Electronic Supplementary Material (ESI) for RSC Advances.

Electrochemical Polymerization of 1,4-Di(aryl)cyclopentadienes: Thin-Film Optical and Electronic Properties

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Electronic Supplementary Information

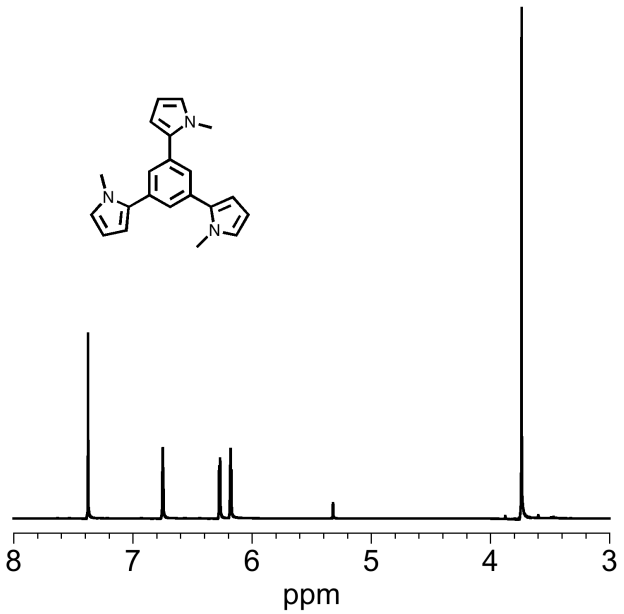

Figure S 1. ^{1}H NMR spectrum of 3PyrB (500 MHz, CD_2Cl_2).

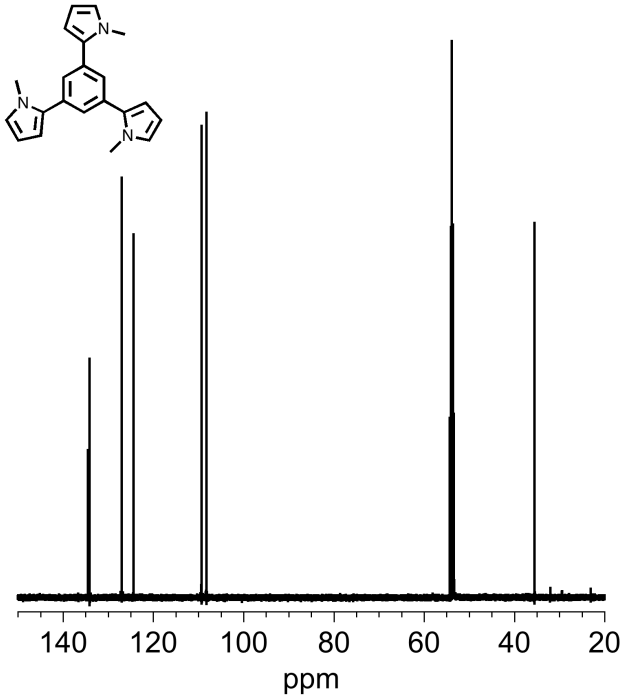

Figure S 2. ^{13}C NMR spectrum of 3PyrB (100 MHz, CD_2Cl_2).

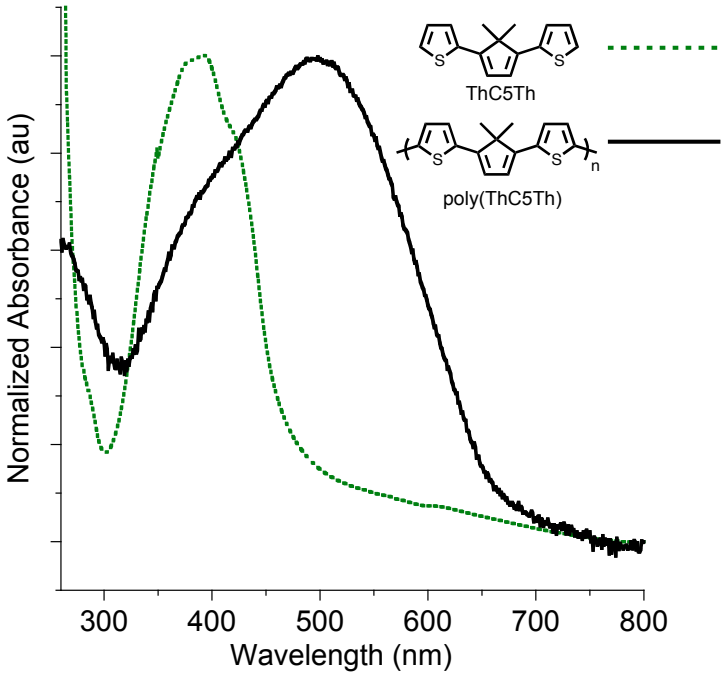

Figure S 3. UV/vis absorbance spectra of ThC5Th (drop-casted film on ITO) and poly(ThC5Th) (electrochemically generated film on ITO).

