

Supporting information

**Segregated *versus* disordered stacking in two low bandgap alternated copolymers for photovoltaic applications : Impact of polymorphism on optical properties**

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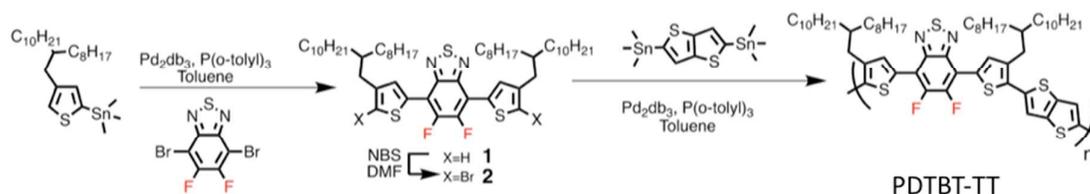
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1) Synthesis of PDTBT-TT.



**Figure S1** : Synthesis route of PDTBT-TT.

**5,6-difluoro-4,7-bis(4-(2-octyldodecyl)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (compound 1).**

A flame dried Schlenk was charged with the 4,7-Dibromo-5,6-difluoro-2,1,3-benzothiadiazole (1.0 equiv) and the 2-(trimethylstannyl)-4-(2-octyldodecyl)thiophene compound (2.2 equiv). Anhydrous and degassed toluene (0.1M) was added under inert gas. Finally, the  $\text{Pd}_2(\text{dba})_3$  (2.0 mol%) and  $\text{P}(\text{o-tolyl})_3$  (8.0 mol%) were added in one portion and the mixture was stirred 24 hours at 120°C. After cooling to room temperature the reaction mixture was filtered through a pad of celite and the toluene solution was evaporated under reduced pressure. Then, the crude material was purified by column chromatography (silica gel, petroleum ether). Yield: 65%.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 8.09 (d,  $^4J$  = 1.1 Hz, 2H), 7.17 (d,  $^4J$  = 1.0 Hz, 2H), 2.65 (d,  $^3J$  = 6.7 Hz, 4H), 1.70 (m, 2H), 1.26 (m, 64H), 0.87 (t,  $^3J$  = 6.0 Hz, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 151.4 (dd,  $J$  = 256.5 and 20.4 Hz), 149.0 (t,  $J$  = 4.23 Hz), 142.37, 132.9 (d,  $J$  = 3.8 Hz), 131.0, 124.81, 111.69 (dd,  $J$  = 9.1 and 4.9 Hz), 39.0, 34.9, 33.4, 31.9, 30.0, 29.7, 29.6, 29.3, 26.7, 22.6, 14.0.

## **4,7-bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (compound 2)**

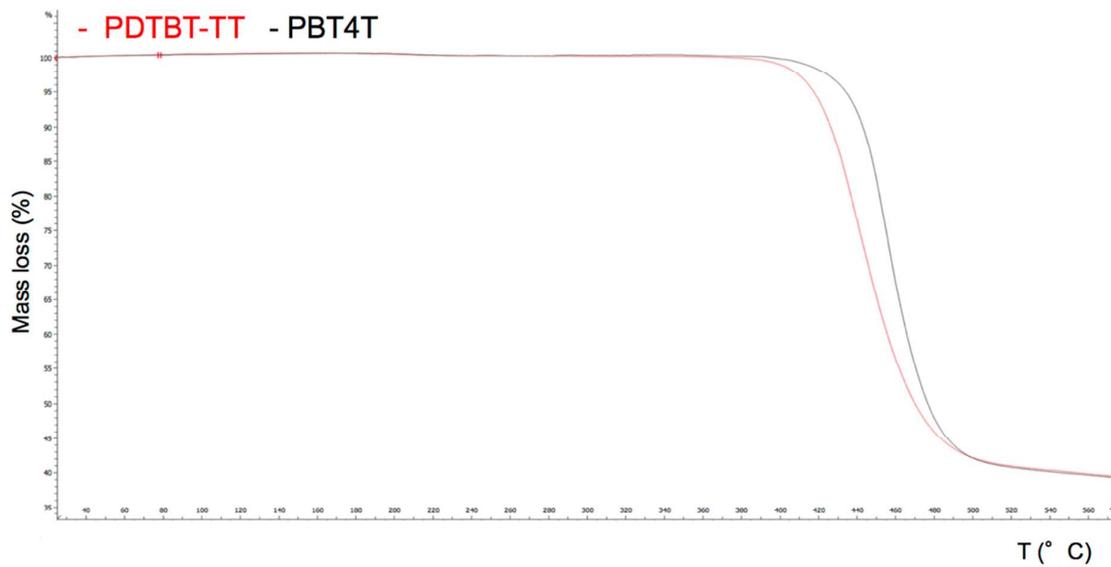
The compound 1 (1.0 equiv) was solubilized in DMF (0.05 M) under argon in the dark. NBS (2.0 equiv) was added portion wise. The resulting solution was stirred at room temperature under argon overnight. Water and diethylether were added and the resulting solution was stirred for 2h. The organic phase was separated from the water phase and extracted with brine (3 x 100 mL). The organic phase was dried with sodium sulfate, filtered and the solvent evaporated under reduced pressure. The crude product was purified by column chromatography. The crude product was purified by column chromatography (silica gel, petroleum ether). Yield: 78%.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 7.90 (s, 2H), 2.57 (d,  $^3J$ = 7.0 Hz, 4H), 1.74 (m, 2H), 1.25 (m, 64H), 0.86 (t,  $^3J$ = 5.4 Hz, 12H).

