Supporting Information

For

Multifunctional Materials for OFETs, LFETs and NIR PLEDs

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Polymer	% DAD loading	M _n ^a (kg/mol)	PDI	$T_d (°C)^b$	$\lambda_{max} (nm)$	$\lambda_{onset} (nm)$
P1	0	6.5	1.2	261	475	547
P2	0	9.4	1.5	293	481	553
P2EC	0	8.9	1.7	394	480	553
P3	0	40	2.5	439	445	522
P4	1	42	2.1	431	441, 785	907
P5	1	92	4.3	434	439, 795	987

Table S1. Physical properties of polymers P1-5.

[a] Molecular weights determined by gpc relative to polystyrene standards using 1,2,4-trichlorobenzene as the eluent (135 °C). [b] Temperature resulting in 1 % weight loss.



Figure S1. Square-wave voltammetry for polymers P1-5.

reference.										
Polymer	Eox, a	E ^{red, a}	$HOMO^{b}$	$LUMO^{b}$	E _g c	E ^{ox, d}	Ered, d	$HOMO^{b}$	$LUMO^{b}$	Ege
	(V)	(V)	(eV)	(eV)	(eV)	(V)	(V)	(eV)	(eV)	(eV)
P1	0.83	-1.74	-5.96	-3.39	2.57	0.94	-1.83	6.07	-3.30	2.77
P2	0.86	-1.68	-5.99	-3.45	2.54	0.96	-1.80	6.09	-3.33	2.76
P2EC	0.91	-1.70	-6.04	-3.43	2.61	1.28	-1.81	6.41	-3.32	3.09
P3	1.18	-1.63	-6.31	-3.50	2.81	1.35	-1.90	-6.48	-3.23	3.25
P4	1.15	-1.64	-6.28	-3.49	2.79	1.35	-1.89	-6.48	-3.24	3.24
P5	1.16	-1.65	-6.29	-3.48	2.81	1.30	-1.85	-6.43	-3.28	3.15

[a] Onset potential verses Fc/Fc⁺. [b] HOMO/LUMO = $-(E_{ox/red} + 5.13)$ eV. [c] Electrochemical band gap using onset potentials. [d] Peak potential verses Fc/Fc⁺. [e] Electrochemical band gap using peak potentials.

Table S3. Summary of C	OFET performance f	or as-spun devi	ices for po	lymers P1-P3.
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Sample	$\mu_{e-, sat'd}$ (cm ² /Vs)	$\mu_{h, sat'd}$ (cm ² /Vs)
P1	~2 x 10 ⁻³	~4 x 10 ⁻³
P2	~3 x 10 ⁻³	~3 x 10 ⁻⁴
P2EC	~2 x 10 ⁻⁵	~8 x 10 ⁻⁵
P3	~5 x 10 ⁻⁴	~4.7 x 10 ⁻⁵



Figure S2. Top (left): Absorption-photoluminescence spectra of **P1** thin film as-spun at 100 °C, excited at 501 nm, PLQE = ~ 20 %. (right): Normalized photoluminescence and electroluminescence of **P1** thin film. Bottom: Transfer characteristics of a light-emitting FET (W = 1 cm, L = 20 μ m) based on **P1** thin film as-spun at 100 °C.



Figure S3. Left: Transfer characteristics of a light-emitting FET (W = 1 cm, L = 20 μ m) based on **P2** thin film as-spun at 100 °C. Right: Transfer characteristics of a light-emitting FET (W = 1 cm, L = 20 μ m) based on **P2EC** thin film as-spun at 100 °C and annealed at 300 °C.



Figure S4. Top (left): Absorption-photoluminescence spectra of **P3** thin film as-spun at 100 °C and annealed at 290 °C, excited at 501 nm, PLQE = \sim 3 %. (Right): Transfer characteristics of a light-emitting FET (W = 1 cm, L = 20 µm) based on **P3** thin film as-spun at 100 °C. Bottom: Transfer characteristics of a light-emitting FET (W = 1 cm, L = 20 µm) based on **P3** thin film annealed at 300 °C



Figure S5. 1H NMR spectra of a) P1, b) P2, c) P3, d) P4, e) P5 and f) P2EC in CDCl₃.