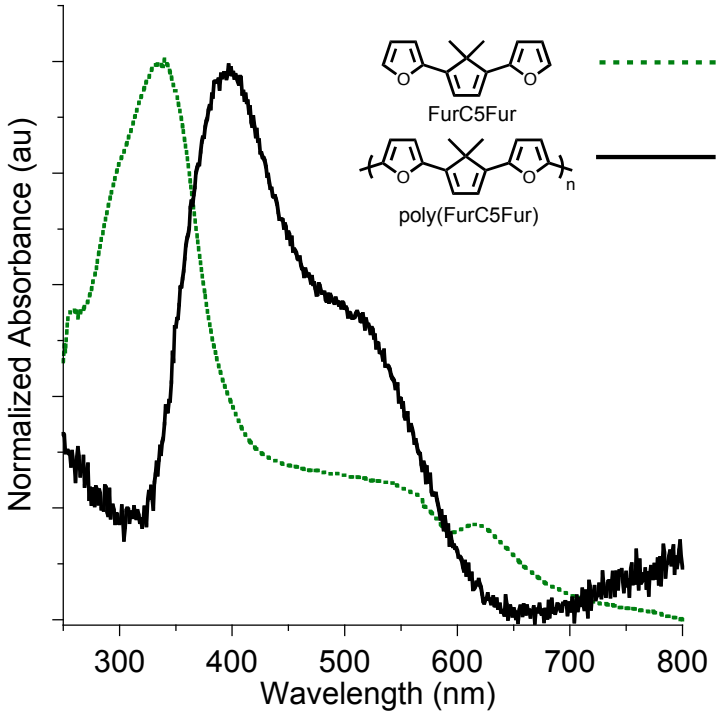

Figure S 4. UV/vis absorbance spectra of FurC5Fur (drop-casted film on ITO) and poly(FurC5Fur) (electrochemically generated film on ITO).

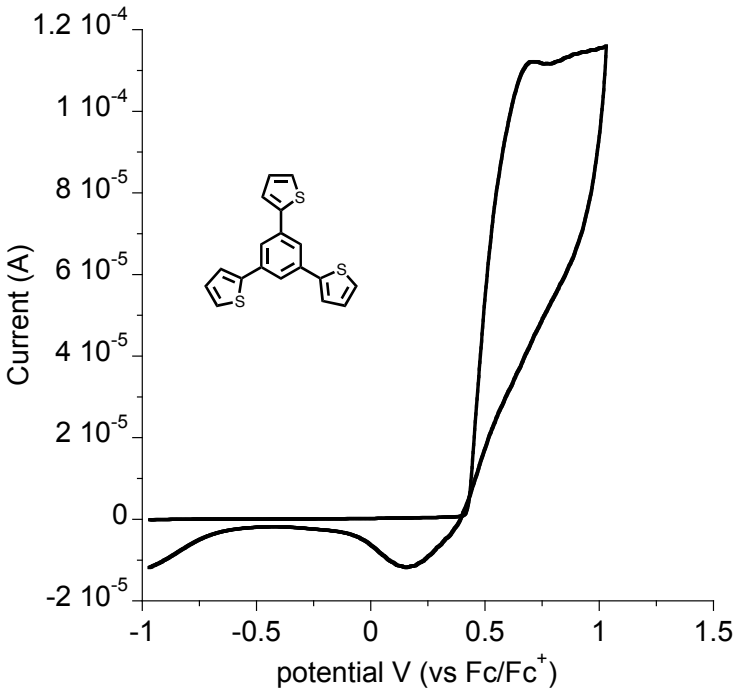

Figure S 5. Cyclic voltammogram of 3ThB [4.2 mM]. Conditions: 0.1 M [*n*-Bu_4N]PF_6 in DCM; scan rate, 100 mV/s, Pt disc working electrode, *E vs.* Fc/Fc^+.

