

Synthesis, thin-film morphology, and comparative study of bulk and bilayer heterojunction organic photovoltaic devices using soluble diketopyrrolopyrrole molecules

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Supplementary Information for

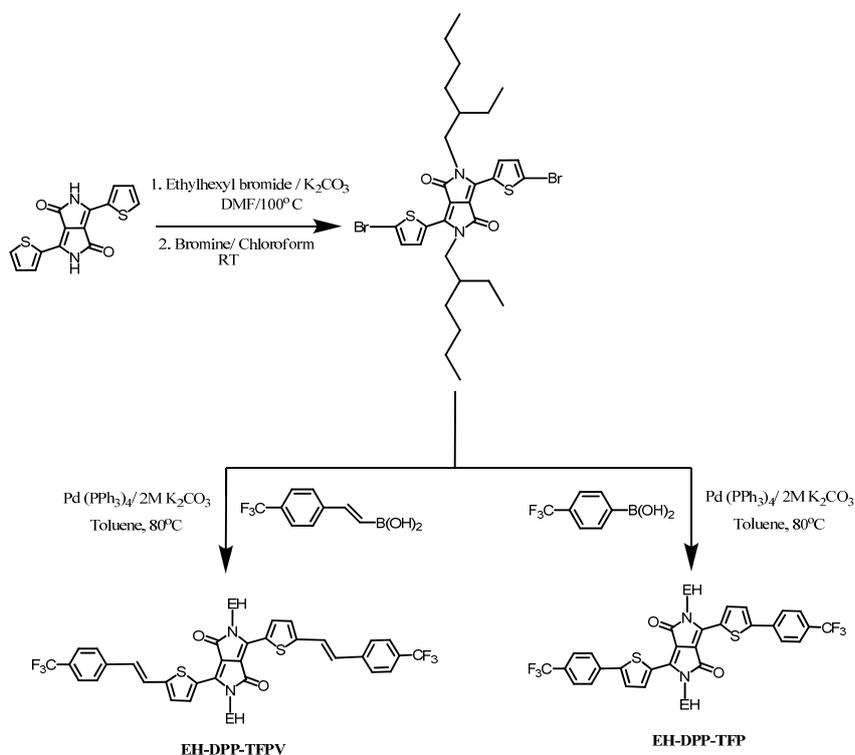
Synthesis, thin-film morphology, and comparative study of bulk and bilayer heterojunction organic photovoltaic devices using soluble diketopyrrolopyrrole molecules

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Details of the chemical synthesis and properties of EH-DPP-TFP and EH-DPP-TFPV



Scheme S1. Synthesis of EH-DPP-TFPV and EH-DPP-TFP via Suzuki coupling.

Synthesis of EH-DPP-TFP

Dibromo-EH-DPP (0.4 g, 0.588 mmol), 4-(trifluoromethyl) phenylboronic acid (0.28 g, 1.47 mmol, 2.5 equiv.) and Pd(PPh₃)₄ (30 mg, 0.025 mmol) were added to a 50 mL schlenk flask and subjected to three vacuum/argon refill cycles. Argon degassed toluene (16 mL), aqueous 2M K₂CO₃ (7 mL) and ethanol (3 mL) were added to the above mixture and stirred for 20 min under argon. After addition of solvent three more vacuum/argon cycles were carried out to fully remove oxygen. The reaction mixture was heated at 80°C for 24 h and monitored via TLC. After completion of the reaction, toluene was removed using a rotovap and the product extracted with chloroform, then successively washed with water, and dried over MgSO₄. Removal of the solvent afforded the crude product which was then purified using column chromatography (silica gel, chloroform as eluent) yielding the product as dark purple crystalline solid (0.250 g, 69%).

