Electronic Supplementary Information

Diketopyrrolopyrrole-based terpolymers with tunable broad band absorption for fullerene and fullerene-free polymer solar cells

Asfaw Negash^{ab}*, Zewdneh Genene^{ac}, Raghavendran Thiruvallur Eachambadi^d, Jurgen Kesters^b, Niko Van den Brande^e, Jan D'Haen^b, Huguette Penxten^b, Birhan Alkadir Abdulahi^a, Ergang Wang^f, Koen Vandewal^b, Wouter Maes^b*, Wendimagegn Mammo^a, Jean Manca^d, Shimelis Admassie^a

^a Department of Chemistry, Addis Ababa University, P.O. Box 33658, Addis Ababa, Ethiopia
^b Institute for Materials Research (IMO-IMOMEC), Hasselt University, Agoralaan 1, B-3590 Diepenbeek, Belgium
^c Department of Chemistry, Ambo University, P.O. Box 19, Ambo, Ethiopia
^d X-LAB, Hasselt University, Universitaire Campus, Agoralaan 1, B-3590 Diepenbeek, Belgium
^e Physical Chemistry and Polymer Science (FYSC), Vrije Universiteit Brussel (VUB), Pleinlaan 2, B-1050 Brussels, Belgium
^f Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

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1. Experimental section

1.1. Instrumentation

¹H and ¹³C NMR spectra were acquired using a Varian Inova 400 MHz spectrometer. Tetramethylsilane was used as an internal standard with deuterated chloroform as the solvent. Size exclusion chromatography (SEC) was performed on an Agilent PL-GPC 220 integrated high temperature SEC system with refractive index and viscometer detectors and 3 sequential PLgel 10 µm MIXED-B LS 300 x 7.5 mm columns. The eluent was 1,2,4-trichlorobenzene and the operating temperature was 150 °C. The concentration of the samples was 0.5 mg mL⁻¹ and they were filtered (0.45 µm) prior to the analysis. The polymer molar masses were calculated according to relative calibration with polystyrene standards. UV-Vis absorption measurements were performed on a Perkin Elmer Lambda 950 UV-Vis-NIR spectrophotometer. The films for the UV-Vis measurements were prepared by casting a solution of the respective polymer in ortho-dichlorobenzene (o-DCB) on a glass substrate. The solid-state UV-Vis absorption spectra were used to estimate the optical gaps. Electrochemical measurements (cyclic voltammetry) were performed with a Autolab PGSTAT 30 potentiostat using a three-electrode microcell with a platinum wire working electrode, a platinum counter electrode and a Ag/AgNO₃ reference electrode, and a solution of 0.1 M tetrabutylammonium hexafluorophosphate [NBu₄PF₆] in anhydrous acetonitrile as the supporting electrolyte. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the polymers were calculated from the onset oxidation and reduction, respectively, as observed by cyclic voltammetry using equations S1 and S2¹ after ferrocene correction.

$$\begin{split} E_{HOMO} &= -(E_{ox} + 4.98)eV \dots S1 \\ E_{LUMO} &= -(E_{red} + 4.98)eV \dots S2 \end{split}$$

1.2. Synthetic procedures

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. Thienothiophene-capped DPP (TTDPP) and thienyl-substituted benzodithiophene (BDTT) were purchased from Solarmer Materials Inc. The fluorinated benzotriazole (FTAZ) monomer was synthesized following our previously reported procedure.²



Synthesis of polymer P1

In a dry 25 mL round-bottom flask, (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5*b*']dithiophene-2,6-diyl)bis(trimethylstannane) (217.1 mg, 0.24 mmol), 4,7-bis(5-bromothiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2*H*-benzo[*d*][1,2,3]triazole (42.1 mg, 0.06 mmol), 3,6-bis(5bromothieno[3,2-*b*]thiophen-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4dione (183.5 mg, 0.18 mmol), tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃) (2.3 mg) and tri(*o*-tolyl)phosphine (P(*o*-tol)₃) (3.04 mg) were dissolved in anhydrous toluene (8 mL) under nitrogen atmosphere. The reaction mixture was vigorously stirred at 75 °C for 4.5 h. 2-Bromothiophene (0.15 mL) and tributyl(thiophen-2-yl)stannane (0.15 mL) were then added into the solution. After cooling to room temperature, the polymer was precipitated by pouring the solution into methanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extractions with acetone, diethyl ether and chloroform, respectively. The chloroform fraction was purified by passing it through a short silica gel plug and then the polymer was precipitated from acetone. Finally, pure polymer **P1** was obtained by filtration through a 0.45 μm Teflon filter and dried under vacuum at 40 °C overnight (280 mg, 86%).

