

## Supplementary information

# Effect of Alkyl Chain Spacer on Charge Transport in n-Type Dominant Polymer Semiconductors with Diketopyrrolopyrrole- Thiophene-Bithiazole Acceptor-Donor-Acceptor Unit †

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## Experimental

**Materials.** All chemicals were purchased from Aldrich and Alfa : 2-bromothiazole, n-butyllithium, N,N-dimethylformamide(DMF), tetrakis(triphenylphosphine) palladium (0) were purchased from Aldrich. 3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione<sup>[1]</sup>, 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decylnonadecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione<sup>[2]</sup> and 5,5'-bis(trimethylstannyl)-2,2'-bithiazole<sup>[3]</sup> were synthesized via published literature procedures.

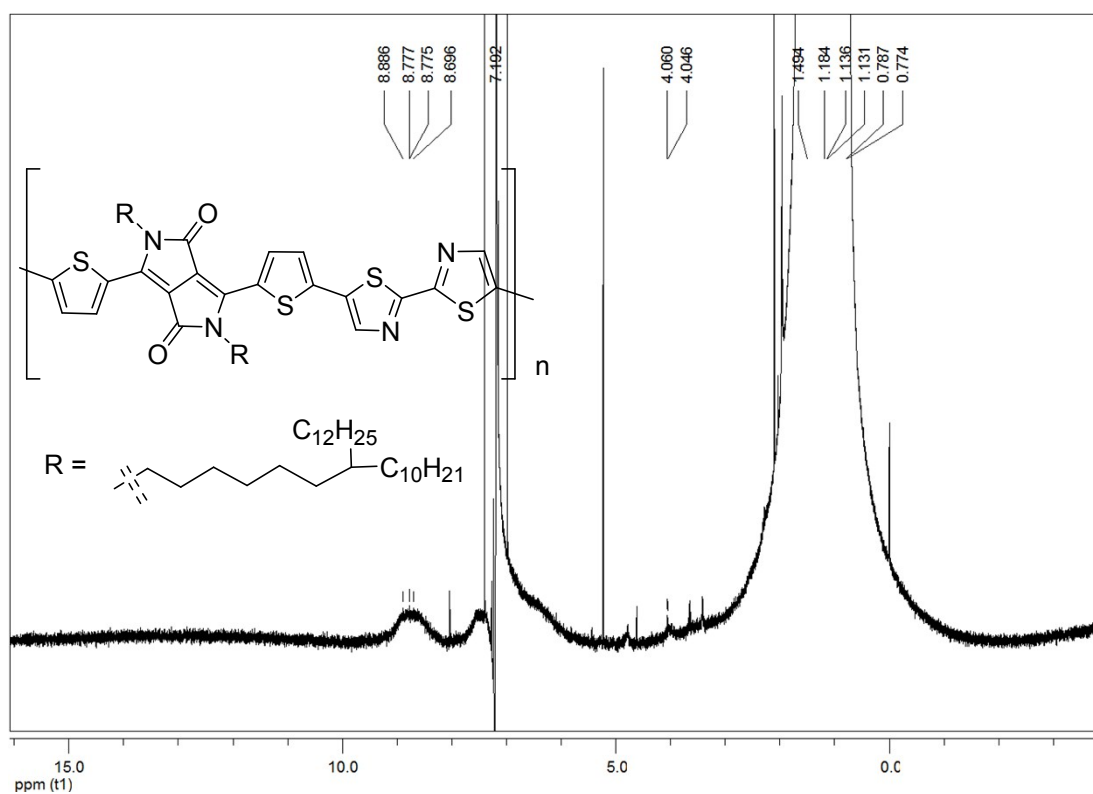
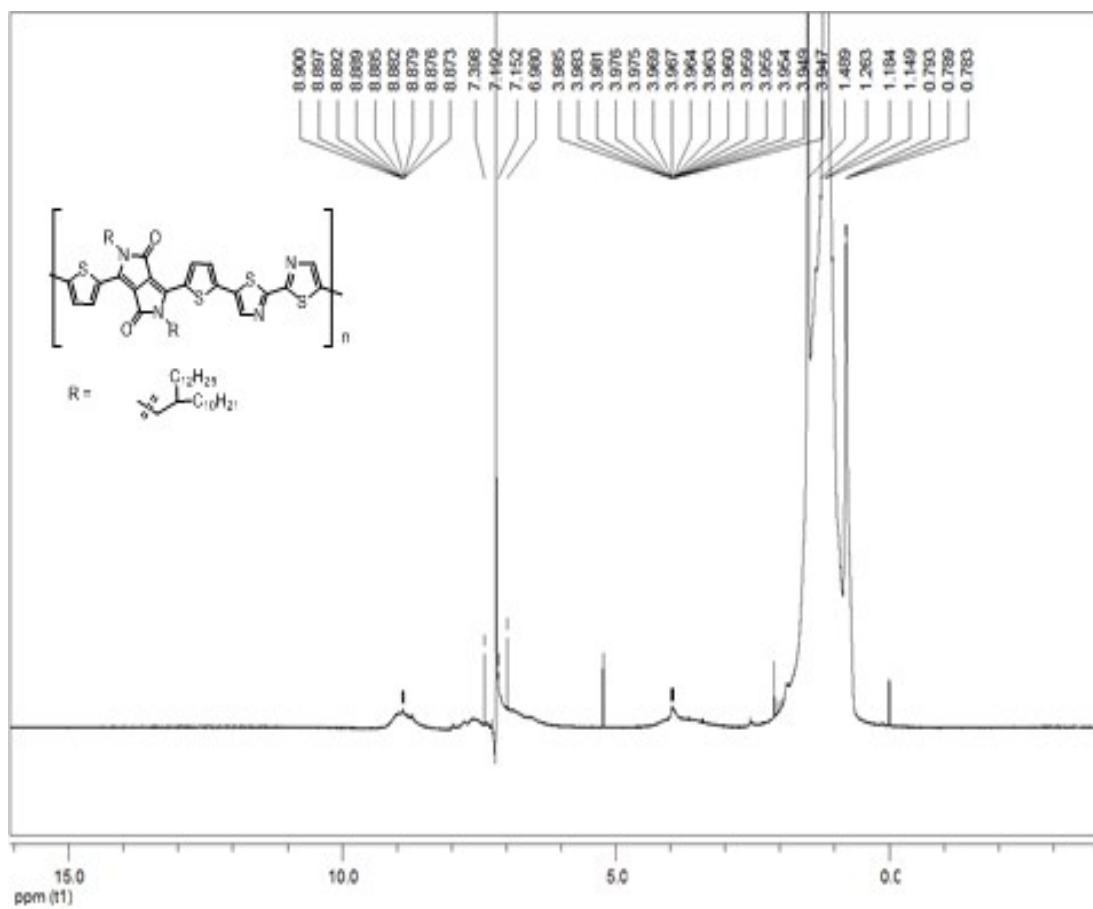
**Measurement.** The <sup>1</sup>H NMR spectra were recorded using a Bruker AM-300 spectrometer. The thermal analysis was performed on a TA TGA 2100 thermogravimetric analyzer in a nitrogen. The sample was heated at 20 °C min<sup>-1</sup>. Differential scanning calorimeter was conducted under nitrogen on a TA instrument 2100 DSC. The sample was heated at 20 °C min<sup>-1</sup> from 0 °C to 250 °C. UV-vis absorption studies were carried out using Perkin-Elmer LAMBDA-900 UV/VIS/IR spectrophotometer. Cyclic voltammetry (CV) was performed on an EG and G Parc model 273 Å potentiostat/galvanostat system with a three-electrode cell in a solution of Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M) in acetonitrile at a scan rate of 100 Mvs<sup>-1</sup>. The polymer films were coated on a square Pt electrode (0.50 cm<sup>2</sup>) by dipping the electrode into the corresponding solvents and then drying in air. A Pt wire was used as the counter electrode, and an Ag/AgNO<sub>3</sub> (0.1 M) electrode was used as the reference electrode.