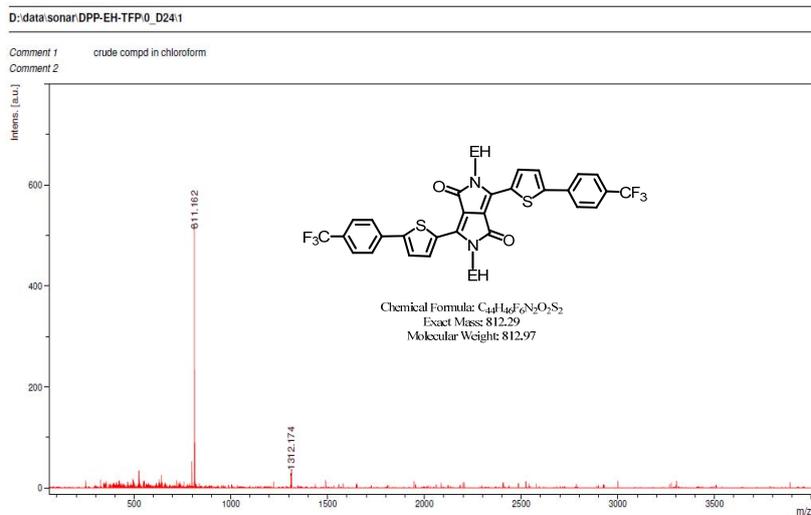
¹H NMR (CDCl₃): δ 0.93-0.85 (m, 12 H), 1.39 - 1.28 (m, 16 H), 1.90-1.88 (s, 2 H), 4.09-4.06 (t, 4 H), 7.55-7.54 (d, 2 H), 7.69-7.67 (d, 4 H), 7.79-7.77 (d, 4 H), 8.95-8.94(d, 2 H).

Calculated for C₄₄H₄₆F₆N₂O₂S₂: C 65.01, H 5.70, F, 14.02, N 3.45, O 3.94, S 7.89 %; Found: C 64.98, H 5.76, N 3.37, S 7.86 %. MS (MALDI-TOF, *m/z*): found 811.16; calcd. for C₄₄H₄₆F₆N₂O₂S₂= 812.29.

Synthesis of EH-DPP-TFPV

This reaction was carried out as described for EH-DPP-TFP using dibromo-EH-DPP (0.4 g, 0.588 mmol), trans-2-[4-(trifluoromethyl)phenyl]vinyl-boronic acid (0.204 g, 0.944 mmol, 2.5 equiv.), Pd(PPh₃)₄ (30 mg, 0.025 mmol) in toluene (16 mL), aqueous 2M K₂CO₃ (7 mL) and ethanol (3 mL) as the solvent mixture. The crude product was purified using column chromatography (silica gel, hexane: chloroform as eluent) and yielded the product as purple solid (11.0 g, 54%).

(a)



(b)

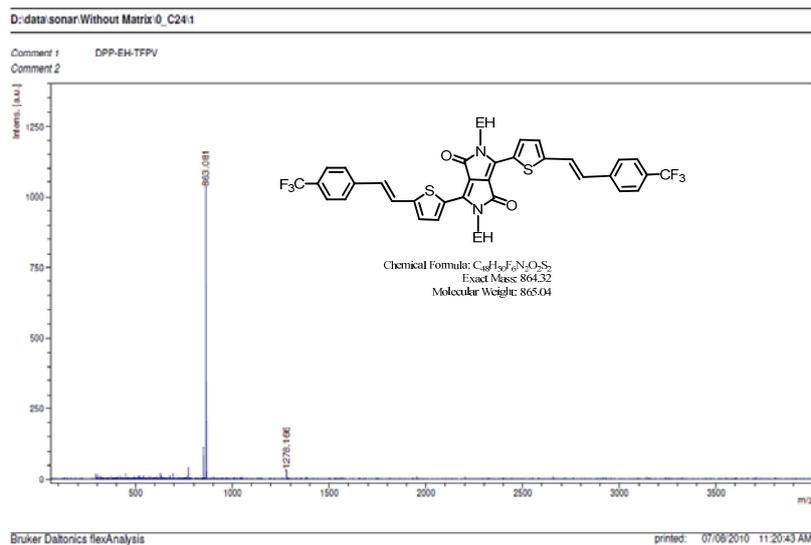
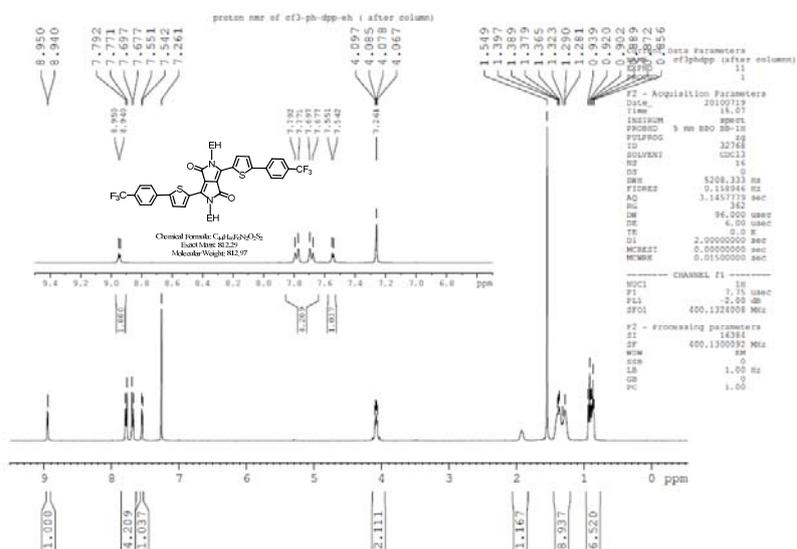