Figure S6. TGA of polymers at a heating rate of 10 °C/min, a) P1, b) P2, c) P2EC and d) P3.



Figure S7. DSC of P3-5 at a scan rate of 10 °C/min.



Figure S8. AFM height images of P1.



Figure S9. XRD on drop-cast films of **P1-3** dried in the dark under ambient conditions for 24 h.



Figure S10. XRD on drop-cast films of P1-3 annealed at 290 °C in the dark under a nitrogen atmosphere for 30 minutes.

Experimental Methods

Characterization

Experimental procedures can be found in the supporting information. ¹H-NMR spectra were measured on an automated Agilent (Varian) MR 400 MHz spectrometer (equipped with "oneprobe") with CDCl3 as the solvent. In all cases, the peak values were calibrated relative to tetramethylsilane. Size exclusion chromatography (SEC) was performed on a Waters Alliance GPCV2000 with refractive index detector columns: Waters Styragel HT GE x 1, Waters Styragel HMW GE x 2. The eluent was 1,2,4-trichlorobenzene. The operating temperature was 135 °C, and the dissolution time was 2 h. The concentration of the samples was 0.5 mg/mL, which were filtered through a 0.45 µm metal filter prior to analysis. The molecular weights were calculated relative to calibration with polystyrene standards. UV-Vis-NIR absorption spectra were measured with a Perkin Elmer Lambda 900 UV-Vis-NIR absorption spectrometer. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA7 Thermo Graphic Analyzer. A temperature range of 25-600 °C was used with a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were done on a Perkin Elmer Pyris over a temperature range of 30-250 °C using a heating/cooling rate of 10 °C/min. Values from the 2nd scan were reported. Square-wave voltammetry (SWV) measurements were carried out on a CH-Instruments 650A Electrochemical Workstation. Experiments were performed in a three-electrode cell using platinum wires as both the working electrode and the counter electrode, and a Ag/Ag^+ reference electrode calibrated to the Fc/Fc⁺ redox couple. A 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu4NPF6) in anhydrous acetonitrile was used as supporting electrolyte. The polymers were deposited onto the working electrode from chloroform solution. In order to remove oxygen from the electrolyte solution, the system was bubbled with nitrogen prior to each experiment.

The nitrogen inlet was then placed above the liquid surface and left there during the scans. The HOMO/LUMO levels were estimated from onset and peak potentials of the third scan using the equation HOMO/LUMO = $-(E_{ox/red} + 5.13) \text{ eV})$.^[28]

For polymers **P1-3** seen in **Figure 3**, **S2** and **S4**, UV-Vis absorption spectra of polymer films were measured in air using a Hewlett-Packard HP845x Visible-UV spectrometer (with quartz Spectrosil B substrates). Photoluminescence (PL) and photoluminescence quantum efficiency (PLQE) measurements were carried out at room temperature with a nitrogen-purged integrating sphere using polymer films on quartz Spectrosil B substrates. The 501 nm line of an argon-ion laser (Coherent Innova305) was used as the excitation source and a cooled CCD camera (Oriel Instaspec IV) was used for photon detection. The PLQE value was calculated as described by de Mello *et al.*^[34] For polymers **P1-3** seen in **Figure S8**, AFM images were obtained in air using a Digital Instruments Dimension 3100 AFM in tapping mode.

For polymers **P3-5** seen in **Figure 4**, photoluminescence measurements of thin films were recorded with an Andor Newton EMCCD camera coupled to an Andor SHAMROCK 163 spectrograph upon excitation with a Kimmon HeCd laser ($\lambda = 325$ nm). Electroluminescence spectra were recorded with the same Andor Newton EMCCD camera coupled to an Andor SHAMROCK 163 spectrograph.

