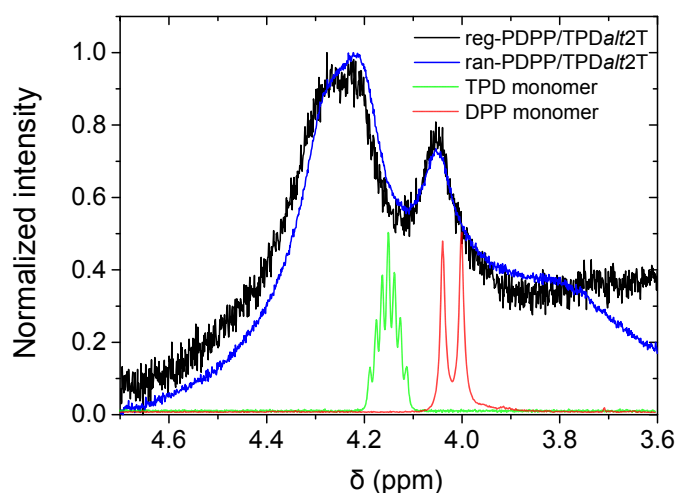


## Electronic Supplementary Information

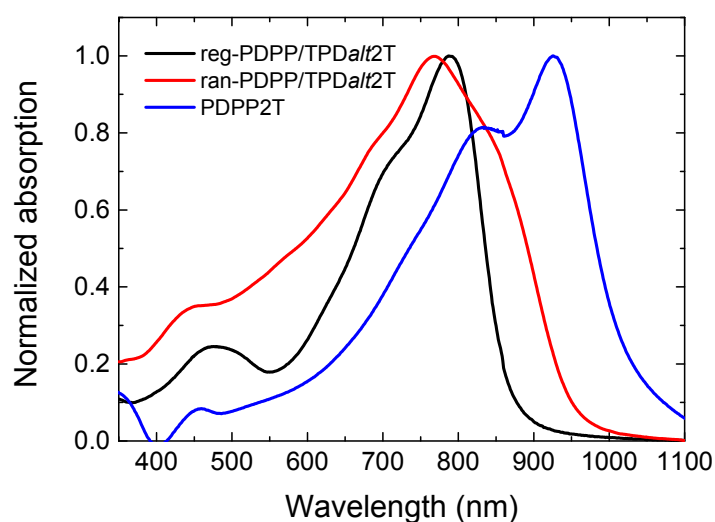
### Comparing Random and Regular Diketopyrrolopyrrole-Bithiophene-Thienopyrrolodione Terpolymers for Organic Photovoltaics