Figure S2. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectra of (a) EH-DPP-TFP and (b) EH-DPP-TFPV.

(a)



(b)

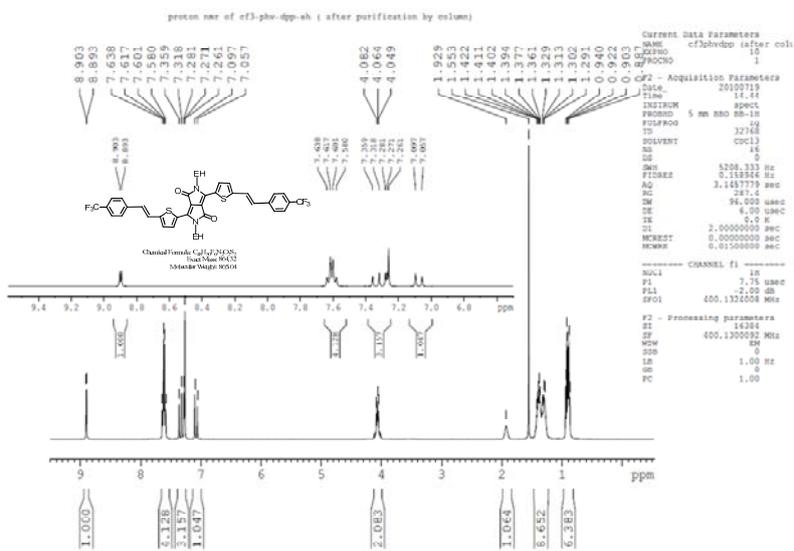


Figure S3. ¹H-NMR spectra of (a) EH-DPP-TFP and (b) EH-DPP-TFPV in CDCl₃.