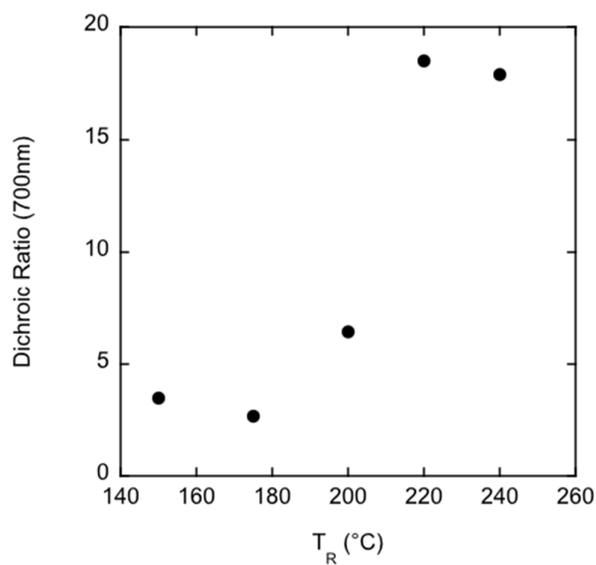
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 152.4 (dd,  $J$ = 260.3 and 20.4 Hz), 148.4 (t,  $J$ = 4.2 Hz), 141.8, 132.3 (t,  $J$ = 4.7 Hz), 131.0, 115.1 (t,  $J$ = 3.6 Hz), 111.0 (dd,  $J$ = 4.7 and 13.3 Hz), 38.6, 34.2, 33.4, 31.9, 30.0, 29.7, 29.65, 29.61, 29.3, 26.6, 22.7, 14.1.

### **PDTBT-TT, Stille polymerization.**

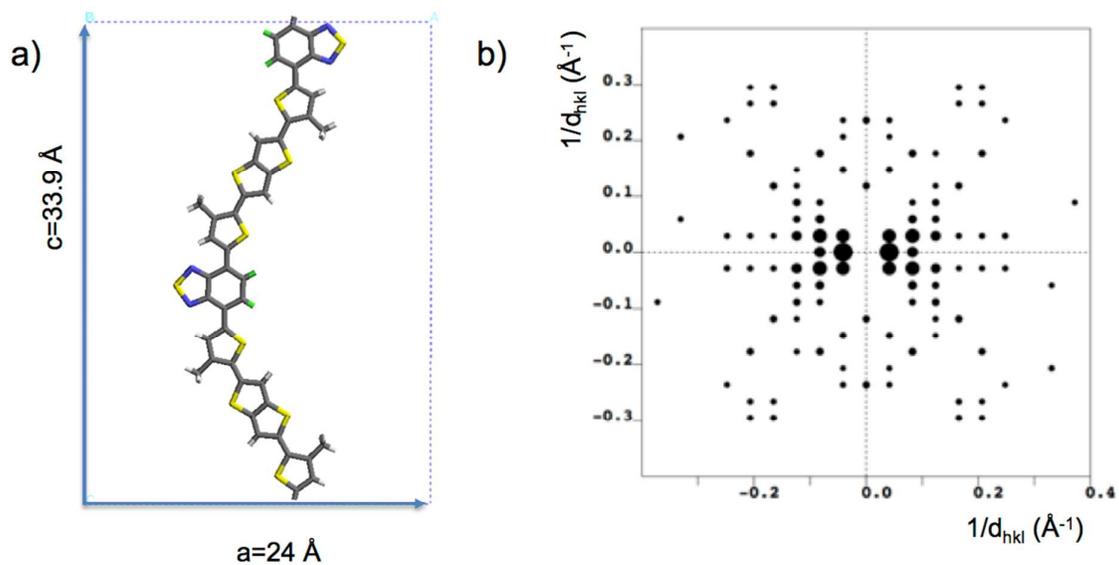
A flame dried Schlenck was charged with dibrominated compound 2 (1.0 equiv) and the 2-5-bis-trimethylstannyl-thieno[3,2-b]thiophene (1.0 equiv). Anhydrous and degassed toluene (0.0125 M) was added under inert gas. Then, the  $\text{Pd}_2(\text{dba})_3$  (2 mol%) and  $\text{P}(\text{o-tolyl})_3$  (8 mol%) were added in one portion and the mixture was stirred 24 hours at 120°C. The reaction was quenched with 2-(trimethylstannyl)-thiophene (0.6 equiv) during 1 hour followed by 2-bromothiophene (0.6 equiv). Then, the polymer crude was purified by precipitation in methanol, filtered and separated by Soxhlet extraction with methanol, acetone, cyclohexane and chlorobenzene. Then, the *sodium diethyldithiocarbamate* solution was *added* in the chlorobenzene fraction *and the mixture was stirred at 60°C during 1 hour*. The organic phase was washed with water, separated and evaporated under reduced pressure. Finally, the polymer was precipitated in methanol, filtered and dried under reduced pressure at 40°C overnight, providing powder with a metallic shine.