Synthesis of polymer P2

In a dry 25 mL round-bottom flask, (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5*b*']dithiophene-2,6-diyl)bis(trimethylstannane) (217.1 mg, 0.24 mmol), 4,7-bis(5-bromothiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2*H*-benzo[*d*][1,2,3]triazole (84.2 mg, 0.12 mmol), 3,6-bis(5bromothieno[3,2-*b*]thiophen-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4dione (122.3 mg, 0.12 mmol), Pd₂(dba)₃ (2.3 mg) and P(*o*-tol)₃ (3.04 mg) were dissolved in anhydrous toluene (8 mL) under nitrogen atmosphere. The reaction mixture was vigorously stirred at 75 °C for 3 h. 2-Bromothiophene (0.15 mL) and tributyl(thiophen-2-yl)stannane (0.15 mL) were then added into the solution. After cooling to room temperature, the polymer was precipitated by pouring the solution into methanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extractions with acetone, diethyl ether and chloroform, respectively. The chloroform fraction was purified by passing it through a short silica gel plug and then the polymer was precipitated from acetone. Finally, pure polymer **P2** was obtained by filtration through a 0.45 µm Teflon filter and dried under vacuum at 40 °C overnight (290 mg, 94%).

Synthesis of polymer P3

In a dry 25 mL round-bottom flask, (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5*b*']dithiophene-2,6-diyl)bis(trimethylstannane) (217.1 mg, 0.24 mmol), 4,7-bis(5-bromothiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2*H*-benzo[*d*][1,2,3]triazole (126.3 mg, 0.18 mmol), 3,6bis(5-bromothieno[3,2-*b*]thiophen-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (61.2 mg, 0.06 mmol), Pd₂(dba)₃ (2.3 mg) and P(*o*-tol)₃ (3.04 mg) were dissolved in anhydrous toluene (8 mL) under nitrogen atmosphere. The reaction mixture was vigorously stirred at 75 °C for 4.5 h. 2-Bromothiophene (0.15 mL) and tributyl(thiophen-2-yl)stannane (0.15 mL) were then added into the solution. After cooling to room temperature, the polymer was precipitated by pouring the solution into methanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extractions with acetone, diethyl ether and chloroform, respectively. The chloroform fraction was purified by passing it through a short silica gel plug and then the polymer was precipitated from acetone. Finally, pure polymer **P3** was obtained by filtration through a 0.45 µm Teflon filter and dried under vacuum at 40 °C overnight (269 mg, 93%).

1.3. Thermal analysis

TGA experiments were performed at 20 K.min⁻¹ in platinum crucibles on a TA Instruments Q5000 TGA using nitrogen (50 mL min⁻¹) as purge gas. DSC measurements were performed at 20 K.min⁻¹ in aluminum crucibles on a TA Instruments Q2000 Tzero DSC equipped with a refrigerated cooling system (RCS), using nitrogen (50 mL.min⁻¹) as purge gas.



Fig. S1. TGA plots of terpolymers P1–P3 at a heating rate of 20 K min⁻¹ under N₂ atmosphere.

1.4. UV-Vis absorption spectra in solution



Fig. S2. UV-Vis absorption spectra of polymers P1-P3 in *o*-DCB solution.

2. Literature overview on the combination of DPP-based donor polymers and nonfullerene acceptors

Table S1. Summary of photovoltaic performances of fullerene-free PSCs based on DPP-baseddonor polymers and non-fullerene acceptors.