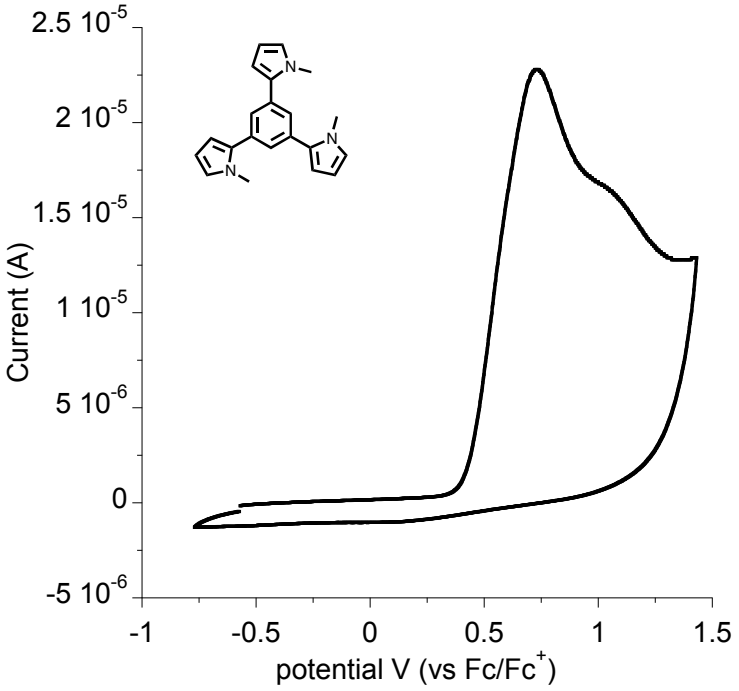

Figure S 6. Cyclic voltammogram of 3PyrB [4.2 mM]. Conditions: 0.1 M [*n*-Bu_4N]PF_6 in DCM; scan rate, 100 mV/s, Pt disc working electrode, *E vs.* Fc/Fc^+.

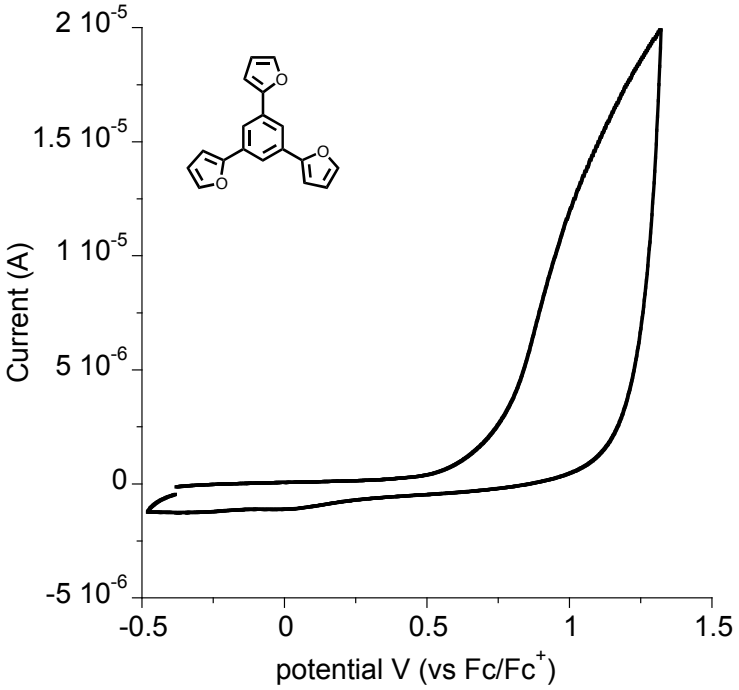

Figure S 7. Cyclic voltammogram of 3FurB [4.2 mM]. Conditions: 0.1 M [*n*-Bu_4N]PF_6 in DCM; scan rate, 100 mV/s, Pt disc working electrode, *E vs.* Fc/Fc^+.

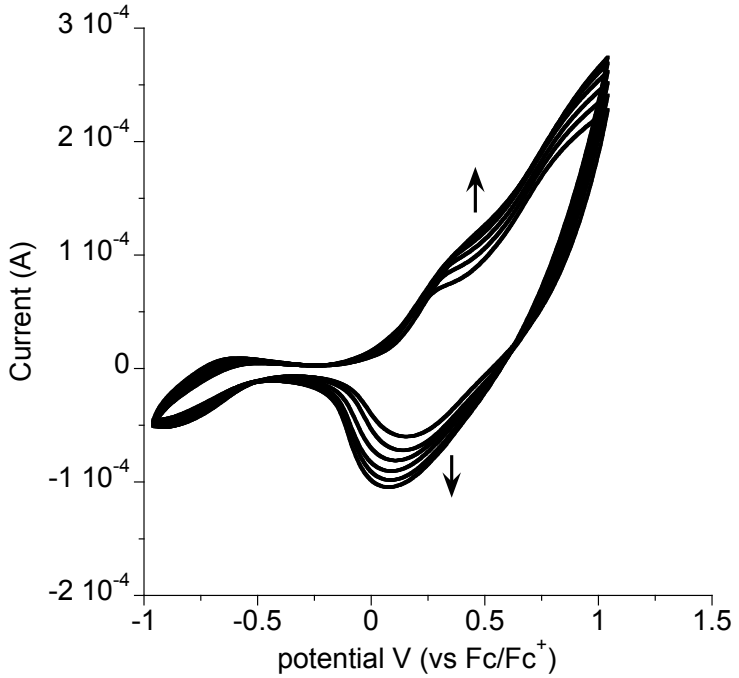

Figure S 8. Cyclic voltammogram of 3ThB [4.2 mM] (10 sweeps). Conditions: 0.1 M [*n*-Bu_4N]PF_6 in DCM; scan rate, 100 mV/s, Pt disc working electrode, *E vs.* Fc/Fc^+.