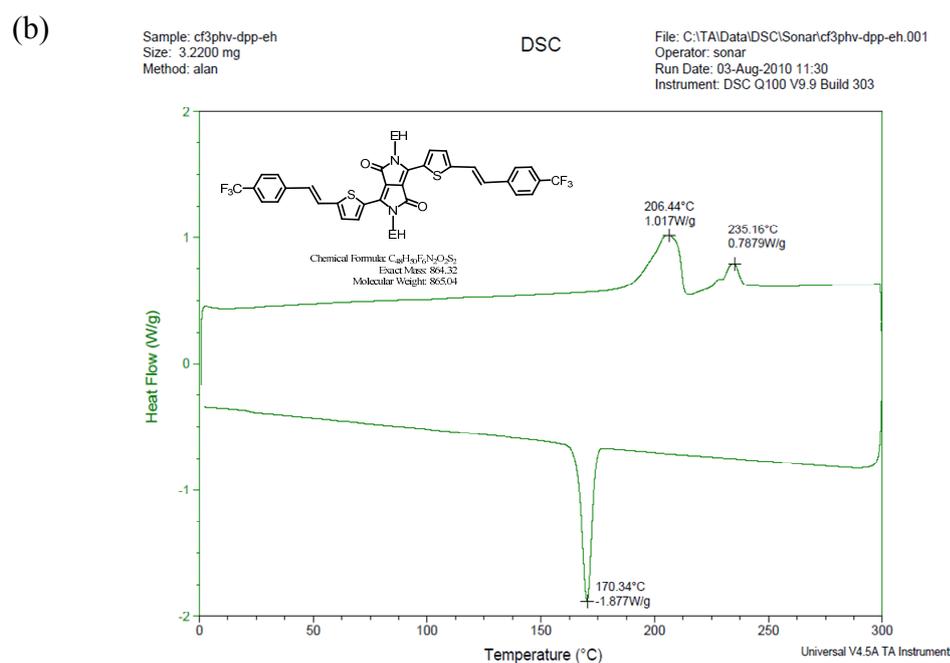
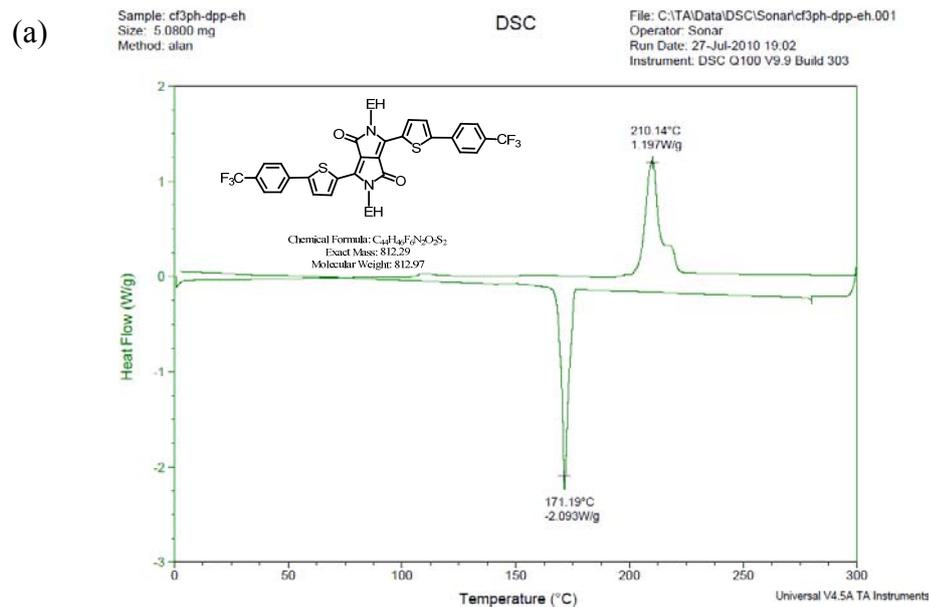


Figure S4. DSC thermograms of (a) EH-DPP-TFP and (b) EH-DPP-TFPV.

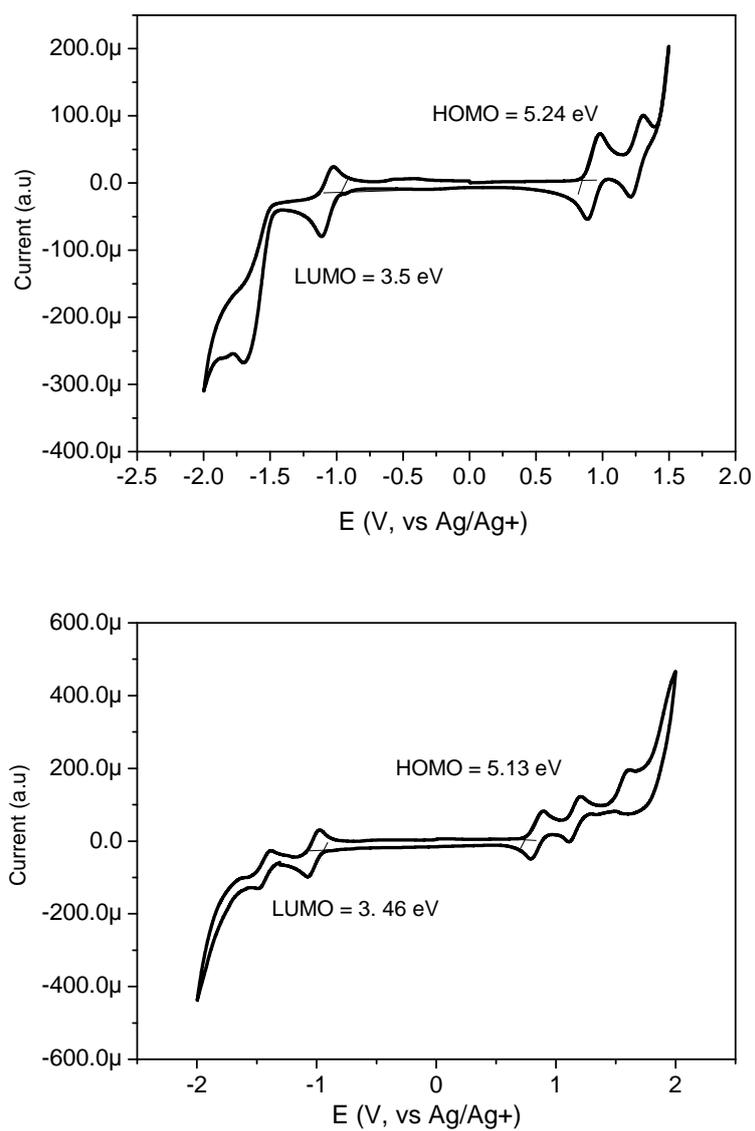


Figure S5. Cyclic voltammograms of (top) EH-DPP-TFP and (bottom) EH-DPP-TFPV.