FET Devices

Top-gate/bottom-contact structure was employed for field effect transistor characteristics of ambipolar semiconducting polymers. Photolithography was used to make interdigitated pattern on glass substrate and gold with Cr adhesion layer underneath was deposited for source and drain contacts. Semiconducting polymer was dissolved in anhydrous 1,2-dichlorobenzene (DCB) on hotplate at 110 °C to make 10 mg/ml and spun at 1500 rpm and

annealed at 100 °C for two hours to dry solvent. Further annealing was carried out on preheated hotplate for 30 minutes when required. Poly(methyl methacrylate) (PMMA, Polymer Source) was dissolved in n-butylacetate (45 mg/ml) and spun on the semiconducting polymer layer as a dielectric layer of 500 nm. Gate electrode was evaporated using a shadow mask. I-V characteristics were measured using HP4155B semiconductor parameter analyzer. Besides HP4155B, for the characterization of LFETs, we also used Keithley 2636A in order to apply higher voltage than 100V. Light emission during FET operation was measured with a silicon photodiode (Hamamatsu, S1133-01) mounted above the semitransparent gold gate of the FETs. The sensitivity of the silicon photodiode is 0.39 A W-1 at $\lambda = 670$ nm, and 0.43 A W-1 at $\lambda = 714$ nm. An Ocean Optics USB 2000 spectrometer was mounted with an optical fiber directly on top of the gold gate to record electroluminescence spectra during FET operations. All device fabrication and measurement procedures were performed in nitrogen atmosphere.

X-Ray Diffraction

X-Ray Diffraction (XRD) was performed on drop-cast polymer thin films on microscope glass slides. Thin films of **P1-3** were drop-cast from ODCB (**P1**: 3.5 mg/mL; **P2**: 3.8 mg/mL) or chloroform (**P3**: 3.3 mg/mL) solutions and dried in the dark under ambient conditions for 24 h. After performing initial XRD analysis, the films were then annealed at 290 °C for 30 minutes under a nitrogen atmosphere and allowed to cool to room temperature under a nitrogen atmosphere. Then XRD analysis was performed again on the annealed films. Diffraction data was collected from a Philips X'Pert Materials Research Diffractometer in 2θ scans (0.05 ° step size, 10 s/step). X-ray tube with Cu anode was used to generate radiation

(K α radiation, k = 1.54184A°) at 45 kV and 40 mA. An X-ray lens with Ni filter was used as incident optics; a thin film collimator was used as diffracted optics.

NIR PLED Devices

Devices were prepared on glass substrates coated with indium tin oxide (ITO) films, cleaned with acetone and isopropanol before being exposed to an oxygen-plasma immediately before the deposition of the hole injection layer. The PEDOT:PSS hole injection layer was spin-coated at 3000 rpm to obtain films ~80 nm thick which were then baked at 180 °C for ten minutes. 2 w.t. % solutions of **P3**, **P4** or **P5** in chlorobenzene were prepared and spin-coated onto the slides at 1500 rpm in a nitrogen glovebox. Lastly, anodes of 30 nm calcium and 150 nm aluminium were evaporated onto the polymer layers. We fabricated three samples (each with 8 pixels) for each polymer. Quoted values and error bars are derived from the mean and standard deviation respectively of the parameters of the tested devices.

Materials





Scheme S2. Synthesis of Bisthienyl(benzotriazolothiadiazole) emitter.



Scheme S3. Synthesis of phthalimide-thiophene copolymers P1-3 and NIR-emitting polymers P4-5.

Compounds 1,^[35] 4,^[9] 6,^[9] 8^[31] and 14^[30] were made according to literature procedure. Potassium phthalimide, dodecylamine and hexadecylamine was purchased from Aldrich Chemical Company and used as received. Compound 15 was purchased from Solamer Chemical Company and used as received. All other reagents and solvents were purchased from Aldrich Chemical Company and used as received. All reactions were performed under nitrogen unless noted. **2**. To a round-bottomed flask containing 14.57 g (35.5 mmol) of **1** was added 45 mL of DMF followed by 7.23 g (39.0 mmol) of potassium phthalimide. The mixture was stirred and heated to 90 °C overnight. Upon cooling, 150 mL of H₂O was added and the mixture was extracted (3 x 50 mL) with dichloromethane. The combined organic layers were washed with 0.2 M KOH (3 x 60 mL) and brine, then dried over anhydrous magnesium sulfate, filtered and the solvent was removed under reduced pressure. Column chromatography (SiO₂, 2:1 hexane:DCM) yielded 6.80 g (50 %) of a clear and colorless oil. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 7.82 (m, 2H), 7.70 (m, 2H), 4.19 (p, *J* = 5.0 Hz, 1H), 2.06 (m, 2H), 1.67 (m, 2H), 1.25-1.21 (m, 24H), 0.85 (t, *J* = 6.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 169.02, 133.96, 132.09, 123.26, 52.54, 32.69, 32.01, 29.64, 29.49, 29.41, 26.88, 22.83, 14.27.