Donor	Non-fullerene	Voc	Jsc	FF	PCE	Pof
polymer	acceptor	[V]	[mA cm ⁻²]	T, T,	[%]	KU.
PDPP5T	PDPP2Tz	0.81	6.9	0.51	2.9	3
PDPP3T	SDIPBI	0.71	3.5	0.40	0.98	4
PDPPTPT	SDIPBI	0.88	5.5	0.43	2.1	5
PDPP5T	SDIPBI	0.63	8.9	0.41	2.3	5
PDPP4T	SDIPBI	0.74	7.5	0.47	2.6	5
PDPP2TDTP	SDIPBI	0.50	7.4	0.43	1.6	5
PDPPTPT	N2200	0.88	1.4	0.38	0.45	6
PDPP5T	N2200	0.68	5.2	0.48	1.7	6
PDPP2TBDT	N2200	0.80	4.0	0.48	1.5	6
PDPP2TDTP	N2200	0.50	5.9	0.38	1.1	6
PDPP5T	PDPP2TzT	0.81	7.1	0.49	2.8	7
PDPP5T	PDPP2Tz10FBDT	0.79	5.7	0.49	2.3	7
PDPP3T	ITIC	0.78	4.2	0.59	1.9	8
PDPP4T	ITIC	0.78	8.0	0.63	3.9	8
PDPP5T	ITIC	0.69	9.6	0.61	4.1	8
PDPP6T	ITIC	0.68	9.3	0.60	3.8	8
P1	IEICO-4F	0.62	15.25	0.55	5.24	This work
P2	IEICO-4F	0.64	15.74	0.54	5.49	This work
P3	IEICO-4F	0.66	17.84	0.54	6.32	This work



Fig. S3. Chemical structures of DPP-based donor polymers and some non-fullerene acceptors.

3. Device fabrication and characterization

Patterned indium tin oxide (ITO) glass substrates (100 nm, Kintec, sheet resistivity 20 Ω sq⁻¹) were ultrasonically cleaned with detergent, distilled water, acetone and isopropanol, and then dried under a nitrogen flow. The substrates were treated with UV/O₃ for 15 min and then PEDOT:PSS (Heraeus, Clevios P VP.AI 4083) was spin-coated on top with a thickness of ~35 nm, followed by heating at 150 °C for 15 min under ambient conditions to remove any residual water. Thereafter, the substrates were transferred into a nitrogen-filled glove box (<1 ppm the conventional device architecture glass/ITO/PEDOT:PSS/ter- O_2/H_2O). Using polymer:PC71BM/Ca/Al, the terpolymer:PC71BM (Solenne, 99%) active layers were deposited via spin-coating. The blend solutions were prepared in different polymer:PC₇₁BM ratios in o-DCB (with a total concentration of 20, 25 and 20 mg mL⁻¹ for the **P1**, **P2** and **P3** blends, respectively) and stirred overnight at 50 °C. Finally, the top electrodes Ca and Al, with layer thicknesses of ~30 and 80 nm, respectively, were deposited by evaporation at a pressure of 3×10^{-6} mbar. In this way, devices with an active area of 0.03 cm² were obtained. For the devices with inverted architecture glass/ITO/ZnO/terpolymer:IEICO-4F/MoO₃/Ag, a ZnO nanoparticles suspension was deposited on cleaned ITO substrates by spin-coating (4000 rpm), followed by annealing on a hot plate at 300 °C for 10 min, affording thin layers of ~30 nm. The top electrodes MoO₃ (10 nm) and Ag (100 nm) were thermally evaporated at a pressure of 3×10^{-6} mbar on top of the active layer. The blend solutions for the fullerene-free polymer solar cells were prepared in different terpolymer:IEICO-4F ratios in o-DCB (with a total concentration of 18, 20 and 20 mg mL⁻¹ for the **P1**, **P2** and **P3** blends, respectively) and stirred overnight at 50 °C. The current-voltage (I-V) characteristics of the photovoltaic devices were measured by a computer-controlled Keithley 2400 source meter under 1 sun, using a Newport class A solar simulator (model 91195A) calibrated with a silicon solar cell to give an AM 1.5G spectrum. External quantum efficiency (EQE) measurements were performed with a Newport Apex illuminator (100 W xenon lamp, 6257) as a light source, a Newport Cornerstone 130° monochromator and a Stanford SR830 lock-in amplifier for the current measurements. A silicon FDS100-CAL photodiode was employed as a reference cell. To analyze the morphology of the photoactive layers, atomic force microscopy (AFM) images were taken using a Bruker Multimode 8 microscope in the peak-force Quantum nanomechanical (PF-QNM) mode. The probe used during imaging (Scanasyst Air, supplied by Bruker) contained a triangular cantilever