UV spectra and X-ray diffractograms of EH-DPP-TFP films from CHCl₃, as-coated, heat-treated and solvent vapour-treated

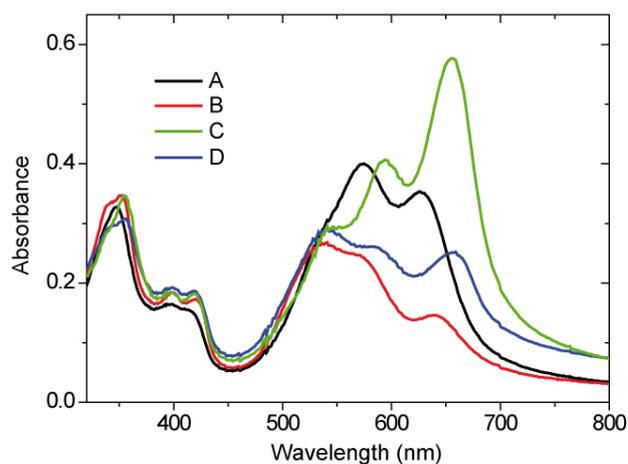


Figure S6. Absorption spectra of EH-DPP-TFP thin films spin-coated on PEDOT:PSS from CHCl₃. A) as-coated, room temperature; B) after annealing at 120 °C for 30 min (A → B); C) after CHCl₃ vapour treatment of as-coated film for 12 h (A → C); D) after CHCl₃ vapour treatment of heated film for 12 h (B → D).

Absorption spectra A and B are recapitulations from Figure 2i, main text, for clarity. Figure S6 shows that CHCl₃ vapour treatment of the as-coated or heated film changes the spectra and a dominant absorption at 660 nm appears. Re-annealing of the vapour-treated films (C, D) restores the spectra of the annealed film (B, data not shown); from this we conclude that the solvent-induced molecular rearrangement is reversible. Repeated CHCl₃ vapour treatment followed by annealing provided a means to grow large, needle-like EH-DPP-TFP crystals (see Figure S7). Note that a similar vapour treatment with chlorobenzene was not effective and the absorption spectrum of an annealed film (B) remained unchanged.

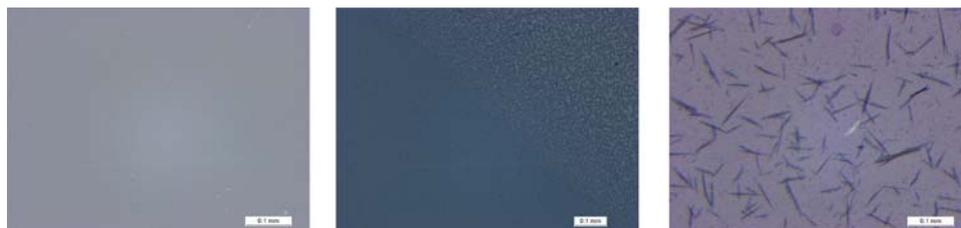


Figure S7. Optical microscope images of EH-DPP-TFP thin films. left) after annealing; middle) after a first CHCl_3 vapour treatment; right) after 3 cycles of CHCl_3 vapour treatment followed by annealing.

Grazing incidence X-ray diffraction measurements were performed on EH-DPP-TFP films coated from CHCl_3 using a PANalytical's X'Pert PRO MRD (see Figure S8). The incident X-rays had a wavelength of 1.5418 \AA ($\text{Cu-K}\alpha$) and the incident angle was 1.0° . The diffraction patterns were scanned from 3° to 10° (2θ) with an angular step interval of 0.02° . All samples displayed diffraction peaks indicating crystallinity in the materials. Heat or solvent annealing changed the diffraction patterns, confirming that the changes in the absorption spectra are accompanied by crystal rearrangements. The diffraction peak at $2\theta \sim 6.47$ degree appears in all diffractograms. The highest degree of crystallinity was induced in an heated film followed by solvent annealing.

