Supporting Information for:

Dithienopyrrole-Based Donor-Acceptor Copolymers:

Low Band-Gap Materials for Charge Transport,

Photovoltaics and Electrochromism

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Figure S1 TGA curves of P1-P5

Figure S2 UV-vis-NIR spectra of P1-P5 in thin films

Figure S3 DPV of P4 and P5

Figure S4 Oxidative spectroelectrochemistry of P2 and P3

Figure S5 Reductive spectroelectrochemistry of P1 and P2

Figure S6 Output (a) and transfer (b) characteristics of an OFET based on P4.

Figure S7 Output (a) and transfer (b) characteristics of an OFET based on P5.

Figure S8 *J-V* characteristics of multiple cells measured in the dark (black line) and under illumination (red line) for films of PCBM blended with **P4** in a 1:1 weight ratio. (Inset shows the same data in a semilogarithmic plot)



Figure S1 TGA curves of P1-P5



Figure S2 UV-vis-NIR spectra of P1-P5 in thin films

a)

b)



Figure S3. DPV of **P4-5** (a and b) on a Pt button with a step size of 2 mV and step time of 0.1 second.



Figure S4a. Oxidative spectroelectrochemistry of **P2** spray-cast onto ITO, from -0.33 V to 1.07 V vs. SCE in 100 mV increments. Bold black line = neutral (-0.33 V) and bold orange line = oxidized state (1.07 V).



Figure S4b. Oxidative spectroelectrochemistry of **P3** spray-cast onto ITO, from -0.13 V to 0.97 V vs. SCE in 100 mV increments. Bold black line = neutral (-0.13 V) and bold olive green line = oxidized state (0.97 V).



Figure S5a Reductive spectroelectrochemistry of **P2** spray-cast onto ITO, from -0.54 V to -1.94 V vs. SCE in 100 mV increments. Bold black line = neutral (-0.54 V), bold yellow line = first reduced state (-1.14 V), and bold orange line = second reduced state (-1.94 V).



Figure S5b. Reductive spectroelectrochemistry of **P3** spray-cast onto ITO from 0.05 V to -1.45 V vs. SCE in 100 mV increments. Bold black line = neutral (0.05 V), bold purple line = first reduced state (-0.85 V), and bold pink line = second reduced state (-1.45 V).

a)



b)



Figure S6. Output (a) and transfer (b) characteristics of an OFET based on P4.



Figure S7. Output (a) and transfer (b) characteristics of an OFET based on P5.



Figure S8. *J-V* characteristics of multiple cells measured in the dark (black line) and under illumination (red line) for films of PCBM blended with **P4** in a 1:1 weight ratio. (Inset shows the same data in a semilogarithmic plot)