ⁻¹)	$\mu_{ m h}/\mu_{ m e}$
PDTBTBz-0F	1.0×10^{-3}	7.5×10^{-4}	1.33
PDTBTBz-1F	1.07×10^{-3}	8.3×10^{-4}	1.29
$PDTBTBz-2F_{syn}$	1.0×10^{-3}	9.0×10^{-4}	1.11
$PDTBTBz\text{-}2F_{anti}$	1.15×10^{-3}	1.1×10^{-3}	1.05
PDTBTBz-4F	1.15×10^{-4}	7.3×10^{-4}	0.16

Table S9 Summary of reference subcells and tandem PSCs.

Device	$J_{\rm SC}$ (mA cm ⁻²)	V _{OC} (V)	FF	PCE (%)
Ref. front cell (PDTBTBz-2F _{anti})	13.0	0.98	0.70	9.0
Ref. back cell (DT-PDPP2T-TT)	16.4	0.69	0.71	8.0
Tandem	9.9	1.58	0.66	10.3



Fig. S14 *J-V* curve and EQE of devices using PDTBTBz-2F_{anti}:PC₇₁BM blend in an inverted structure.





Fig. S15 Comparison of air stabilities for single- and tandem-junction solar cells with different electrodes and device structures.

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