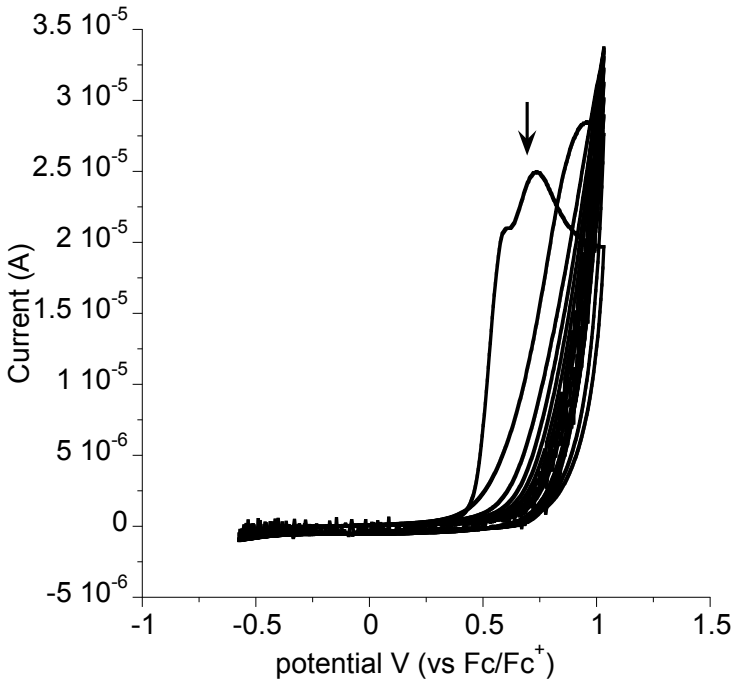

Figure S 9. Cyclic voltammogram of 3PyrB [4.2 mM] (10 sweeps). Conditions: 0.1 M [*n*-Bu_4N]PF_6 in DCM; scan rate, 100 mV/s, Pt disc working electrode, *E vs.* Fc/Fc^+.

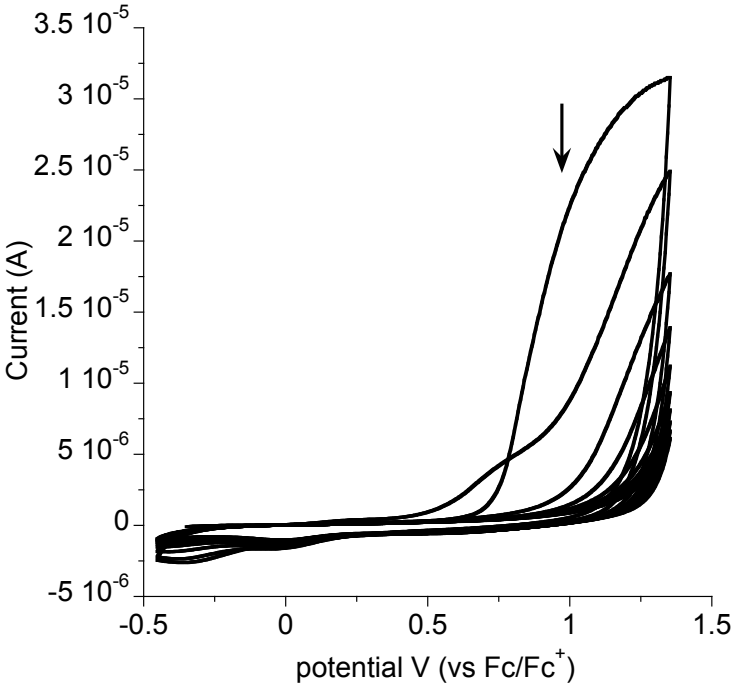

Figure S 10. Cyclic voltammogram of 3FurB [4.2 mM] (10 sweeps). Conditions: 0.1 M [*n*-Bu_4N]PF_6 in DCM; scan rate, 100 mV/s, Pt disc working electrode, *E vs.* Fc/Fc^+.