3. To a round-bottomed flask containing 7.56 g (19.6 mmol) of **2** was added 12 mL of ethanolamine. The reaction was stirred and heated to 90 °C for 4 h. Upon cooling, 100 mL of water was added and the reaction mixture was extracted with dichloromethane. The combined organic layers were washed with water, dried over anhydrous magnesium sulfate, filtered and the solvent was removed under reduced pressure yielding a colorless oil (quantitative), which was used without further purification. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 2.66 (m, 1H), 1.37-1.28 (m, 28H), 0.85 (t, *J* = 6.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 51.39, 38.35, 32.07, 30.01, 29.80, 29.48, 26.36, 22.84, 14.26.

5.^[9] This serves as a representative procedure for compound 7. To a round-bottomed flask containing 5.72 g (22.4 mmol) of **3** was added 4.56 g (14.9 mmol) of **4** followed by 90 mL of acetic acid. The reaction mixture was stirred and heated to reflux for 3 h. Upon cooling, the solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO₂, 4:1 hexane:DCM) yielding 4.80 g (59 %) of a white solid. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 7.66 (s, 2H), 4.20 (m, *J* = 5.0 Hz, 1H), 2.04 (m, 2H), 1.71 (m, 2H), 1.27-1.22 (m, 24H), 0.85 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ

(ppm): 165.27, 139.68, 131.07, 117.68, 53.38, 32.46, 32.00, 29.59, 29.44, 29.40, 26.90, 22.83, 14.28. MS (MALDI): calcd for C₂₅H₃₇Br₂NO₂ (M⁺) 543.1, found 542.3.

7.^[9] Column chromatography (SiO₂, 1:1 hexane:DCM) yielded 1.27 g (89 %) of a white solid. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 7.65 (s, 2H), 3.69 (t, *J* = 7.3 Hz, 2H), 1.67 (p, *J* = 7.2 Hz, 2H,), 1.32-1.25 (m, 26H), 0.88 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 165.03, 139.67, 131.52, 117.69, 38.88, 32.14, 29.91, 29.90, 29.87, 29.83, 29.78, 29.65, 29.57, 29.35, 28.52, 27.04, 22.91, 14.34 (Note: 2 peaks overlap in the ¹³C NMR spectrum).

9. To a dry 50 mL 2-neck round-bottomed flask was added 12 mL of triflic acid (d = 1.696 g mL). The solution was then cooled to 0 °C. Next, 1.5 mL of fuming nitric acid (d = 1.52 g mL) was added and the mixture was stirred for 30 minutes at 0 °C. Upon stirring, a white solid crashed out of the solution. Then 4.18 g of **6** was added drop-wise at 0 °C over 1.33 h. The reaction was stirred for another 50 min at 0 °C, then at room temperature for 4 h. Then the mixture was poured into 150 mL of ice/H₂O and extracted with diethyl ether. The combined ether layers were washed with saturated sodium bicarbonate and dried over anhydrous magnesium sulfate, filtered and the solvent was removed under reduced pressure. Column chromatography (SiO₂, 1:1 hexane:DCM) yielded 2.09 g (41 %) of a pale yellow solid. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 4.78 (d, *J* = 7.1 Hz, 2H), 2.30 (sp, *J* = 6.4 Hz, 1H), 1.42-1.27 (m, 8H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 143.29, 142.08, 107.45, 62.06, 40.75, 30.43, 28.39, 23.93, 22.99, 14.16, 10.55. MS (MALDI): calcd for C₁₄H₁₇Br₂N₅O₄ (M⁺) 479.0, found (M⁺) 478.2.