### Synthesis of 5,5'-bis(trimethylstannyl)-2,2'-bithiazole

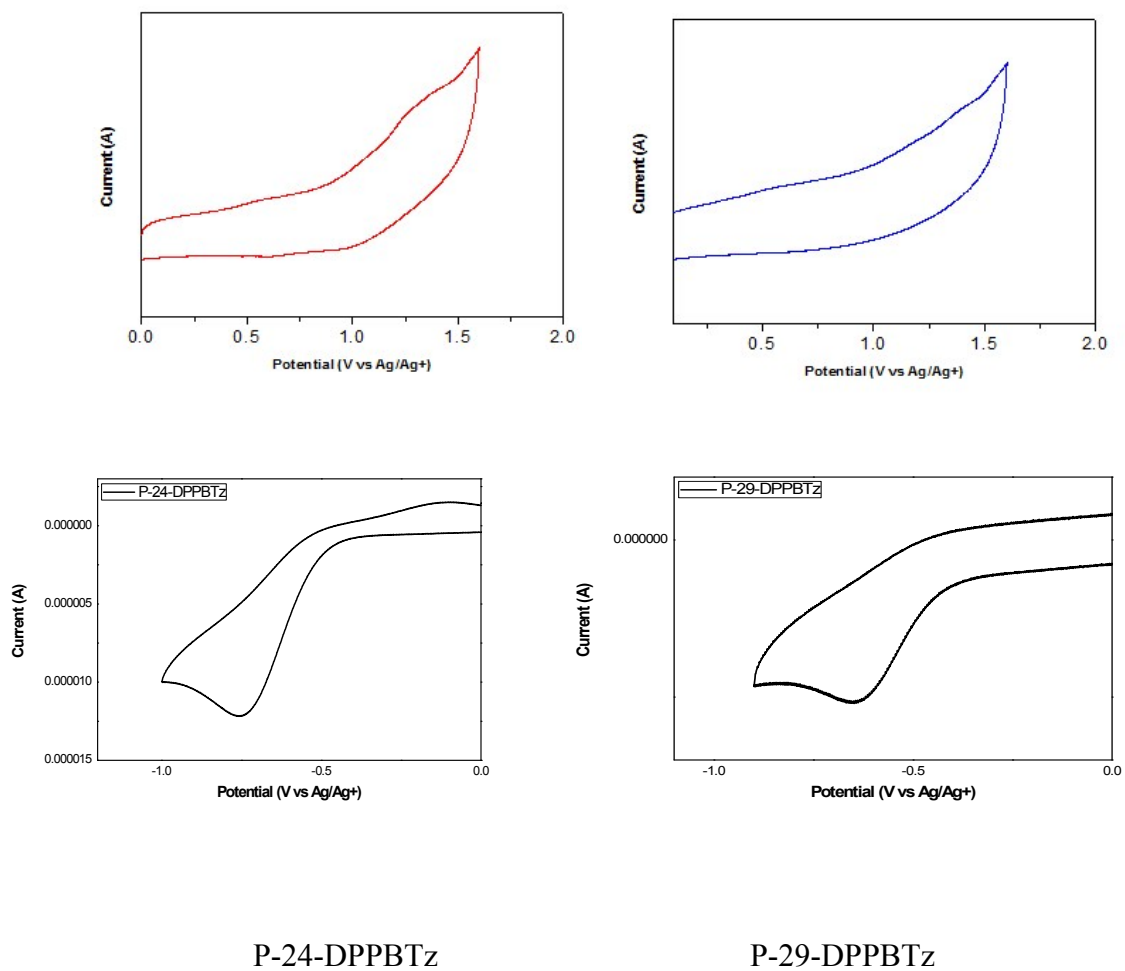
5,5'-bis(trimethylstannyl)-2,2'-bithiazole was prepared according to the procedures reported in the literature. <sup>[3]</sup> (1.3g, yield: 43%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.819 (s, 2 H), 0.465 (s, 18H).