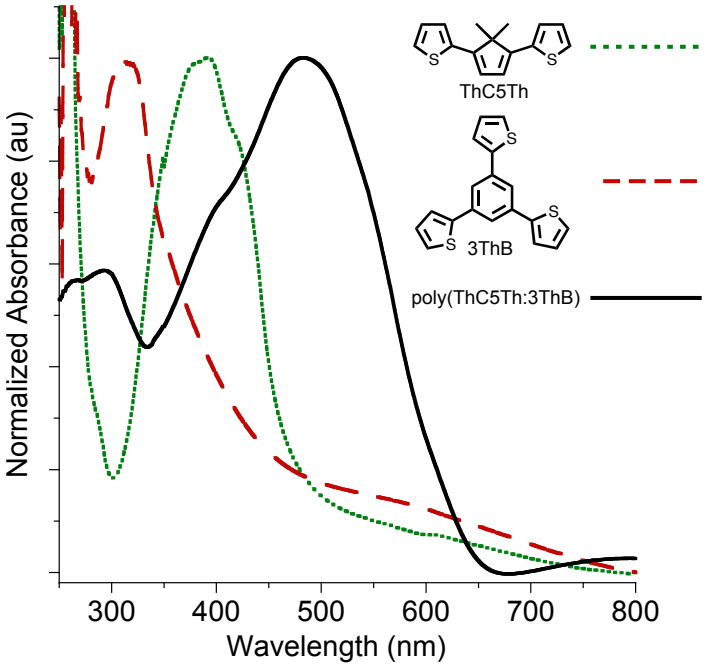

Figure S 11. UV/vis absorbance spectra of ThC5Th (drop-casted film on ITO), 3ThB (drop casted film on ITO), and poly(ThC5Th:3ThB, 60:40) (electrochemically generated film on ITO).

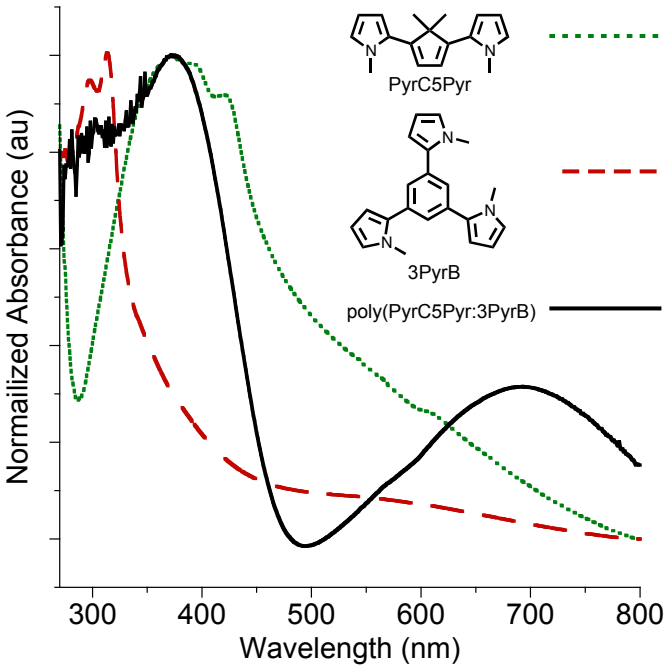

Figure S 12. UV/vis absorbance spectra of PyrC5Pyr (drop-casted film on ITO), 3PyrB (drop casted film on ITO), and poly(PyrC5Pyr:3PyrB) (electrochemically generated film on ITO).

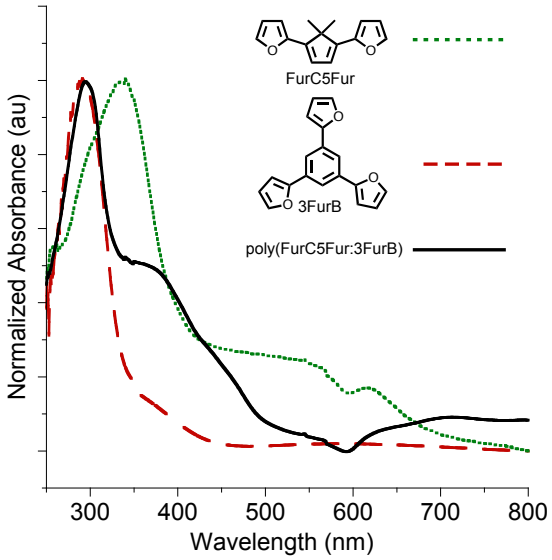

Figure S 13. UV/vis absorbance spectra of FurC5Fur (drop-casted film on ITO), 3FurB (drop casted film on ITO), and poly(FurC5Fur:3FurB) (electrochemically generated film on ITO).

