Supplementary Information

Dramatically Different Charge Transport Properties of Bisthienyl Diketopyrrolopyrrole-Bithiazole Copolymers Synthesized via Two Direct (Hetero)arylation Polymerization Routes

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Scheme S1. Possible α’-β and α-β’ coupling side reactions in Route A and Route B, respectively, between a C-Br in a terminal thiazole (α’) or thiophene (α) unit of a polymer chain or monomer and a β C-H in a thiophene (β) or thiazole (β’) unit of a polymer chain or monomer, where C-Hα in the α’-β defect and C-Hα’ in the α-β’ defect have much higher reactivity than that of other β C-H groups on the polymer backbone, resulting in branched and cross-linked structures.
**Fig. S1** The 300 MHz $^1$H-NMR spectrum of 2-(trimethylstannyl)thiazole (I) measured in CDCl$_3$. 
Fig. S2 The 300 MHz $^1$H-NMR spectrum of 2,2′-bithiazole (2) measured in CDCl$_3$. 
Fig. S3 The 300 MHz $^1$H-NMR spectrum of di(tritriacontan-17-yl) 4,4’-(1,4-dioxo-3,6-di thiophen-2-yl)pyrrolo[3,4-c]pyrrole-2,5(1H,4H)-diyl)dibutanoate (4-2) measured in CDCl$_3$. 
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Fig. S4 The 100 MHz $^{13}$C-NMR spectrum of di(tritriacontan-17-yl) 4,4'-(1,4-dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-2,5(1H,4H)-diyl)dibutanoate (4-2) measured in CDCl$_3$. 

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Fig. S5 The 300 MHz $^1$H-NMR spectrum of di(tritriacontan-17-yl) 4,4'-(3,6-bis(5-bromothiophen-2-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1$H$,4$H$)-diyl)dibutanoate (5-2) measured in CDCl$_3$. 
Fig. S6 The 100 MHz $^{13}$C-NMR spectrum of di(tritriacontan-17-yl) 4,4'-(3,6-bis(5-bromothiophen-2-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-diyl)dibutanoate (5-2) measured in CDCl$_3$. 
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Fig. S7 The 300 MHz $^1$H-NMR spectra of PA-1 and PB-1 (chloroform extracted fractions) measured at room temperature in CDCl$_3$. The poor resolution is due to the strong aggregation of polymer chains in solution.
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**Fig. S8** UV-Vis absorption spectra of PA-2 and PB-2 in chloroform solutions and as thin films.
Fig. S9 AFM images (2 µm × 2 µm) of PA-1 (top) and PB-1 (bottom) thin films (~50-60 nm) on silicon dioxide substrates annealed at 100, 150, 200 and 250 °C.
Fig. S10 GPC traces of PA-1 chloroform (CF) and 1,1,2,2-tetrachloroethane (TCE) extracted fractions measured at 140 °C using 1,2,4-trichlorobenzene as eluent.
Fig. S11 GPC traces of PB-1 chloroform (CF) and 1,1,2,2-tetrachloroethane (TCE) extracted fractions measured at 140 °C using 1,2,4-trichlorobenzene as eluent.
**Fig. S12** GPC trace of PA-2 (hexane extracted fraction) measured at 140 °C using 1,2,4-trichlorobenzene as eluent.
Fig. S13 GPC trace of PB-2 (hexane extracted fraction) measured at 140 °C using 1,2,4-trichlorobenzene as eluent.
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Fig. S14 DSC thermogram of PA-1 (chloroform extracted fraction) measured with a heating rate of 10 °C min⁻¹ under nitrogen.
Fig. S15 DSC thermogram of PB-1 (chloroform extracted fraction) measured with a heating rate of 10 °C min\(^{-1}\) under nitrogen.
Fig. S16 TGA thermograms of PA-1 and PB-1 (chloroform extracted fractions) at a heating rate of 10 °C min\(^{-1}\) under nitrogen.