Koen H. Hendriks, Gaël H. L. Heintges, Martijn M. Wienk, René A. J. Janssen\*

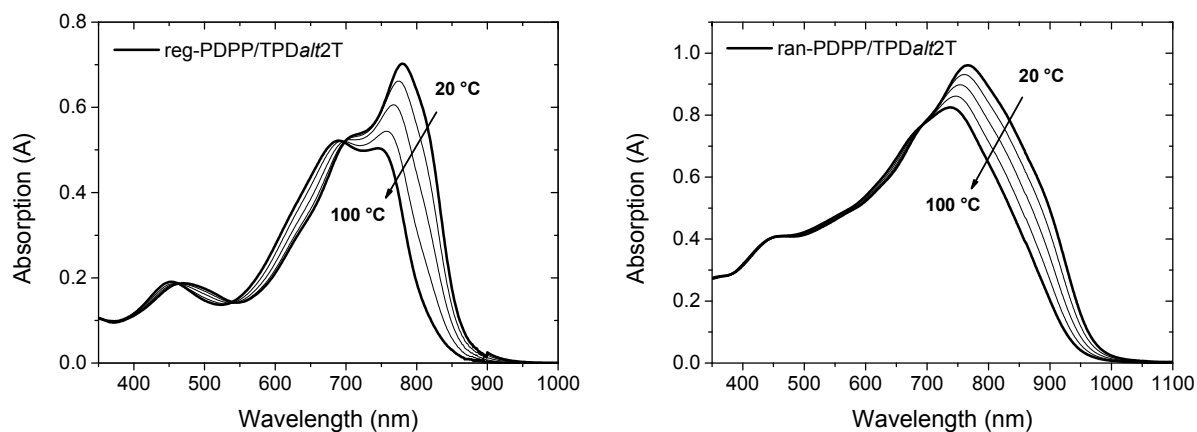
#### Additional figures



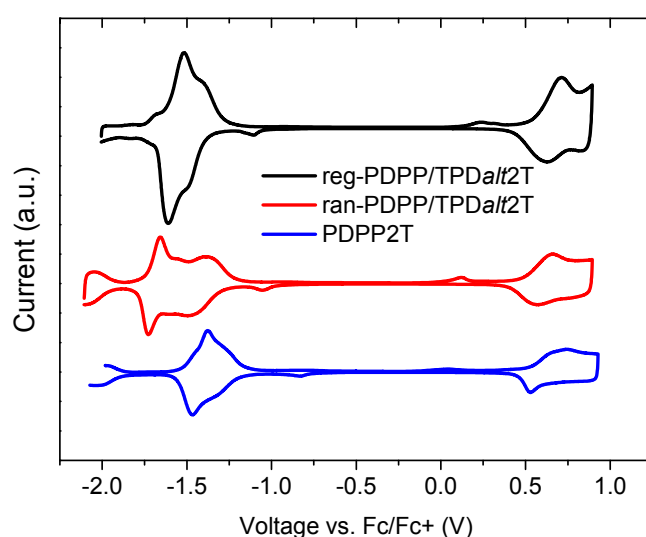
**Fig. S1.** Normalized  $^1\text{H}$ -NMR spectra of reg-PDPP/TPDalt2T and ran-PDPP/TPDalt2T between 4.7 and 3.6 ppm displaying the signals of the  $\alpha$ -protons on the alkyl side chains of TPD and DPP.



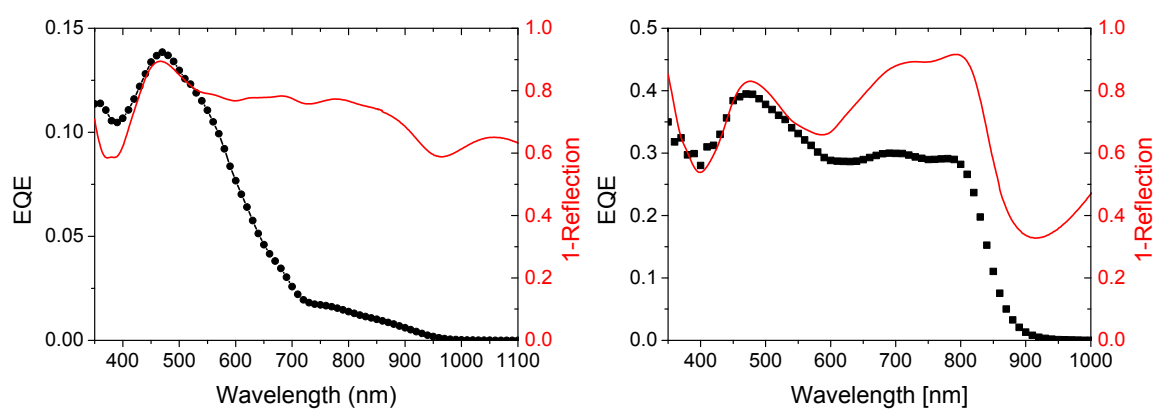
**Fig. S2.** Absorption spectra of reg-PDPP/TPDalt2T, ran-PDPP/TPDalt2T, and PDPP2T in thin films.