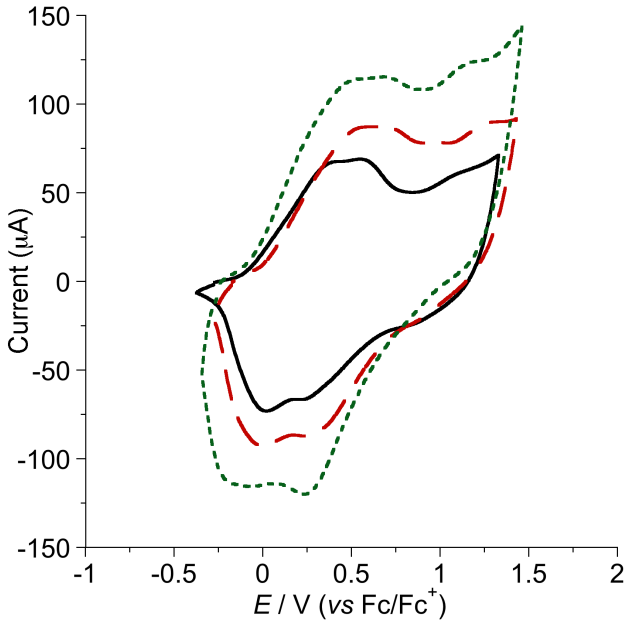

Figure S 14. CV scans (in monomer-free electrolyte) of poly(ThC5Th:3ThB) films (deposited onto platinum disc electrodes) grown from comonomer solution with molar ratios: a) 60:40 (black line), b) 75:25 (red, long dash line), and c) 90:10 (green, short dash line).

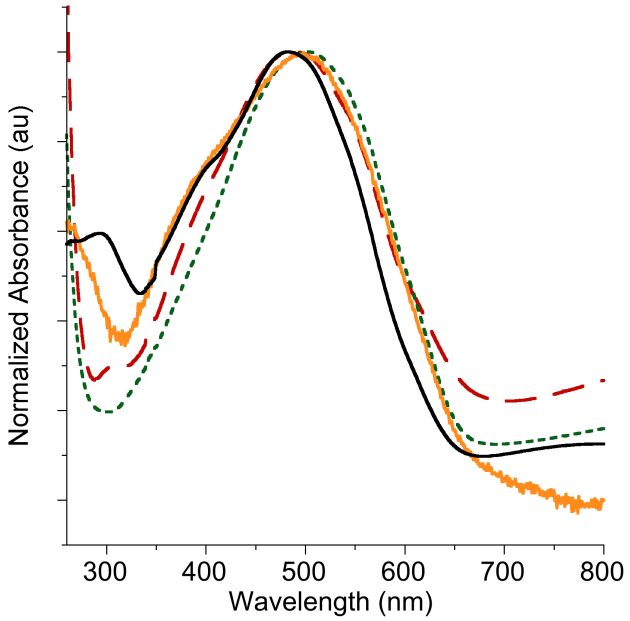

Figure S 15. UV/vis absorbance spectra of poly(ThC5Th:3ThB) films (grown on ITO) prepared from comonomer solutions at molar ratios of 60:40 (black solid line), 75:25 (red long dash line), and 90:10 (green, short dash line). For comparison, the UV/vis absorbance spectrum of poly(ThC5Th) is shown as well (orange solid line).

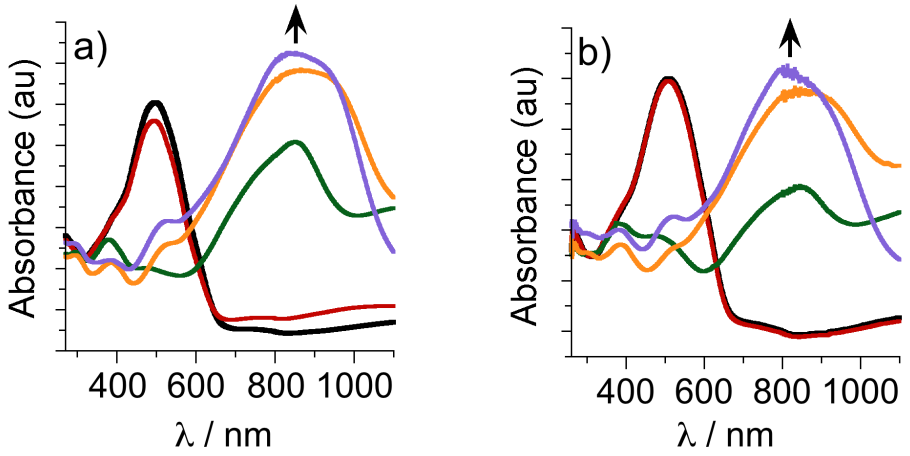

Figure S 16. Spectroelectrochemical profiles of poly(ThC5Th:3ThB) prepared from comonomer solutions at molar ratios of (a) 75:25, and (b) 90:10. All black UV/Vis/NIR spectra where taken from films in their neutral state. All subsequent spectra (*i.e.* red, green, orange, violet, black dashed, and red dashed lines) were taken at progressively higher potentials at 200 mV intervals over the range of *ca.* -0.1 V and 1.1 V (*E vs.* Fc/Fc^{+}).