with a pyramidal tip with a nominal tip radius of 2 nm. The thicknesses of the active layers were determined with a DektakXT surface profilometer. The XRD studies were performed with a Bruker D8 diffractometer. This theta-theta diffractometer is equipped with a Göbel mirror (line focus, mostly Cu K_{α} radiation). The X-rays were detected with a 1D lynxeye detector.

4. Determination of the voltage losses for strongly absorbed photons

A lower limit to the energy lost for a photon absorbed by either the donor or the acceptor in a blend is given by the difference between the absorption edge energy (E_{edge}) and eV_{oc} , where e is the elementary charge. E_{edge} is determined for devices containing **P1**, **P2** and **P3**, mixed with either PC₇₁BM or IEICO-4F, via the procedure outlined in literature.^{9,10} Values are listed in Table S2. The minimum energy losses for strongly absorbed photons (E_{loss}), determined by E_{edge} - eV_{oc} are listed in Table 2 and 4 of the main text and are more relevant than the often reported difference between the onset of absorption and eV_{oc} , as discussed in literature.^{9,10}



Fig. S4. Determination of *E*_{edge} for polymers P1, P2 and P3 blended with PC₇₁BM or IEICO-4F.

Blend	Additive	Eedge [eV]	Blend	Additive	Eedge [eV]
P1 :PC ₇₁ BM	-	1.59	P1:IEICO-4F	-	1.41
	1% DIO	1.59		0.5% CN	1.41
P2 :PC ₇₁ BM	-	1.63	P2:IEICO-4F	-	1.40
	3% DIO	1.61		0.5% CN	1.42
P3 :PC ₇₁ BM	-	1.63	P3:IEICO-4F	-	1.43
	3% DIO	1.62		0.5% CN	1.42

Table S2. *E*_{edge} values for polymers P1, P2 and P3 blended with PC₇₁BM or IEICO-4F.

5. Additional information on the polymer solar cells

Terpolymer	Ratio	Voc	$J_{ m sc}$	FF	PCE ^a
		[V]	[mA cm ⁻²]		[%]
P1	1:1	0.62	13.50	0.58	4.85
	1:1.5	0.62	15.70	0.59	5.74
	1:2	0.62	13.30	0.62	5.11
	1:3	0.62	11.60	0.67	4.82
P2	1:1	0.64	7.10	0.57	2.59
	1:1.5	0.64	8.42	0.59	3.18
	1:2	0.64	7.32	0.59	2.76
	1:3	0.62	6.41	0.56	2.23
	1:1	0.66	10.60	0.53	3.70
D2	1:1.5	0.66	8.38	0.58	3.21
r J	1:2	0.64	8.20	0.59	3.10
	1:3	0.64	7.52	0.58	2.79

Table S3. Donor: acceptor blend ratio optimization for the polymer solar cells based on the terpolymers and $PC_{71}BM$.

^a Best efficiencies are reported.

Townolsee	Datia	DIO	Thickness	Voc	$J_{ m sc}$	$J_{\rm EQE}{}^{\rm a}$		PCE ^b
Terpolymer	Katio	DIO	[nm]	[V]	[mA cm ⁻²]	[mA cm ⁻²]	ГГ	[%]
P1	1:1.5	w/o	140±3	0.62	15.70	15.07	0.59	5.74
		0.5%	136±2	0.62	14.70		0.60	5.47
		1%	130±2	0.60	16.60	15.78	0.56	5.58
		3%	124±3	0.60	15.10		0.55	4.98
		5%	120±2	0.58	14.70		0.52	4.43
P2	1:1.5	w/o	115±3	0.64	8.42	7.76	0.59	3.18
		0.5%	112±2	0.62	10.60		0.65	4.27
		1%	110±2	0.62	11.60		0.63	4.53
		3%	105±4	0.62	13.33	12.83	0.67	5.54
		5%	100±2	0.60	11.90		0.67	4.78
P3	1:1	w/o	110±3	0.66	10.60	10.03	0.53	3.70
		0.5%	107±2	0.66	11.10		0.54	3.96
		1%	105±3	0.64	10.80		0.61	4.20
		3%	101±4	0.62	12.40	11.88	0.65	5.00
		5%	96±4	0.62	11.10		0.66	4.54

Table S4. Influence of the amount of additive (DIO) on the photovoltaic performance of the terpolymer:PC₇₁BM solar cells.