10. To a 500 mL round-bottomed flask was added 1.99 g (4.15 mmol) of 7, 2.80 g (50.1 mmol) of Fe powder and 95 mL of acetic acid. The reaction was stirred and heated at 60 °C for 3 h. Upon cooling the reaction was poured into 200 mL of H_2O and extracted with ethyl

acetate. The combined organic layers were washed with water, saturated sodium bicarbonate, water and dried over anhydrous magnesium sulfate, filtered and the solvent was removed under reduced pressure. Column chromatography (SiO₂, DCM) yielded 1.27 g (73 %) of a yellow solid. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 4.54 (d, *J* = 7.4 Hz, 2H), 4.13 (br s, 4H), 2.25 (sp, *J* = 6.4 Hz, 1H), 1.37-1.23 (m, 8H), 0.91-0.84 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 139.19, 135.95, 92.44, 60.10, 40.31, 30.39, 28.42, 23.86, 23.09, 14.18, 10.57. MS (MALDI): calcd for C₁₄H₂₁Br₂N₅ (M⁺) 419.0, found 418.2.

11. To a dry 50 mL 2-neck round-bottomed flask containing 0.68 g (1.62 mmol) of **8** was added 14 mL of anhydrous pyridine. After dissolution of **8**, 0.39 mL (3.50 mmol) of N-thionylaniline was added followed by 0.38 mL (1.84 mmol) of trimethylsilyl chloride. The reaction mixture was heated to 80 °C overnight. Upon cooling, the reaction mixture was poured into 150 mL of water and a dark maroon colored solid was collected by filtration. The solid was rinsed with water and dried. Column chromatography (SiO₂, DCM) yielded 0.59 g (82 %) of a bright orange solid. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 4.85 (d, *J* = 7.3 Hz, 2H), 2.45 (sp, *J* = 6.4 Hz, 1H), 1.42-1.25 (m, 8H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 151.50, 145.62, 98.86, 62.62, 40.77, 30.52, 28.42, 24.03, 23.03, 14.17, 10.59. MS (MALDI): calcd for C₁₄H₁₇Br₂N₅S (M⁺) 447.0, found 446.2.

12. To a 25 mL 2-neck round-bottomed flask was added 0.35 g (0.78 mmol) of **9**, 0.55 mL (1.72 mmol) of 2-tributylstannylthiophene and 10 mL of THF. The solution was degassed with nitrogen for 30 minutes. Then 0.027 g of PdCl₂(PPh₃)₂ was added and the solution was stirred at 75 °C overnight. The solvent was then removed under reduced pressure and the residue was purified by column chromatography (SiO₂, Hex:CHCl₃ 2:1) yielding 0.17 g (48 %) of a dark blue solid. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 8.76 (d, *J* = 3.8 Hz, 2H), 7.58 (d, *J* = 5.0 Hz, 2H), 7.27 (m, 2H), 4.80 (d, *J* = 6.7 Hz, 2H), 2.33 (sp, *J* = 6.2 Hz,

1H), 1.42-1.25 (m, 8H), 1.01 (t, , *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 149.98, 142.80, 137.39, 131.12, 129.46, 127.81, 112.08, 61.12, 40.82, 30.91, 28.71, 24.33, 23.14, 14.27, 10.83.

13. To a 150 mL round-bottomed flask was added 0.17 g (0.38 mmol) of **10** followed by 70 mL of DMF. The solution was degassed with nitrogen for 30 minutes. Then 0.15 g (0.82 mmol) of N-Bromosuccinimide was added and the reaction was stirred in the dark for 24 h. The solution was then poured into 150 mL of water and extracted (3 x) with dichloromethane. The combined organic layers were then washed with brine, 3 M HCl, water and then dried over anhydrous magnesium sulfate. The solution was then filtered and the solvent removed under reduced pressure. The residue was purified by column chromatography (SiO₂, Hex:CH₂Cl₂ 2:1) yielding 0.17 g (74 %) of a dark blue solid. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 8.22 (d, *J* = 4.0 Hz, 2H), 7.08 (d, *J* = 4.1 Hz, 2H), 4.65 (d, *J* = 6.7 Hz, 2H), 2.23 (sp, *J* = 6.2 Hz, 1H), 1.45-1.29 (m, 8H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 149.00, 141.83, 138.71, 131.10, 130.57, 117.85, 110.78, 61.05, 40.77, 30.87, 28.65, 24.32, 23.21, 14.35, 10.84. MS (MALDI): calcd for C₂₂H₂₁Br₂N₅S₃ (M⁺) 610.9, found 610.4.