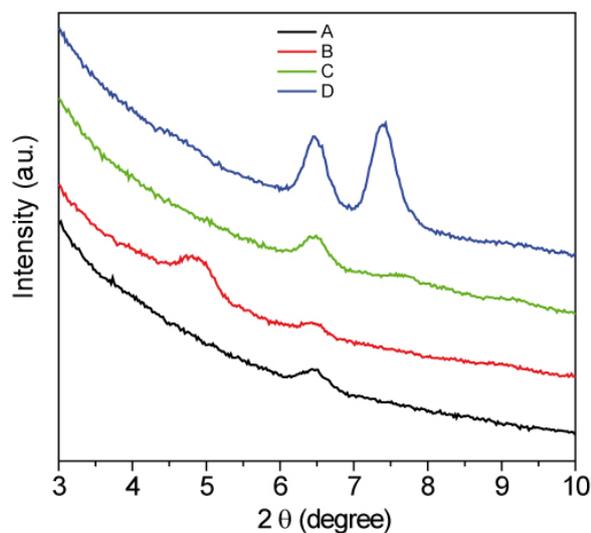


Figure S8. X-ray diffractograms of EH-DPP-TFP thin films spin-coated on PEDOT:PSS from CHCl_3 . A) as-coated, room temperature; B) after annealing at $120\text{ }^\circ\text{C}$ for 30 min (A \rightarrow B); C) after CHCl_3 vapour treatment of as-coated film for 12 h (A \rightarrow C); D) after CHCl_3 vapour treatment of heated film for 12 h (B \rightarrow D). The diffractograms were vertically offset for clearer presentation.

Table with peak positions and calculated d -spacings from Figure S8.

Sample	Peak position (2Θ)	d -spacing (\AA)
A	6.46	13.67
B	4.87	18.13
C	6.47	13.65
	6.46	13.67
D	7.70	11.48
	6.47	13.65
	7.40	11.94

AFM and optical microscope images of EH-DPP-TFP and EH-DPP-TFPV thin films

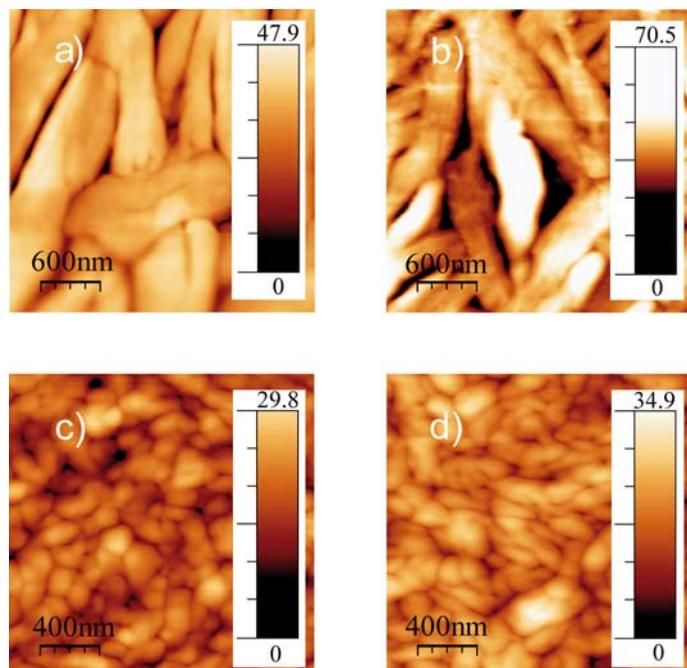


Figure S9. AFM topographical images of spin-coated films on PEDOT:PSS of (a,b) EH-DPP-TFP and (c,d) EH-DPP-TFPV dissolved in chlorobenzene : chloroform = 3 : 2; concentrations always 20 mg dye/mL solvent; (a,c) as-coated films, (b,d) after annealing at 120 °C for 30 min.