^a Integrated current densities from the EQE spectra of the best devices.

^b Best efficiencies are reported.

Terpolymer	Ratio	Additive	Thickness	Voc	$J_{\rm sc}$	FF	PCE ^a
			[nm]	[V]	[mA cm ⁻²]		[%]
P1	1:1.5	-	140±3	0.62	15.70	0.59	5.74
	1:1.5	3% CN	126±2	0.62	14.23	0.55	4.84
P2	1:1.5	-	115±3	0.64	8.42	0.59	3.18
	1:1.5	3% CN	107±2	0.64	9.97	0.65	4.17
P3	1:1	-	110±3	0.66	10.60	0.53	3.70
	1:1	3% CN	105±2	0.64	8.84	0.68	3.77

Table S5. Influence of the addition of 3% CN on the photovoltaic performance of the terpolymer:PC₇₁BM solar cells.

^a Best efficiencies are reported.

Table S6. Donor:acceptor blend ratio optimization for the polymer solar cells based on the terpolymers and IEICO-4F.

Terpolymer	Ratio	Voc	$J_{\rm sc}$	FF	PCE ^a
		[V]	[mA cm ⁻²]		[%]
P1	1.5:1	0.58	13.35	0.469	3.63
	1:1	0.60	13.71	0.464	3.82
	1:1.5	0.60	14.02	0.497	4.03
P2	1.5:1	0.64	14.20	0.474	4.31
	1:1	0.64	14.57	0.489	4.56
	1:1.5	0.62	13.54	0.518	4.35
P3	1.5:1	0.66	14.15	0.487	4.55
	1:1	0.65	15.95	0.458	4.75
	1:1.5	0.65	15.90	0.439	4.52

^a Best efficiencies are reported.

Polymer	Thickness		$J_{\rm sc}$	FF	PCE ^a
	[nm]		[mA cm ⁻²]		[%]
P1	85±2	0.60	11.60	0.63	4.36
	102±3	0.60	13.59	0.55	4.50
	116±2	0.60	14.70	0.52	4.59
	125±3	0.60	15.59	0.51	4.72
	132±2	0.60	16.82	0.45	4.52
P2	80 ± 1	0.64	12.03	0.59	4.56
	90±2	0.64	13.12	0.57	4.82
	102±3	0.64	14.00	0.54	4.86
	118±2	0.64	15.15	0.51	4.96
	124±2	0.64	16.05	0.46	4.76
P3	75±3	0.66	13.23	0.59	5.13
	90±2	0.66	14.10	0.57	5.28
	101±2	0.66	15.53	0.54	5.52
	108±3	0.65	17.01	0.52	5.72
	113±3	0.66	17.24	0.49	5.61
	120±2	0.66	18.20	0.45	5.38

Table S7. Thickness optimization for the polymer solar cells based on the terpolymers andIEICO-4F.

^a Best efficiencies are reported.