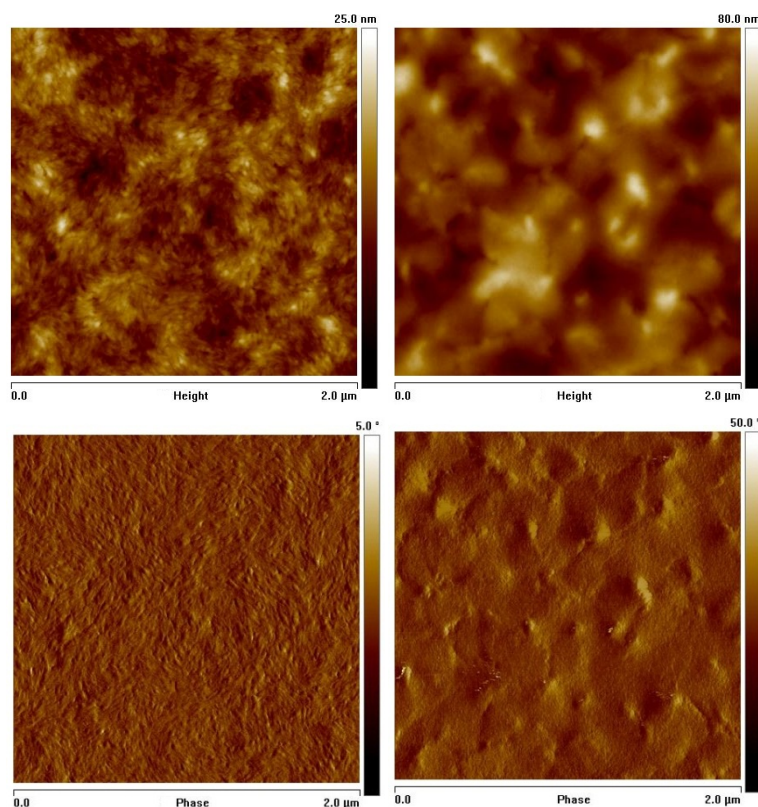
**Fig. S3.** UV/vis spectra of reg-PDPP/TPDalt2T and ran-PDPP/TPDalt2T at elevated temperatures in dilute *o*-DCB solution.



**Fig. S4.** Cyclic voltammograms of reg-PDPP/TPDalt2T, ran-PDPP/TPDalt2T, and PDPP2T in thin film vs. Fc/Fc<sup>+</sup>.



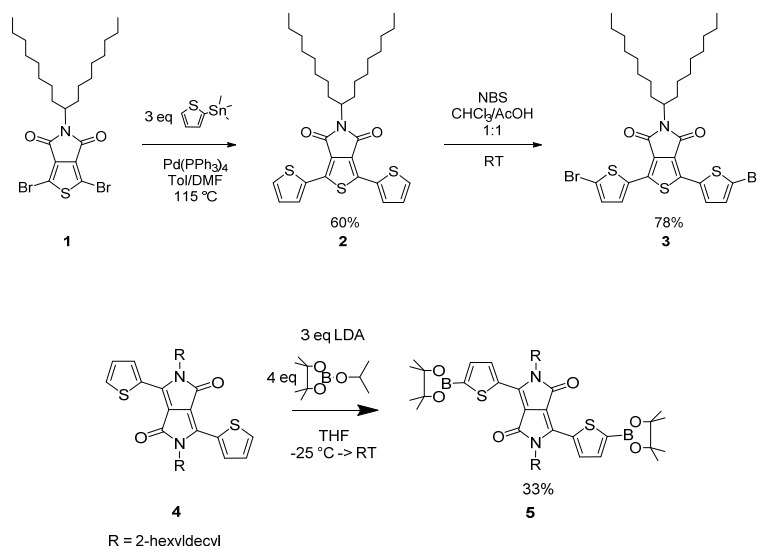
**Fig. S5.** Reflection (red line) and EQE (solid circles) spectra of reg-PDPP/TPDalt2T:[70]PCBM cell (left) and ran-PDPP/TPDalt2T:[70]PCBM (right) solar cells.



**Fig. S6.** AFM height (top) and phase (bottom) images of the active layers of reg-PDPP/TPDalt2T:[70]PCBM ( $R_a = 1.78$  nm) and ran-PDPP/TPDalt2T:[70]PCBM ( $R_a = 6.38$  nm).

## Synthesis

Commercial solvents and reactants were used without further purification unless stated otherwise. 1,3-Dibromo-5-(heptadecan-9-yl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (**1**), 3,6-Bis(thiophen-2-yl)-2,5-bis(2-hexyldecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**4**), and 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione were synthesized according to literature procedures.<sup>S1,S2</sup> 2,5-Bis(2-hexyldecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**5**) was prepared according to a slightly modified literature procedure.<sup>S3</sup> PDPP2T was synthesized as described previously.<sup>S4</sup> NMR spectra were recorded on a Varian Mercury (<sup>1</sup>H 400 MHz or 500 MHz, <sup>13</sup>C 100 MHz) spectrometer. Chemical shifts are given in ppm with respect to tetramethylsilane as internal standard. Fourier transform infrared spectroscopy (FTIR) was performed on a Perking Elmer Spectrum Two spectrometer in ATR mode. Matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectroscopy was performed on a Bruker Autoflex Speed spectrometer.