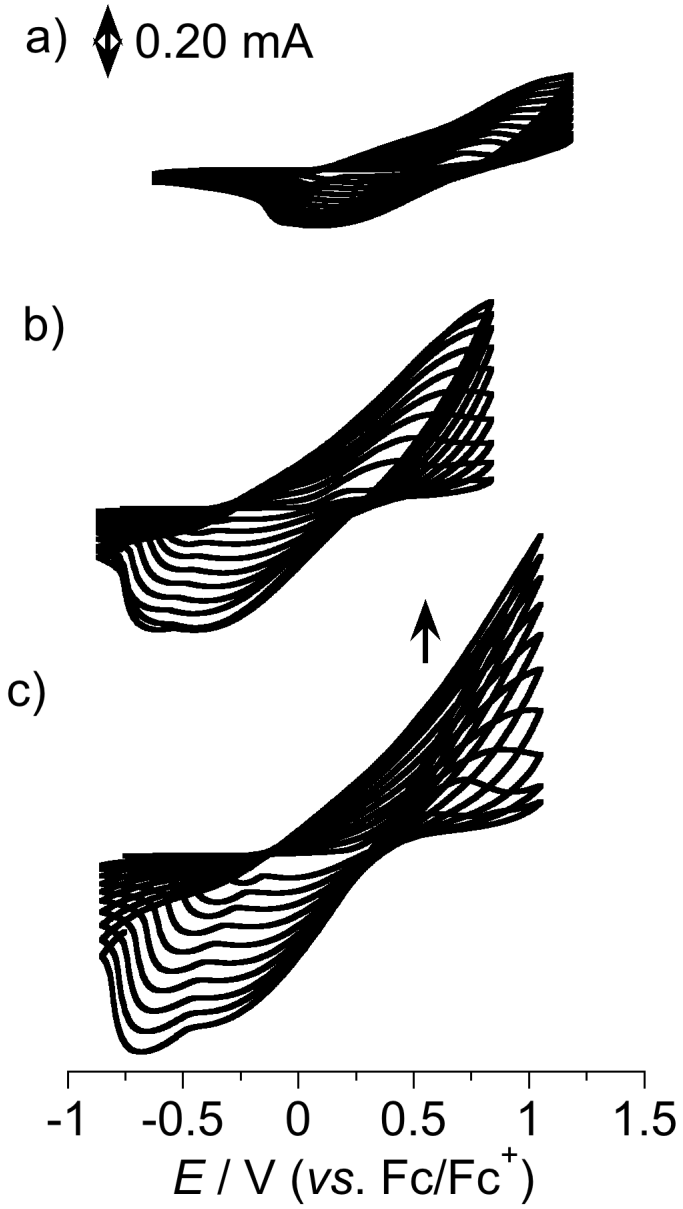

Figure S 17. CV scans (10 cycles) of Th_3:3ThB at molar ratios: a) 60:40, b) 75:25, and c) 90:10. Conditions: concentration of electropolymerizable species, 4.2 mM in 0.1 M [*n*-Bu_4N]PF_6 in DCM; scan rate, 100 mV/s, Pt disc working electrode, *E vs.* Fc/Fc^+.

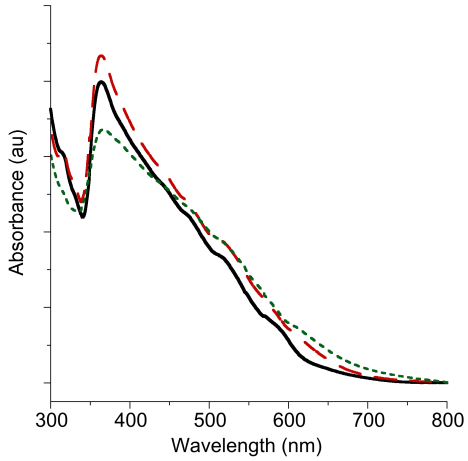

Figure S 18. UV/vis absorbance spectra of poly(Th_3:3ThB) films (grown on ITO) prepared from comonomer solutions at molar ratios of 60:40 (black solid line), 75:25 (red long dash line), and 90:10 (green, short dash line).