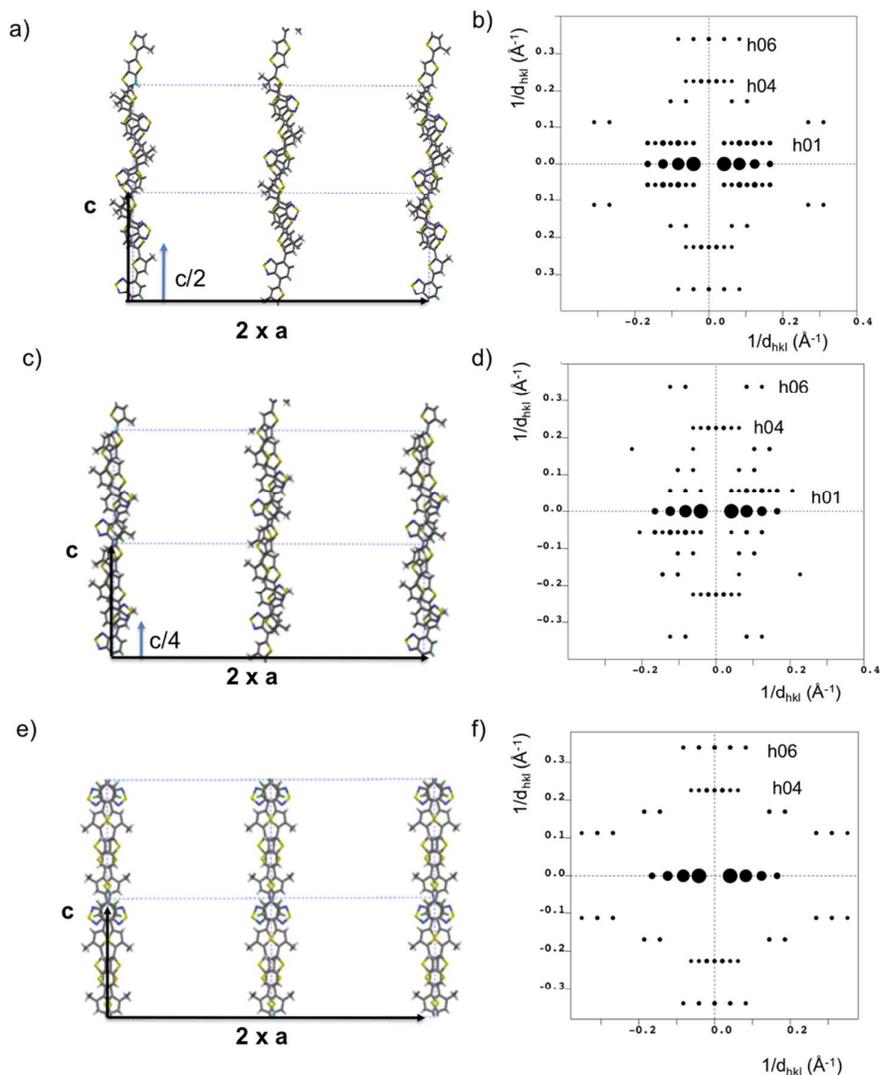
**Figure S2.** TGA trace of PDTBT-TT and PBT4T showing the high thermal stability of the two polymers..



