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Polymer-polymer solar cells with near-infrared spectral response

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The supporting information contains the experimental part, molecular weight data of the polymers (Table S1), absorption spectra of the polymers and P3HT:DPP-polymers in thin films (Fig. S1 and Fig. S2); the AFM images of P3HT:PDPP2TzT films without or with thermal annealing (Fig. S3); influence of solvent with or without additive, thermal annealing and thickness of active layer on P3HT:DPP-polymers solar cells (Table S2 – Table S3); refractive index and extinction coefficient of the P3HT:DPP-polymer layers (Fig. S4); and AFM images of P3HT:PDPP2TzT films spin coated from different solvents (Fig. S5).

Materials and Measurements

Commercial chemicals were used as received. Optical absorption spectra were recorded on a Perkin Elmer Lambda 900 UV/vis/nearIR spectrophotometer. Cyclic voltammetry was performed under an inert atmosphere with a scan rate of 0.1 V s^{-1} and 1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte. An ITO glass slide cover with a thin layer of polymer (approx. 20 nm) was used as working electrode, and a silver rod as counter 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.

Inverted configuration photovoltaic devices were made by spin coating a ZnO sol-gel[S1] at 4000 rpm for 60 s onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). A 40 nm thick ZnO layer was formed and baked at 150 °C for 5 min. in air. The photoactive layer was deposited by spin coating a chloroform solution containing the P3HT and DPP-polymer with ratio of 2:1 (w/w) and the appropriate amounts of additive in air. MoO_3 (10 nm) and Ag (100 nm) were deposited by vacuum evaporation at ~2×10^{-7} mbar as the back electrode. The cells were exposed to UV light (365 nm) for 15 min. before measurement.

The active area of the cells was 0.09 or 0.16 cm^2 and no size dependence was found between these two dimensions. *J–V* characteristics were measured under ~100 mW cm^{-2} white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB 120 daylight filter, using a Keithley 2400 source meter. Short circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The spectral response was measured under simulated 1 sun operation conditions using bias light from a 532 nm solid state laser (Edmund Optics). Light from a 50 W tungsten halogen lamp (Osram64610) was used as probe light and modulated with a mechanical chopper before passing the monochromator (Oriel, Cornerstone 130) to select the wavelength. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford Research Systems SR 830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak 150 profilometer.

The IQE was determined by optical modeling of the entire layer stack using the wavelength dependent refractive index (*n*) and extinction coefficient (*k*).[S 2] Calculations of the optical electric field were performed with Setfos 3 (Fluxim AG, Switzerland). The averaged IQE was determined by convolution of the solar spectrum with the EQE of the solar cell and the absorbed photon flux.

PDPP2TzT with 2-octyldecyl side chains was synthesized analogous to the synthesis of PDPP2TzT with 2-hexyldecyl side chains reported in Ref S3, using

3,6-bis(5-bromothiazol-2-yl)-2,5-bis(2-octyldecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione and 5,5′-bis(trimethylstannyl)thiophene as a monomers. M_n = 74.0 kg/mol and PDI = 2.8.

Table S1. Molecular weight and polydispersity of thiazole-bridged DPP polymers.

Polymer	M_n[a] (kg/mol)	PDI
PDPP2TzT	74.0	2.8
PDPP2TzBDT	85.2	3.8
PDPP2Tz2T	108.9	1.8
PDPP2TzDTP	88.5	3.10

[a] Determined with GPC at 140 °C using *o*-DCB as the eluent.

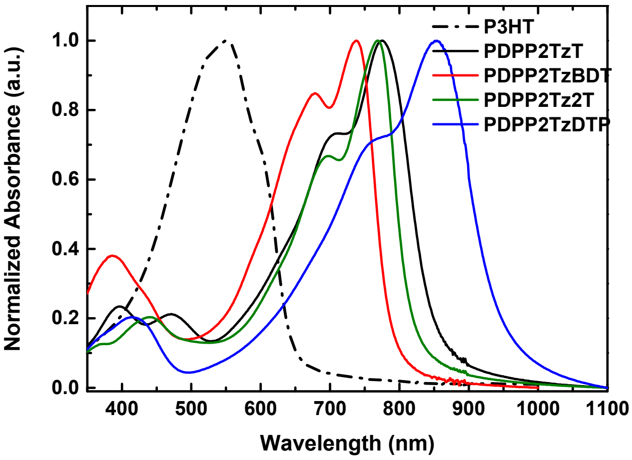

Fig. S1. Absorption spectra in films of P3HT and DPP-polymers.