Additives	Thickness	Voc	$J_{\rm sc}$	$J_{\rm EQE}{}^{\rm a}$	FF	PCE ^b
	[nm]	[V]	[mA cm ⁻²]	[mA cm ⁻²]		[%]
_*	125±5	0.60	15.59	15.30	0.505	4.71
0.25% CN	122±4	0.62	12.36		0.504	3.86
0.25% CN*	118±5	0.62	13.26		0.555	4.56
0.5% CN	120±5	0.62	14.38		0.537	4.79
0.5% CN*	115±2	0.62	15.25	14.94	0.554	5.24
0.5% DBE	117±2	0.57	11.20		0.593	3.75
0.5% DIO	112±2	0.58	15.18		0.459	4.04
_*	118±3	0.64	15.15	14.86	0.512	4.96
0.25% CN	117±3	0.64	14.67		0.527	4.95
0.25% CN*	115±2	0.64	15.04		0.523	5.03
0.5% CN	112±3	0.64	15.15		0.524	5.10
0.5% CN*	110±2	0.64	15.74	15.13	0.545	5.49
0.5% DBE	114±3	0.62	8.63		0.464	2.48
0.5% DIO	108±2	0.64	13.72		0.526	4.62
_ *	108±3	0.65	17.01	16.62	0.517	5.72
0.25% CN	104±3	0.66	15.39		0.537	5.46
0.25% CN*	105±2	0.65	16.15		0.537	5.55
0.5% CN	106±2	0.64	17.15		0.531	5.83
0.5% CN*	102±3	0.66	17.84	17.03	0.537	6.32
0.5% DBE	108±2	0.61	17.70		0.376	2.69
0.5% DIO	100±3	0.66	13.63		0.544	4.89
	Additives	AdditivesFhickness[nm]-*125±50.25% CN122±40.25% CN118±50.5% CN120±50.5% CN115±20.5% DBE117±20.5% CN112±30.25% CN115±20.5% CN115±20.5% CN115±20.5% CN112±30.5% CN112±30.5% CN110±20.5% CN110±20.5% CN104±30.5% CN108±20.5% CN104±30.25% CN105±20.5% CN<	AdditivesFhicknessVoc[m][V]-*125±50.600.25% CN122±40.620.5% CN118±50.620.5% CN115±20.620.5% CN117±20.570.5% DBE117±20.640.5% DBE117±30.640.5% CN115±20.640.5% CN115±20.640.25% CN115±20.640.5% CN112±30.640.5% CN110±20.640.5% CN108±20.640.5% CN108±30.640.5% CN108±30.640.5% CN105±20.640.5% CN105±20.640.5% CN105±20.640.5% CN105±20.640.5% CN105±20.640.5% CN105±20.640.5% CN105±20.640.5% CN102±30.640.5% CN1	AdditivesThicknessVocJsc[mm][V][mA cm²]-*125±50.6015.590.25% CN122±40.6212.360.25% CN*118±50.6213.260.5% CN*120±50.6214.380.5% CN*115±20.6215.250.5% DBE117±20.5711.200.5% DBE112±20.5815.18-*118±30.6415.150.25% CN115±20.6415.040.25% CN115±20.6415.040.5% CN*110±20.6415.150.5% CN*110±20.6415.740.5% CN*108±20.6413.720.5% DBE104±30.6517.010.5% CN*105±20.6415.390.5% CN*105±20.6415.390.5% CN*105±20.6417.150.5% CN*102±30.6417.150.5% CN*102±30.6417.840.5% DBE108±20.6117.840.5% DBE108±20.6117.840.5% DBE108±20.6117.840.5% DBE108±20.6117.840.5% DBE108±20.6117.840.5% DBE108±20.6117.840.5% DBE108±20.6117.840.5% DBE108±20.6113.63	Additives Thickness Voc Jsc JEQE ⁴ [m] [V] [mA cm ⁻²] [mA cm ⁻²] -* 125±5 0.60 15.59 15.30 0.25% CN 122±4 0.62 12.36 - 0.25% CN* 118±5 0.62 13.26 - 0.5% CN* 120±5 0.62 14.38 - 0.5% CN* 120±5 0.62 15.25 14.94 0.5% CN* 115±2 0.62 15.15 14.94 0.5% DBE 117±2 0.58 15.18 - 0.5% DIO 112±2 0.58 15.15 14.86 0.25% CN 117±3 0.64 15.04 - 0.5% CN 112±3 0.64 15.15 15.13 0.5% CN* 110±2 0.64 15.74 15.13 0.5% DBE 114±3 0.62 8.63 - 0.5% DIO 108±3 0.65 17.01 16.62 0.5% CN* 1	AdditivesThickness V_{oc} J_{sc} J_{EQE^a} FF $[nm]$ $[V]$ $[mA cm^{-2}]$ $[mA cm^{-2}]$ $[mA cm^{-2}]$ $-^*$ 125 ± 5 0.60 15.59 15.30 0.505 $0.25\% CN$ 122 ± 4 0.62 12.36 -503 0.504 $0.25\% CN$ 118 ± 5 0.62 13.26 -40.537 0.557 $0.5\% CN$ 120 ± 5 0.62 14.38 -40.537 0.537 $0.5\% CN$ 115 ± 2 0.62 15.25 14.94 0.593 $0.5\% DBE$ 117 ± 2 0.57 11.20 0.593 0.593 $0.5\% DBE$ 117 ± 2 0.58 15.18 -48.69 0.512 $0.5\% DBE$ 117 ± 3 0.64 15.15 14.86 0.512 $0.25\% CN$ 115 ± 2 0.64 15.04 -524 0.523 $0.5\% CN$ 110 ± 2 0.64 15.15 -44.64 0.512 $0.5\% CN$ 110 ± 2 0.64 15.74 15.13 0.545 $0.5\% DBE$ 114 ± 3 0.62 8.63 -54.64 $0.5\% DBE$ 108 ± 3 0.65 17.01 16.62 0.537 $0.5\% CN$ 105 ± 2 0.64 15.79 -53.67 0.537 $0.5\% CN$ 105 ± 2 0.64 15.15 -54.64 0.537 $0.5\% CN$ 105 ± 2 0.65 16.15 -54.64 0.537 $0.5\% CN$ 105 ± 2 0.66 17.84 17.03 0.537 $0.5\% CN$