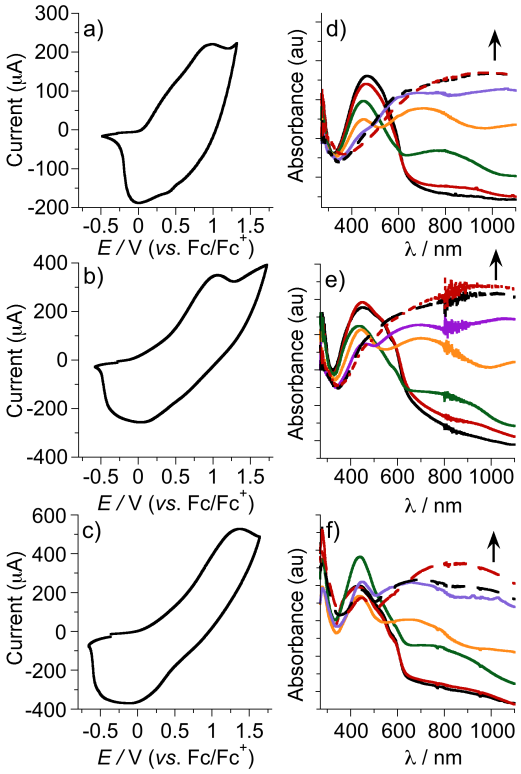

Figure S 19. CV scans (in monomer-free electrolyte) of poly(Th_3:3ThB) prepared from comonomer solutions at molar ratios of (a) 60:40, (b) 75:25, and (c) 90:10. Spectroelectrochemical profiles of poly(Th_3:3ThB) prepared from comonomer solutions at molar ratios of (d) 60:40, (e) 75:25, and (f) 90:10. All black UV/Vis/NIR spectra where taken from films in their neutral state. All subsequent spectra (*i.e.* red, green, orange, violet, black dashed, and red dashed lines) were taken at progressively higher potentials at 200 mV intervals over the range of *ca*. 0.3 V and 1.3 V (*E vs.* Fc/Fc^+).

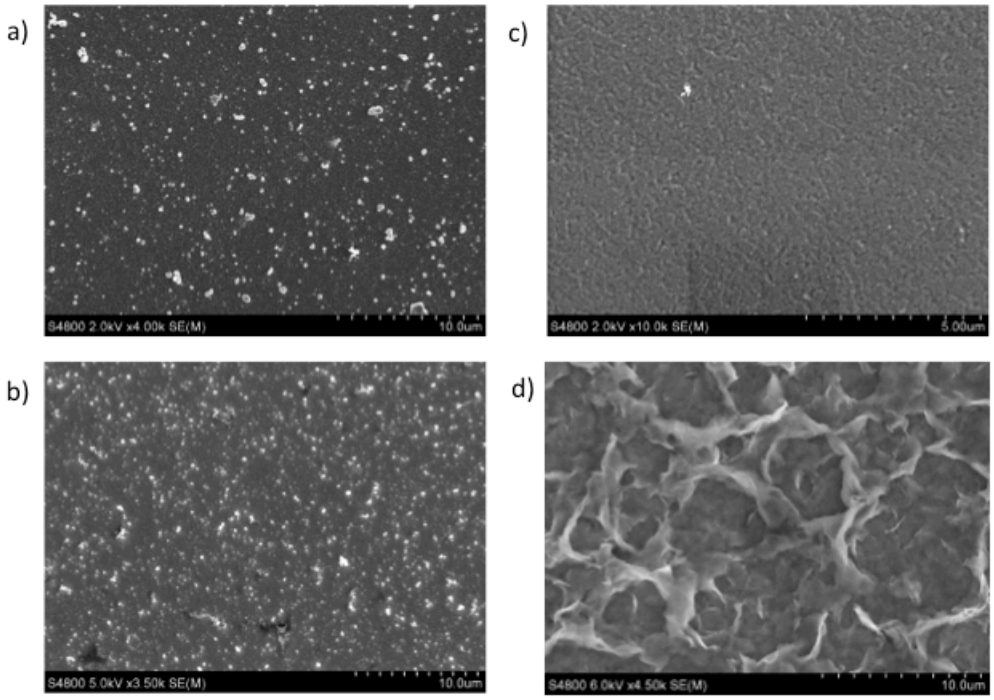

Figure S 20. SEM micrographs of a) poly(ThC5Th:3ThB), b) poly(PyrC5Pyr:3PyrB), c) poly(FurC5Fur:3FurB), and d) poly(Th_3:3ThB) films deposited on ITO electrodes.

Table S 1. (Co)polymer and monomer E_{on} and $E_{p,a}$ values.[a]

Compound	E_{on} (V)	$E_{p,a}$ (V)
ThC5Th	0.32	1.27
3ThB	0.42	0.70
PyrC5Pyr	-0.09	0.35
3PyrB	0.40	0.72
FurC5Fur	0.19	1.55
3FurB	0.72	-
poly(ThC5Th:3ThB) 60:40	-0.10	0.54
poly(PyrC5Pyr:3PyrB) 60:40	-0.18	0.20
poly(FurC5Fur:3FurB) 60:40	0.00	0.30
poly(ThC5Th:3ThB) 75:25	-0.10	0.63
poly(ThC5Th:3ThB) 90:10	-0.10	0.70
poly(Th_3:3ThB) 60:40	0.24	0.63
poly(Th_3:3ThB) 75:25	0.24	1.05
poly(Th_3:3ThB) 90:10	0.24	1.43

[a] 0.1 M $[Bu_4N]PF_6$ in DCM; scan rate, 100 mV/s, Pt disc working electrode, *E vs.* Fc/Fc^+.