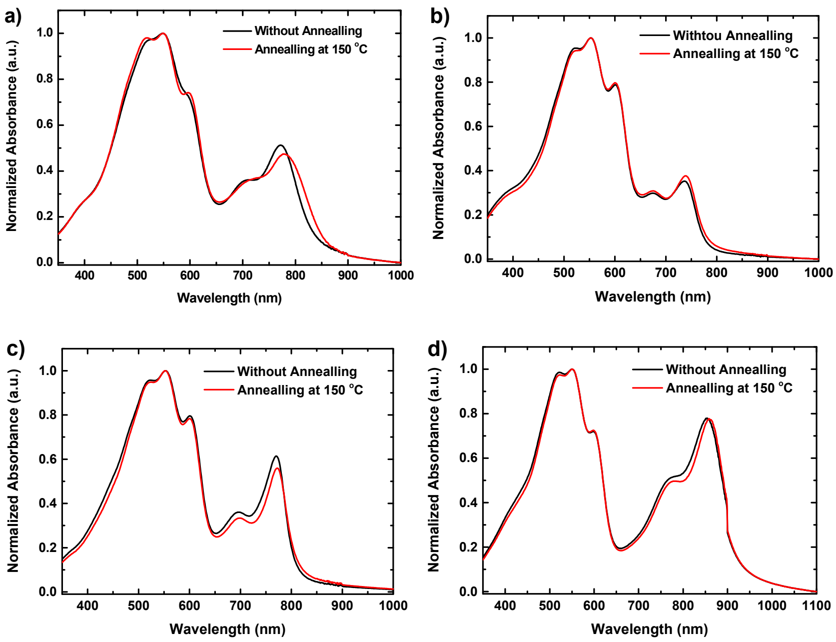

Fig. S2. Absorption spectra of P3HT:DPP-polymer blends (2:1 w/w) as thin films without or with thermal annealing at 150 °C for 10 min. (a) P3HT:PDPP2TzT, (b) P3HT:PDPP2TzBDT, (c) P3HT:PDPP2Tz2T and (d) P3HT:PDPP2TzDTP. The thin film of P3HT:PDPP2TzT was spin coated from chloroform solution with 5% DIO. The other blend films were spin coated from chloroform solution with 10% *o*-DCB. All films were put into a high vacuum chamber to remove the possible solvent before measurement.

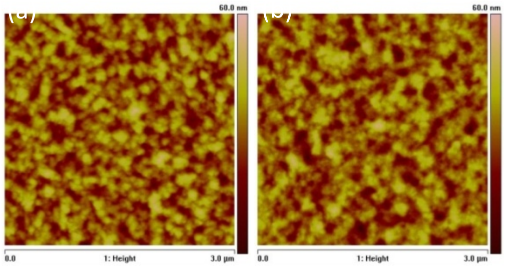

Fig. S3. AFM height image of P3HT:PDPP2TzT films spin coated from $CHCl_3$:2.5% DIO of (a) without thermal and (b) with thermal annealing at 150 °C for 10 min. The RMS roughness for (a) and (b) is 7.22 nm and 7.16 nm.

Table S2. Characteristics of P3HT:DPP-polymer solar cells fabricated from chloroform with different additive. The active layers were thermal annealed at 150 °C for 10 min. before metal evaporation except for note.

Acceptor	Solvent	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
PDPP2Tz-BDT	$CHCl_3$	1.9	0.73	0.47	0.66
	$CHCl_3$:DIO 2.5%	3.3	0.65	0.43	0.95
	$CHCl_3$:1-CN 3%	4.6	0.74	0.54	1.8
	$CHCl_3$: *o*-DCB 10%	4.9	0.73	0.58	2.1
	$CHCl_3$: *o*-DCB 10% [a]	4.6	0.74	0.54	1.8
PDPP2Tz-2T	$CHCl_3$	4.8	0.76	0.49	1.8
	$CHCl_3$:DIO 2.5%	3	0.48	0.37	0.53
	$CHCl_3$:1-CN 3%	4	0.77	0.53	1.6
	$CHCl_3$:*o*-DCB 10%	5.5	0.76	0.50	2.1
	$CHCl_3$:*o*-DCB 10% [a]	3.7	0.76	0.46	1.3
PDPP2Tz-DTP	$CHCl_3$	1.3	0.71	0.38	0.35
	$CHCl_3$:DIO 2.5%	2.5	0.69	0.42	0.7
	$CHCl_3$:1-CN 3%	1.7	0.67	0.44	0.5
	$CHCl_3$:*o*-DCB 10%	4	0.72	0.51	1.5
	$CHCl_3$:*o*-DCB 10% [a]	3.4	0.72	0.48	1.2

[a] Without thermal annealing. The thickness of active layers is 70 nm.

Table S3. Influence of thickness of active layer on device performance based on P3HT:DPP-polymer (2:1) solar cells. The cells were fabricated from the optimized spin coating method as indicated in the manuscript.