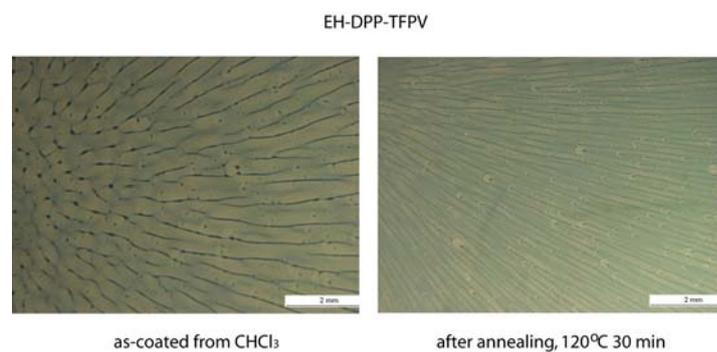


Figure S10. Optical microscope images of thin spin-coated EH-DPP-TFPV films on PEDOT:PSS from CHCl_3 , before and after annealing. The images demonstrate the poor dye film formation when coated from CHCl_3 .

Absorbance spectra of EH-DPP-TFPV film and EH-DPP-TFPV / C₆₀ bilayer

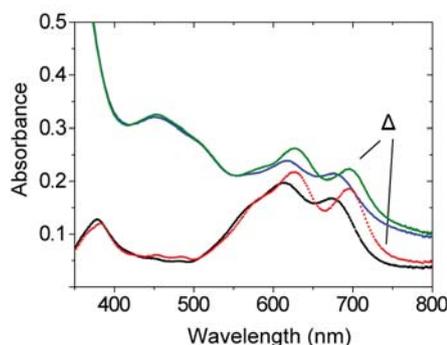


Figure S11. Absorbance spectra of pure 20 nm thick EH-DPP-TFPV film (dotted lines) as-spin coated (black) and after annealing (red, Δ) at 120 °C for 30 min on a digitally controlled hotplate inside the glovebox; corresponding spectra (solid lines) of a EH-DPP-TFPV (20 nm) / C₆₀(40 nm) bilayer before (blue) and after (green) annealing.

Bulk heterojunction solar cells based on EH-DPP-TFP / EH-DPP-TFPV and poly-3-hexylthiophene (P3HT)

Recently, we successfully fabricated BHJ solar cell devices using DPP-TFP and DPP-TFPV with straight dodecyl side chains as acceptor molecules with P3HT as electron donor and achieved PCE close to 1%.¹ However, device fabrication was difficult due to solubility reasons of the blends and films had to be spin coated from hot solutions onto substrates immediately to prevent material precipitation. By replacing the side chains with ethyl hexyl, the solubility of EH-DPP-TFP and EH-DPP-TFPV was enhanced, and attempts were made to fabricate similar BHJ devices with P3HT. We used, as in Ref. 1, a 1:2 blend mixture between P3HT and EH-DPP-TFP or EH-DPP-TFPV (10 mg/mL and 20 mg/mL, respectively). For the solvent chloroform, only very thick films (between 300 nm and 400 nm) could be coated, also for very high acceleration (3000 rpm/s) and final spin speeds (5000 rpm). No working solar

cells could be fabricated with such thick films. Using chlorobenzene, we were able to prepare thinner films, ~ 60 nm for P3HT/ EH-DPP-TFP, and ~150 nm for P3HT/ EH-DPP-TFPV.

Solar cells performed as follows:

Table S1. Performance data of bulk heterojunction solar cells using EH-DPP-TFP and EH-DPP-TFPV as electron acceptors with P3HT as donor. The illumination intensity was 100 mW cm⁻².

From Chlorobenzene		J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF	η (%)
EH-DPP-TFP : P3HT	As prepared	0.3	0.11	0.12	0.004
	Annealed, 150 °C, 30 min	1.1	0.38	0.14	0.06
EH-DPP-TFPV : P3HT	As prepared	0.14	0.09	0.08	0.001
	Annealed	0.12	0.41	0.24	0.012

Obviously, cell performances were very poor, and much below the 1% efficiency that was obtained when using the corresponding DPP derivatives with a straight C12 side chain. At this moment, we suggest that the blend mixture develops a very unfavorable film morphology. This resembles recent findings where low performance was obtained for BHJ solar cells consisting of DPP ethyl hexyl substituted derivatives and P3HT due to a coarse morphology of the blend.²

- 1 P. Sonar, G.-M. Ng, T. T. Lin, A. Dodabalapur and Z.-K. Chen, *J. Mater. Chem.*, 2010, **20**, 3626.
- 2 B. P. Karsten, J. C. Bijleveld and R. A. J. Janssen, *Macromol. Rapid Commun.* 2010, **31**, 1554.