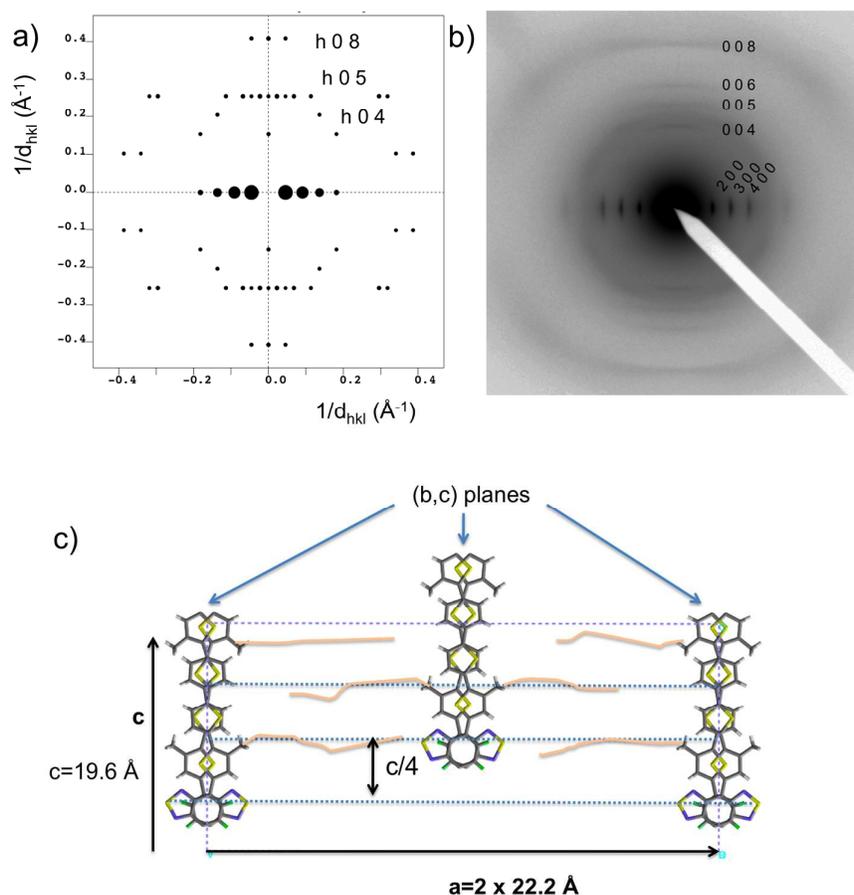
**Figure S3.** Dependence of the dichroic ratio of the 0-0 component at 697 nm versus rubbing temperature  $T_R$  for thin films of PDTBT-TT aligned by high-T rubbing.



**Figure S4.** (a) Zig zag conformation of the backbone of PDTBT-TT as proposed by Zhang et al. (*Macromolecules* 2016, 49, 120) and corresponding electron diffraction pattern with a zone axis  $[0\ 1\ 0]$ . Please note the strong intensity in the first layer line of the 101, 201 and 301 reflections that are not observed in the experimental ED pattern.



**Figure S5.** Two PDTBT-TT unit cells corresponding to two non-segregated stacking modes (a and c) and corresponding ED pattern for the [010] zone (b and d). In addition, the model corresponding to fully segregated stacking is also shown (e and f). *The two models and the respective calculated electron diffraction patterns are obtained for two different values of the relative shift between the chains  $\Delta c$  parallel to the chain direction. In (a)  $\Delta c = c/2$  whereas in (c)  $\Delta c = c/4$  and in (e)  $\Delta c = 0$ . In the cases  $\Delta c \neq 0$ , a strong intensity of reflections in the first layer lines with  $l=1$  is observed in the calculated ED patterns but not observed in the experimental ED pattern.*



**Figure S6.** Comparison of the calculated (a) and experimental (b) ED patterns for the  $[0\ 1\ 0]$  zone of PBT4T. (c)  $(010)$  projection of the refined model corresponding to a segregated stacking of the chains. Disordered side chains are schematically drawn in pink. The unit cell is doubled along the  $\mathbf{a}$  axis to take into account the  $c/4$  shift between successive  $(b,c)$  planes of  $\pi$ -stacked chains that is required for a good interdigitation of side chains. In the true structure, the shift between successive  $(b,c)$  planes is statistical in essence and it is given by  $\pm(2n+1)c/4$  ( $n$  is an integer). Note that the intensity of  $h\ 0\ 4$  reflections is underestimated as the alkyl side chains are not taken into account for the calculation of the ED pattern. Including such side chains would strongly enhance the  $h\ 0\ 4$  reflections.