**Scheme S1.** Synthesis of monomers **3** and **5**.

### **5-(Heptadecan-9-yl)-1,3-di(thiophen-2-yl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (**2**)**

A dried Schlenk flask was charged with **1** (750 mg, 1.37 mmol) and 2-tributylstannylthiophene (1.3 mL, 4.09 mmol). Toluene (40 mL) and DMF (8 mL) were added and the solution was degassed with argon. After addition of tetrakis(triphenylphosphine)palladium (94.6 mg, 0.082 mmol), the mixture was reacted at 115 °C overnight. The cooled solution was then washed with water, dried over magnesium sulfate and the solvents were removed under reduced pressure. The residue was purified using column chromatography (9:1 heptanes:dichloromethane, gradient 7:3), after which **2** was obtained as a yellow solid which was recrystallized in a mixture of methanol and toluene. The product was obtained in a yield of 59% (445 mg). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.03 (d, *J* = 3.9 Hz, 2H); 7.43 (d, *J* = 5.1 Hz, 2H); 7.13 (dd, *J* = 5.0, 3.8 Hz, 2H); 4.17 (h, *J* = 5.1 Hz, 1H); 2.08 (m, 2H); 1.69 (m, 2H); 1.33-1.17 (br, 24H); 0.84 (t, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 163.00; 136.33; 132.45; 129.90; 128.56; 128.41; 128.33; 52.87; 32.36; 31.83; 29.45; 29.34; 29.23; 26.79; 22.64; 14.09. MALDI-TOF-MS: [M<sup>+</sup>] calc: 555.23, found: 555.24.

### **1,3-Bis(5-bromothiophen-2-yl)-5-(heptadecan-9-yl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione (**3**)**

A solution of **2** (425 mg, 0.765 mmol) in chloroform and acetic acid (1:1, 10 mL) was cooled to 0 °C and kept in the dark. *N*-bromosuccinimide (283 mg, 2.1 mmol) was added in portions and the mixture was allowed to warm to room temperature. *N*-bromosuccinimide was added

until the reaction was found to be complete via TLC. (in total 200 mg NBS was added additionally) The solution was subsequently washed with water, dried over magnesium sulfate and reduced in volume under reduced pressure. The obtained solids were purified using column chromatography (9:1 heptanes:dichloromethane, gradient 7:3), followed by precipitation in methanol from toluene. The product (**3**) was obtained as yellow needles in a yield of 73% (399 mg). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.64 (d, *J* = 4.3 Hz, 2H); 7.07 (d, *J* = 3.9 Hz, 2H); 4.15 (h, *J* = 5.1 Hz, 1H); 2.05 (m, 2H); 1.70 (m, 2H); 1.34-1.17 (br, 24H); 0.85 (t, *J* = 6.7 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 162.79; 135.04; 133.73; 131.07; 129.71; 128.49; 116.69; 53.06; 32.31; 31.83; 29.43; 29.29; 29.23; 26.76; 22.64; 14.09. MALDI-TOF-MS: [M<sup>+</sup>] calc: 711.05, found: 711.07.

**2,5-Bis(2-hexyldecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**5**)**

To a cooled solution (0 °C) of diisopropylamine (0.18 mL, 1.24 mmol) in dry THF (4 mL), a 2.5 M solution of *n*-butyllithium in hexane (0.48 mL, 1.20 mmol) was added drop wise over the course of 10 minutes. The mixture was kept at 0 °C during 15 minutes, after which it was allowed to warm to room temperature and stirred another 45 minutes. This mixture was then added drop wise to a solution of 2,5-bis(2-hexyldecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**4**) (0.3 g, 0.40 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.32 mL, 1.60 mmol) in dry THF (4 mL) at -25 °C during 25 minutes. This mixture was kept 10 minutes at -25 °C and subsequently stirred at room temperature for 1 hour. A 1.2 M solution of HCl (7 mL) was then added, after which the mixture was extracted with dichloromethane. The combined organic layers were then washed with water, dried over magnesium sulfate and the solvents were removed under reduced pressure. The solids were then dissolved in dichloromethane and precipitated in acetone at 0 °C. This process was repeated one more time before drying the solids in *vacuo*. The product (**5**) was recovered as a pink solid in a yield of 33% (133 mg). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.89 (d, *J* = 3.9 Hz, 2H); 7.70 (d, *J* = 3.9 Hz, 2H); 4.05 (d, *J* = 7.4 Hz, 4H); 1.89 (br, 2H); 1.33-1.17 (br, 48H); 0.85 (t, *J* = 6.3 Hz, 12H); 0.83 (t, *J* = 6.3 Hz, 24H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 161.73, 140.52, 137.63, 136.10, 135.64, 108.73, 84.60, 46.23, 37.76, 31.87, 31.77, 29.51, 29.28, 24.77, 22.66, 22.59, 14.11, 14.09. MALDI-TOF-MS: [M<sup>+</sup>] calc: 1001.13, found: 1001.35.