**Synthesis of P-24-DPPBTz** : The polymer was prepared using a palladium-catalyzed Stille coupling reaction. In a Schlenk flask 24-DPPBr (0.40 g, 0.35 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiazole (0.175 g, 0.35 mmol) were dissolved in dry chlorobenzene (6 mL). After degassing under nitrogen for 60 min, Pd<sub>2</sub>(dba)<sub>3</sub> (6.4 mg) and P(oTol)<sub>3</sub> (8.6 mg) were added to the mixture, which was then stirred for 48 h at 110 °C. 2-Bromothiophen and tributyl(thiophen-2-yl)stannane were injected sequentially into the reaction mixture for end-capping, and the solution was stirred for 6 h after each addition. The polymer was precipitated in methanol. The crude polymer was collected by filtration and purified by Soxhlet extraction with methanol, acetone, hexane, toluene, and chloroform, successively. The final product, poly[2,5-bis(2-decyltetradecyl)-3-(5-(5'-methyl-2,2'-bithiazol-5-yl)thiophen-2-yl)-6-(5-methylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione] (P-24-DPPBTz) was obtained by precipitation in methanol.

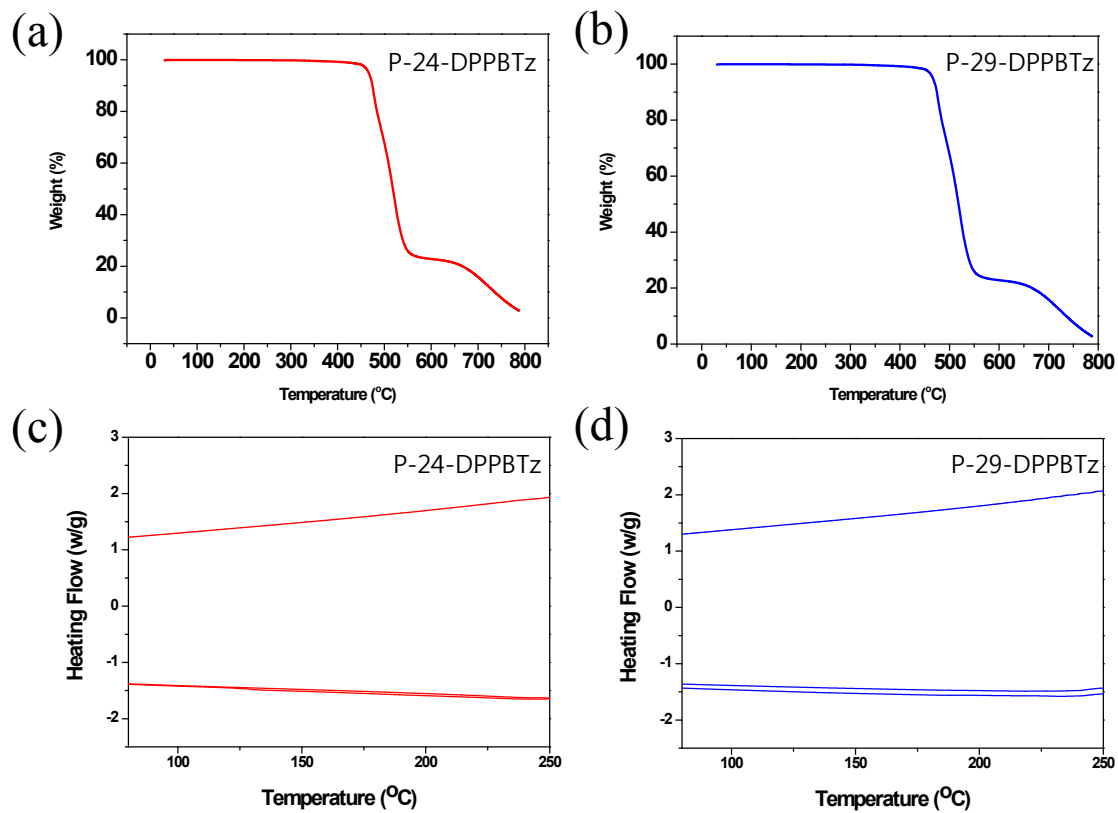
**Synthesis of P-29-DPPBTz** : The polymer was prepared using a palladium-catalyzed Stille coupling reaction. In a Schlenk flask 29-DPPBr (0.4 g, 0.31 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiazole (0.15 g, 0.31 mmol) were dissolved in dry chlorobenzene (6 mL). After degassing under nitrogen for 60 min, Pd<sub>2</sub>(dba)<sub>3</sub> (2.8 mg) and P(oTol)<sub>3</sub> (2.8 mg) were added to the mixture, which was then stirred for 48 h at 110 °C. 2-Bromothiophen and tributyl(thiophen-2-yl)stannane were injected sequentially into the reaction mixture for end-capping, and the solution was stirred for 6 h after each addition. The polymer was precipitated in methanol. The crude polymer was collected by filtration and purified by Soxhlet extraction with methanol, acetone, hexane, toluene, and chloroform, successively. The final product, poly[2,5-bis(7-decylnonadecyl)-3-(5-(5'-methyl-2,2'-bithiazol-5-yl)thiophen-2-yl)-6-(5-methylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione] (P-29-DPPBTz) was obtained by precipitation in methanol.



