

## Supporting Information

### Superheated high temperature SEC with chloroform as the mobile phase for $\pi$ -conjugated polymers

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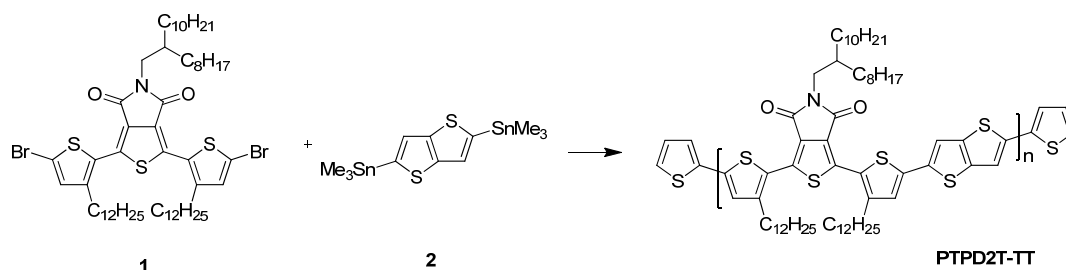
#### Superheated high temperature size-exclusion chromatography

The instrumental set-up of the Superheated HT SEC system has been described in detail elsewhere.<sup>S1</sup> Briefly, A FD-53 oven (Binder, Tuttlingen, Germany) was used to control the SEC temperature. HPLC grade chloroform (Biosolve, Valkenswaard, the Netherlands) was delivered at 1 mL/min at room temperature with a LC-20 AD pump (Shimadzu, Kyoto Japan) and was heated up to the oven temperature before reaching the SEC column by passing through a heater exchanger made from a 1.5 m narrow-bore stainless steel tubing (1/16 in. (o.d.)  $\times$  0.004 in. (i.d.), Alltech-Grace, Lokeren, Belgium) located in the oven. Another piece of 1.2 m of narrow bore stainless steel tubing (1/16 in. (o.d.)  $\times$  0.004 in. (i.d.), Alltech-Grace) was connected after the column to depressurize the eluent and to cool it down to room temperature before reaching the UV/Vis detector (SPD-20A, Shimadzu). Detection was at 254 or 550 nm. A PLgel mixed-C column (300  $\times$  7.5 mm i.d., 5  $\mu$ m particles, linear molecular weight range up to 2,000 kg/mol based on polystyrene, Agilent Technologies, Amsterdam, the Netherlands) was used for the SEC measurements.

## General synthesis

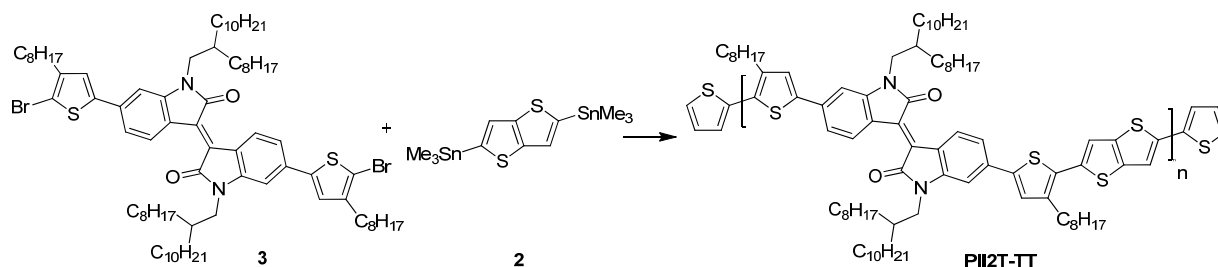
1,3-Bis(5-bromo-3-dodecylthiophen-2-yl)-5-(2-octyldodecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (**1**) was synthesized following literature procedures,<sup>S2,S3</sup> (*E*)-6,6'-bis(5-bromo-4-octylthiophen-2-yl)-1,1'-bis(2-octyldodecyl)-[3,3'-biindolinylidene]-2,2'-dione (**3**) was synthesized similar to literature procedure<sup>S4</sup> and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (**2**) was obtained from Sigma-Aldrich. All monomers were recrystallized and dried prior to use.

## Synthesis of PTPD2T-TT



Toluene:DMF (10:1, 2 mL) was added to a mixture of **1** (70.0 mg, 64.1  $\mu\text{mol}$ ) and **2** (29.9 mg, 64.1  $\mu\text{mol}$ ) under argon atmosphere and degassed for 20 minutes by bubbling argon through the mixture. Tris(dibenzylideneacetone)dipalladium(0) ( $\text{Pd}_2(\text{dba})_3$ ) (2 mol%, 1.28  $\mu\text{mol}$ , 1.17 mg) and triphenylphosphine ( $\text{PPh}_3$ ) (8 mol%, 5.15  $\mu\text{mol}$ , 1.35 mg) were added and the mixture was stirred overnight at 115  $^\circ\text{C}$ . To remove any remaining bromine and trimethyltin end groups, first tributyl(thiophen-2-yl)stannane (80  $\mu\text{L}$ , 256  $\mu\text{mol}$ ) was added and stirred for 1 hour at 115  $^\circ\text{C}$ , followed by 2-bromothiophene (50  $\mu\text{L}$ , 512  $\mu\text{mol}$ ) which was allowed to react for another hour at 115  $^\circ\text{C}$ . The resulting polymer was precipitated in methanol and filtered through a Soxhlet thimble. The precipitate was purified via Soxhlet extraction with acetone, hexane, DCM, and chloroform. The chloroform fraction was concentrated by evaporation under reduced pressure and precipitated in methanol to afford PTPD2T-TT (47 mg, 69%). The remaining solids in the thimble were boiled in 1,1,2,2-tetrachloroethane (TCE) to dissolve it and precipitated in methanol to afford a second sample of PTPD2T-TT (13 mg, 19%). This high molecular weight fraction was used in this study. SEC (Sup-HT  $\text{CHCl}_3$ , 145  $^\circ\text{C}$ ):  $M_n = 64 \text{ kg mol}^{-1}$ , PDI = 2.88 (chloroform fraction). SEC (Sup-HT  $\text{CHCl}_3$ , 145  $^\circ\text{C}$ ):  $M_n = 106 \text{ kg mol}^{-1}$ , PDI = 2.2 (TCE fraction).