Table S8. Influence of the amount of additive (CN) on the photovoltaic performance of the terpolymer:PC₇₁BM solar cells.

* Inverted geometry (ITO/ZnO/active layer/MoO₃/Ag).

^a Integrated current densities from the EQE spectra of the best devices.

^b Best efficiencies are reported.

6. AFM images



Fig. S5. AFM images $(1 \times 1 \ \mu m^2)$ of the highest efficiency PSCs based on (a) **P1**:PC₇₁BM without DIO, b) **P1**:PC₇₁BM with 1% DIO, (c) **P2**:PC₇₁BM without DIO, (d) **P2**:PC₇₁BM with 3% DIO, e) **P3**:PC₇₁BM without DIO and (f) **P3**:PC₇₁BM with 3% DIO.



Fig. S6. AFM images $(1 \times 1 \ \mu m^2)$ of the highest efficiency PSCs based on (a) **P1**:IEICO-4F without CN, (b) **P1**:IEICO-4F with 0.5% CN, (c) **P2**:IEICO-4F without CN, (d) **P2**:IEICO-4F with 0.5% CN, (e) **P3**:IEICO-4F without CN and (f) **P3**:IEICO-4F with 0.5% CN.

7. Space charge limited current (SCLC) fittings

The hole (μ_h) and electron (μ_e) mobilities of the photoactive layers were determined by the SCLC method using hole-only devices with configuration ITO/PEDOT:PSS/terpolymer:acceptor/Au and electron-only devices with configuration ITO/ZnO/terpolymer:acceptor/Ca/Al. The SCLC could be estimated using the Mott-Gurney equation (S3)^{11,12}

$$J = \frac{9\varepsilon_0 \varepsilon_r \mu_{h/e} (V)^2}{8L^3} \dots S3$$

where *J* is the current density, $\varepsilon_{\rm r}$ is the relative permittivity of the terpolymer ($\varepsilon_{\rm r} = 3 \text{ Fm}^{-1}$), $\varepsilon_{\rm o}$ is the free space permittivity (8.85×10⁻¹² Fm⁻¹), $\mu_{\rm h/e}$ is the hole/electron mobility, *L* is the thickness of the active layer and *V* is the effective voltage ($V = V_{\rm appl} - V_{\rm bi}$, where $V_{\rm appl}$ is the applied voltage and $V_{\rm bi}$ the built-in voltage that results from the work function difference between the anode and the cathode).



Fig. S7. $J_{sc}^{1/2}-V$ plots for the **P1–P3**:PC₇₁BM blends applied to determine hole and electron mobilities by the SCLC method.



Fig. S8. $J_{sc}^{1/2}-V$ plots for the **P1–P3**:IEICO-4F blends applied to determine hole and electron mobilities by the SCLC method.

8. References

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