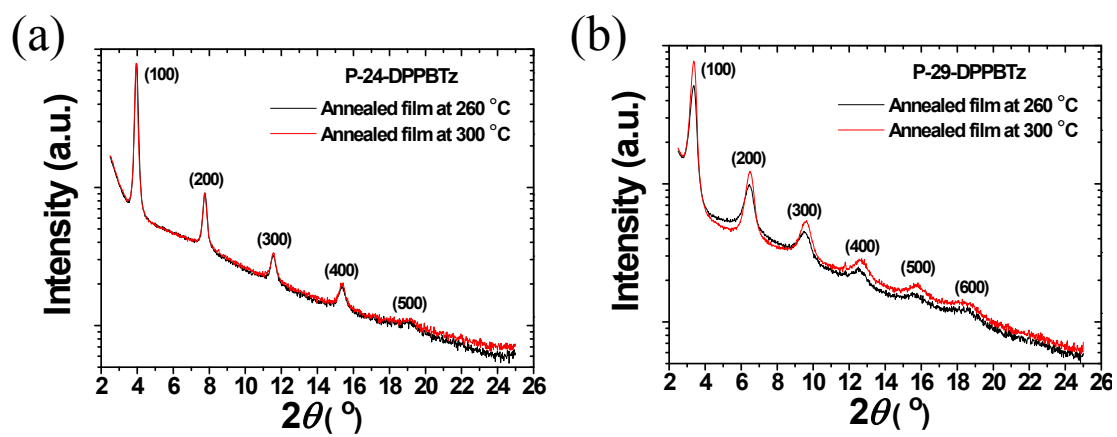
**Figure S1.**  $^1\text{H-NMR}$  data of P-24-DPPBTz and P-29-DPPBTz