### **reg-PDPP/TPDalt2T**

A Schlenk flask was charged with **5** (100 mg, 0.10 mmol), **3** (71.8 mg, 0.10 mmol) and tri(*tert*-butyl)phosphonium tetrafluoroborate (3.50 mg, 0.012 mmol) and placed under argon. 4 mL of THF and 0.25 mL of a degassed, 2 M solution of potassium phosphate in water were added and degassed with argon. Tris(dibenzylideneacetone)dipalladium (2.74 mg, 0.0030 mmol) was then added and the reaction flask was sealed. After stirring at room temperature for 15 minutes the mixture was heated to 70 °C in the course of 1.5 hours and left to react overnight. The solid mixture was subsequently dissolved in chloroform and precipitated in methanol. The crude product was then dissolved in chloroform, EDTA (300 mg) was added and refluxed for one hour, after which water was added and the mixture was refluxed for another hour. The organic phase was cooled and washed with water, reduced in volume under reduced pressure and precipitated in methanol. The solids were subjected to Soxhlet extraction with acetone, hexane, dichloromethane and chloroform. The polymer was then precipitated in methanol and recovered as a dark blue film. (59 mg in dichloromethane fraction, Y = 44%, 75 mg in chloroform fraction, Y = 55%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ): 9.7-8.4 (br); 8.3-7.3 (br, low intensity); 7.5-6.2 (br); 4.7-3.2 (br, 2 peaks); 2.6-1.0 (br); 1.0-0.0 (br). GPC (*o*-DCB, 80 °C):  $M_n = 50.0$  kDa,  $M_w = 137$  kDa, PDI = 2.74.

### **ran-PDPP/TPDalt2T**

Bis(cyclooctadiene)nickel(0) (153 mg, 0.555 mmol) and 2,2'-bipyridine (90 mg, 0.574 mmol) were charged in a dried Schlenk flask under nitrogen atmosphere and 3 mL of dry toluene was added. This mixture was stirred at 70 °C for one hour, and subsequently transferred to a Schlenk flask containing a degassed solution of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (83.9 mg, 0.093 mmol) and **3** (66.1 mg, 0.093 mmol) in 3 mL of dry toluene. The resulting mixture was then stirred at 70 °C overnight, before adding 0.1 mL of bromobenzene, followed by another 30 minutes of stirring. 15 mL of a 0.1 M HCl, methanol and acetone mixture (1:1:1) was then added, followed by extraction with chloroform. The organic layers were then combined, washed with water, reduced in volume and precipitated in methanol. The solids were then dissolved in 1,1,2,2-tetrachloroethane at 115 °C, before ethylenediaminetetraacetic acid (300 mg) was added and the mixture was stirred at 115 °C for one hour. Water was subsequently added and the mixture was refluxed further for 2 hours. The organic layer was then separated and washed with water, before reducing it in volume and precipitating the polymer in methanol. The crude product was then subjected to Soxhlet extraction with acetone, hexane and

chloroform. The chloroform fraction was reduced in volume and precipitated in methanol. The polymer was recovered as a dark blue powder (52 mg, Y = 43%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ): 9.7-8.4 (br); 8.3-7.3 (br, low intensity); 7.5-6.2 (br); 4.7-3.2 (br, 2 peaks); 2.6-1.0 (br); 1.0-0.0 (br). GPC (*o*-DCB, 80 °C):  $M_n = 34.6$  kDa,  $M_w = 116$  kDa, PDI = 3.36.

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