Active Layer	Thickness (nm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
P3HT:PDPP2TzT	80	4.9	0.65	0.57	1.8
	90	6.5	0.66	0.61	2.6
	100	6.2	0.65	0.57	2.3
	115	7.8	0.64	0.61	3
	160	6.5	0.63	0.57	2.3
P3HT:PDPP2TzBDT	80	5.9	0.73	0.54	2.3
	95	4.8	0.73	0.54	1.9
	125	5.4	0.71	0.49	1.9
P3HT:PDPP2Tz2T	70	5.5	0.76	0.50	2.1
	140	3.9	0.74	0.44	1.3
	240	3.8	0.74	0.47	1.3
P3HT:PDPP2TzDTP	70	4	0.72	0.51	1.5
	115	3.8	0.71	0.44	1.2
	150	2.6	0.70	0.4	0.7

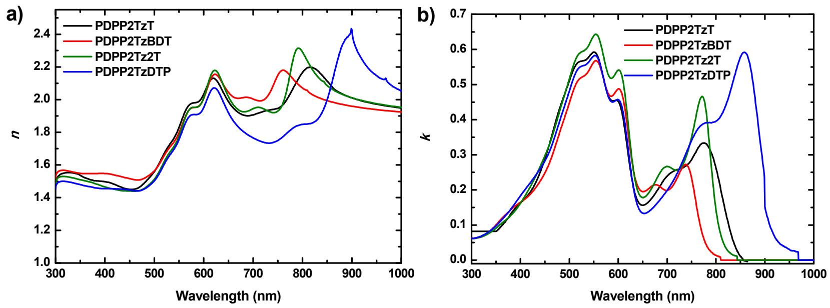

Fig. S4. Refractive index (*n*) and extinction coefficient (*k*) of the P3HT:DPP-polymer layers vs. wavelength. The thin films were spin coated on quartz following the same procedure as for the optimized solar cells.

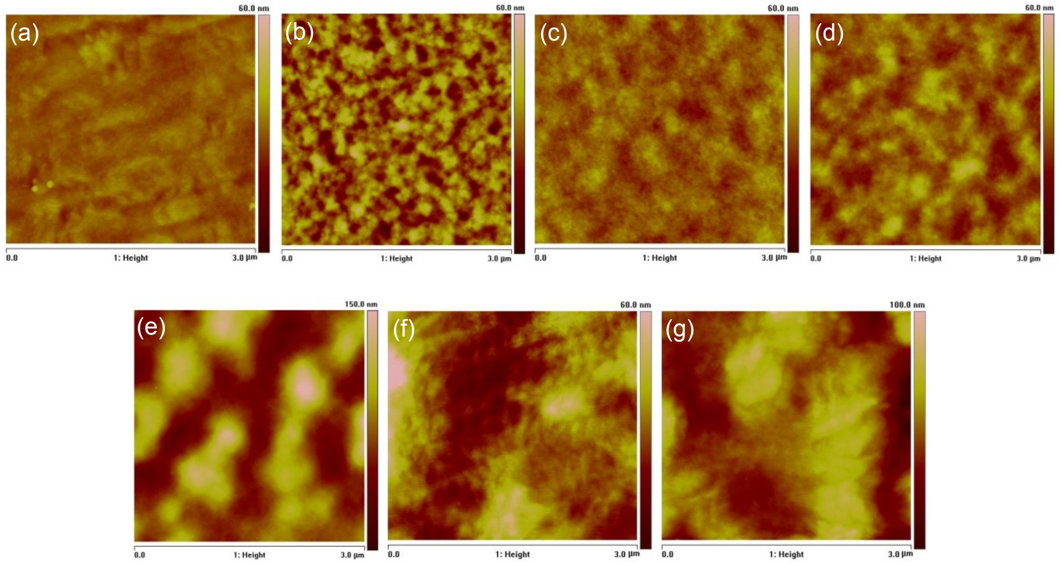

Fig. S5. AFM height image of P3HT:PDPP2TzT films spin coated from $CHCl_3$ (a) without additive or with additive (b) 2.5% DIO, (c) 5% DIO, (d) 10% DIO, (e) 5% DIO+10% *o*-DCB, (f) 3% 1-CN and (g) 10% *o*-DCB. All films were annealed at 150 °C for 10 min. The RMS roughness for (a) to (g) is 2.30 nm, 7.16 nm, 3.18 nm, 4.69 nm, 24.60 nm, 9.72 nm and 15.3 nm.

S1 Y. Sun, J. H. Seo, C. J. Takacs, J. Seifter, A. J. Heeger, *Adv. Mater.*, 2011, 23, 1679-1683.

S2 J. Gilot, M. M. Wienk, R. A. J. Janssen, *Adv. Mater.*, 2010, **22**, E67-E71.

S3 W. Li, W. S. C. Roelofs, M. Turbiez, M. M. Wienk and R. A. J. Janssen, *Adv. Mater.*, 2014, **26**, 3304-3309.