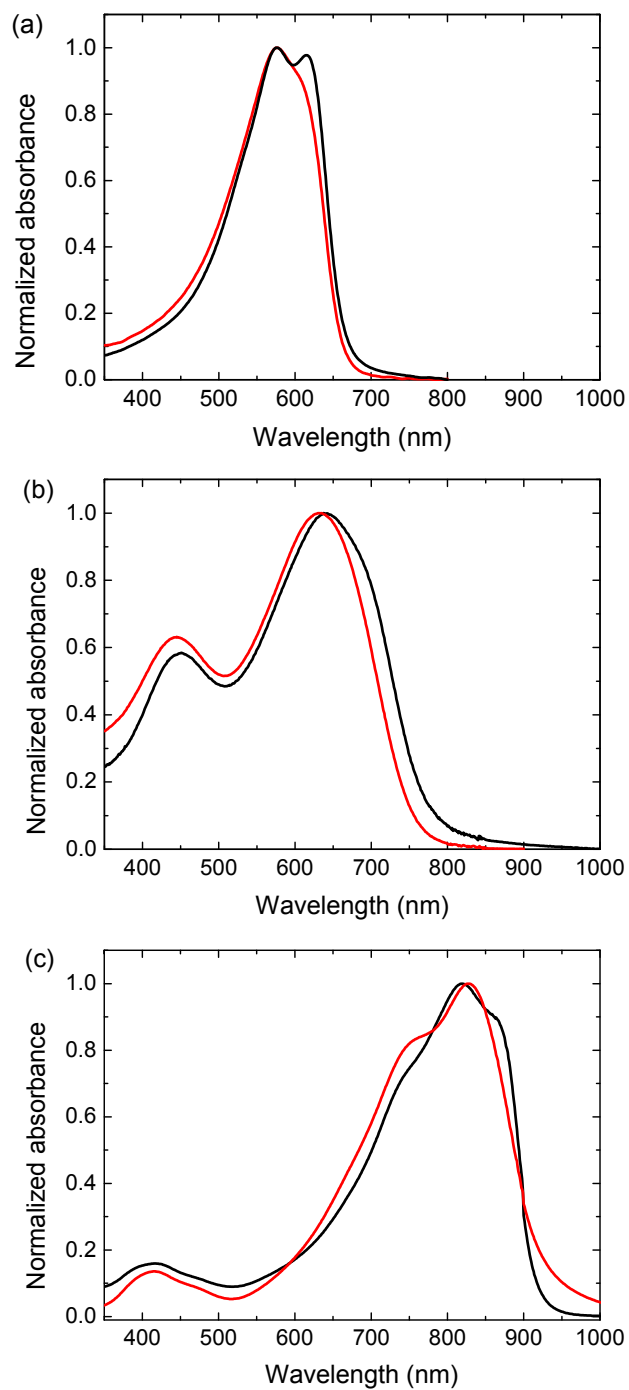
### Synthesis of PII2T-TT



A mixture of **3** (49.98 mg, 36.5  $\mu\text{mol}$ ) and **2** (17.00 mg, 36.5  $\mu\text{mol}$ ) was dissolved in dry toluene:DMF (10:1 1 ml) and argon was bubbled through. After 30 minutes tris(dibenzylideneacetone)dipalladium(0) (0.67 mg, 0.73  $\mu\text{mol}$ ) and triphenylphosphine (0.76 mg, 2.92  $\mu\text{mol}$ ) were added and the reaction mixture was heated to 115  $^{\circ}\text{C}$  for 64 h. Trimethyl(thiophen-2-yl)stannane (69  $\mu\text{L}$ , 0.217 mmol) and 2-bromothiophene (42  $\mu\text{L}$ , 0.435 mmol) were added with an interval of 30 min to end cap the polymer. After 30 min the reaction was allowed to cool to room temperature and was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was extracted with acetone, hexanes and chloroform. The volume of the chloroform fraction was reduced to a minimal amount and precipitated in methanol. The polymer was filtered over a PTFE filter and dried overnight in a vacuum oven at 40  $^{\circ}\text{C}$  to give 46 mg of the polymer. SEC (Sup-HT CHCl<sub>3</sub>, 145  $^{\circ}\text{C}$ ):  $M_n = 58 \text{ kg mol}^{-1}$  and PDI = 2.1.

### Synthesis of PDPP3T

The synthesis of PDPP3T using the Stille coupling was performed according the procedure described in reference S5. SEC (Sup-HT CHCl<sub>3</sub>, 145  $^{\circ}\text{C}$ ):  $M_n = 78 \text{ kg mol}^{-1}$  and PDI = 3.1



**Figure S1.** Normalized absorption spectra of (a) PTPD2T-TT, (b) PII2T-TT, and (c) PDPP3T in a chloroform solution (red lines) and in a solid state film (black lines), both recorded at room temperature.

## References

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- S5 Hendriks, K. H.; Heintges, G. H. L.; Gevaerts, V. S.; Wienk, M. M.; Janssen, R. A. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 8341–8344.