Supporting Information

Toward n-type analogues to poly(3-alkylthiophene)s: Impact of side-chain variation on bulk-morphology and electron transport characteristics of head-to-tail regioregular poly(4-alkylthiazole)s

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Figure S1. Thermogravimetric analyses a) **PTzTIB**, b) **PTzTNB**, and c) **PTzTHX**. Scan rate 15 °C/min.



Figure S2. UV-PES ion current-curve for **PTzTHX**. Vertical axis: arbitrary unit. Horizontal axis: eV.



Figure S3a. Comparison of GIXD-refractogramms of different batches of **PTzTHX**. The broad peak between 5 and 15° stems from the glass substrate. See also Figure S3b.



Figure S3b. Background corrected GIXD pattern of PTzTNB.



Figure S4: Architecture of the electron-only and hole-only based devices on PTzTNB/PTzTHX.



Figure S5: Semi-logarithmic plots of J-V (left) and log (J)-log(V) (right) curves of the electrononly devices based on **PTzTHX**, with the film measured as-spun, and annealed at 185°C for 10 minutes



Figure S6: Semi-logarithmic plots of J-V (left) and log (J)-log(V) (right) curves of the hole-only devices based on **PTzTHX**, with the film measured as-spun, and annealed at 185°C for 10 minutes.



Figure S7: Semi-logarithmic plots of J-V (left) and log (J)-log (V) (right) curves of the electrononly and hole-only devices based on **PTzTHX**, measured as-spun.



Figure S8: Semi-logarithmic plots of J-V (left) and log (J)-log(V) (right) curves of the electrononly and hole-only devices based on **PTzTHX**, with film annealed at 185°C for 10 minutes.



Figure S9: Semi-logarithmic plots of J-V (left) and log (J)-log(V) (right) curves of the hole-only devices based on **PTzTNB**, with the film measured as-spun, and annealed at 150°C for 30 minutes.



Figure S10: Semi-logarithmic plots of J-V (left) and log (J)-log(V) (right) curves of the electrononly devices based on **PTzTNB**, with the film measured as-spun, and annealed at 150°C for 30 minutes



Figure S11: Semi-logarithmic plots of J-V (left) and log (J)-log (V) (right) curves of the electron-only and hole-only based devices on **PTzTNB**, measured as-spun



Figure S12: Semi-logarithmic plots of J-V (left) and log (J)-log (V) (right) curves of the electron-only and hole-only based devices on **PTzTNB**, with film annealed at 150°C for 30 minutes.

Supplementary Analytical Data



Figure S13. ¹H NMR-spectrum of 5-bromo-2-chloro-4-(triisobutylsilyloxymethyl)-thiazole (**2a**). For ¹H NMR data of *rr*-**PTz**s recorded under similar conditions see: F. Pammer, J. Jäger, B. Rudolf, Y. Sun, *Macromolecules*, **2014**, *47*, 5904-5912.



Figure S14. ¹³C NMR-spectrum of 5-bromo-2-chloro-(triisobutylsilyloxymethyl)-thiazole (2a).



Figure S15. ¹H NMR-spectrum of 5-bromo-2-chloro-4-(tri(*n*-butyl)silyloxymethyl)-thiazole (**2b**).



Figure S17. ¹H NMR-spectrum of 5-bromo-2-chloro-4-(tri(*n*-hexyl)silyloxymethyl)-thiazole (2c).



Figure S19. ¹H NMR-spectrum of PTzTIB in 1,2-dichlorobenzene-d₄ at 100 °C.



Figure S21. ¹H NMR-spectrum of PTzTHX in CDCl₃ at 20 °C.



Figure S22. ¹³C NMR-spectrum of PTzTHX in CDCl₃.