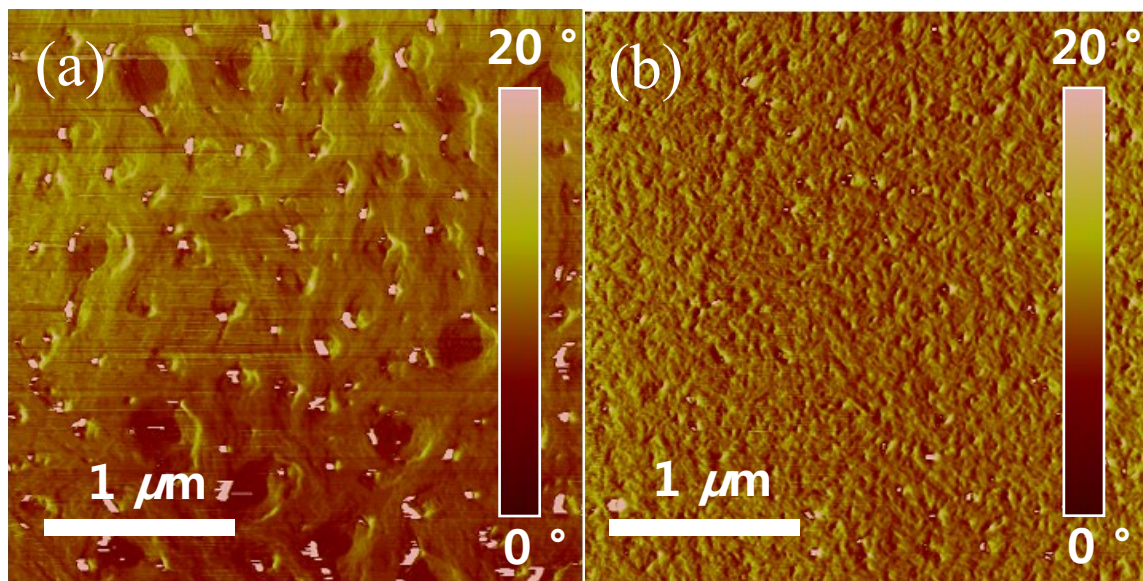
**Figure S2.** Cyclic voltammetry curve of P-24-DPPBTz and P-29-DPPBTz



**Figure S3.** TGA and DSC thermograms of P-24-DPPBTz and P-29-DPPBTz

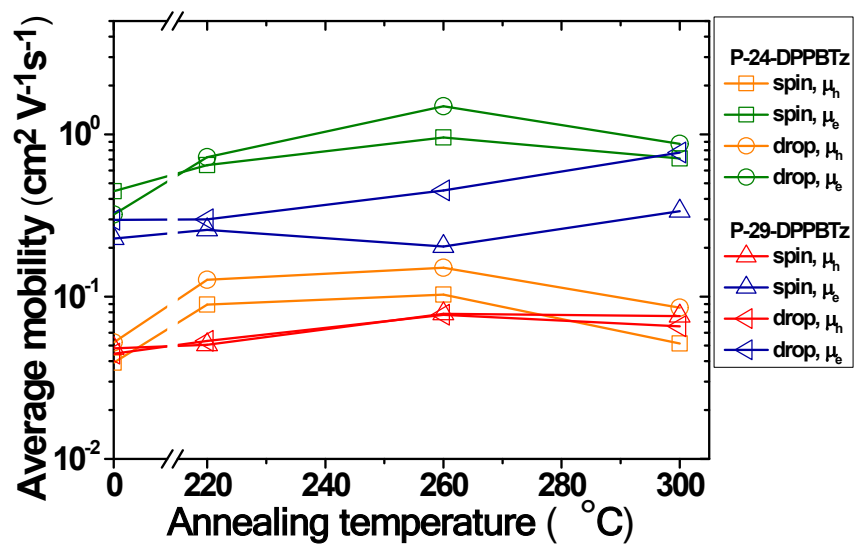


**Figure S4.** Out-of-plane X-ray diffraction (XRD) patterns of annealed (a) P-24-DPPBTz and (b) P-29-DPPBTz thin films at 260  $^{\circ}$ C and 300  $^{\circ}$ C.



**Figure S5.** AFM phase images of annealed (a) P-24-DPPBTz and (b) P-29-DPPBTz films on OTS-treated SiO<sub>2</sub>/Si substrates.





**Figure S6.** Average field-effect mobility variations with standard deviation values under various annealing temperatures

## References

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- [2] Il Kang, Hui-Jun Yun, Dae Sung Chung, Soon-Ki Kwon, and Yun-Hi Kim. *J. Am. Chem. Soc.*, 2013, **135**, 14896-14899.
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