P1. To a 50 mL 2-neck round bottom flask was added 0.3012 g (0.6365 mmol) of **6**, 0.2608 g (.6365 mmol) of **15**, 0.0058 g (0.0064 mmol) of Pd₂dba₃ and 0.0154 g (0.0508 mmol) of tri(o-tolyl)phosphine. The flask was subjected to 6 x vacuum/nitrogen backfill cycles. Then 12 mL of degassed toluene was added and the flask was placed in a pre-heated oil bath at 88 °C and stirred. As the reaction progressed, the solution fluorescence went from green to yellow to orange. After 20 minutes an orange precipitate was seen and the reaction was more viscous, and thus was stopped. The reaction was precipitated into 150 mL of methanol and an orange solid was collected by filtration. Then the polymer was dissolved in 100 mL of CHCl₃ and stirred with an aqueous solution of sodium diethyldithiocarbamate trihydrate (5 g in 100

mL H₂O) overnight. Then the CHCl₃ layer was separated, washed 3 X with water,

concentrated and precipitated into 200 mL of methanol. The polymer was then collected by filtration, placed in a thimble and subjected to Soxhlet extraction with methanol, acetone, hexane and CHCl₃ (overnight, ~15-20 h). Then the CHCl₃ solution was concentrated, precipitated into 200 mL of methanol and an orange solid (54 %) was collected by filtration. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 7.89 (br s, 2H), 7.85 (br s, 2H), 3.72 (br, 2H), 1.71(br, 2H), 1.35-1.25 (br, 17H), 0.86 (br t, *J* = 5.4 Hz, 3H). GPC: M_n =6.5 kg/mol, M_w = 8.1 kg/mol, PDI = 1.2. TGA (N₂) T_{d99} = 261 °C, T_{d95} = 454 °C. DSC: No transitions observed.

P2. To a 50 mL 2-neck round bottom flask was added 0.3008 g (0.5682 mmol) of 7, 0.2328 g (.5682 mmol) of **15**, 0.0052 g (0.0057 mmol) of Pd₂dba₃ and 0.0138 g (0.0454 mmol) of tri(o-tolyl)phosphine. The flask was subjected to 6 x vacuum/nitrogen backfill cycles. Then 12 mL of degassed toluene was added and the flask was placed in a pre-heated oil bath at 88 °C and stirred. As the reaction progressed, the solution fluorescence went from green to yellow to orange. After 12 minutes the reaction was orange in color, hazy and more viscous, and thus was stopped. The reaction was precipitated into 150 mL of methanol and an orange solid was collected by filtration. Then the polymer was dissolved in 100 mL of CHCl₃ and stirred with an aqueous solution of sodium diethyldithiocarbamate trihydrate (5 g in 100 mL H₂O) overnight. Then the CHCl₃ layer was separated, washed 3 X with water, concentrated and precipitated into 200 mL of methanol. The polymer was then collected by filtration, placed in a thimble and subjected to Soxhlet extraction with methanol, acetone, hexane and CHCl₃ (overnight, ~15-20 h). Then the CHCl₃ solution was concentrated, precipitated into 200 mL of methanol and an orange solid (62 %) was collected by filtration. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 7.89 (br s, 2H), 7.85 (br s, 2H), 3.72 (br, 2H), 1.71(br, 2H), 1.35-1.25 (br, 26H), 0.87 (br t, J = 6.0 Hz, 3H). GPC: M_n =9.4 kg/mol, M_w = 14.5 kg/mol, PDI = 1.5. TGA (N₂) T_{d99} = 293 °C, T_{d95} = 462 °C. DSC: No transitions observed.

P2EC. An additional batch of P2 was synthesized in the same manner as above. Then endcapping was performed as follows. To a 2-neck round bottom flask was added 0.2183 g (0.4833 mmol) of P2, 0.1138 g (0.7248 mmol) of PhBr, 0.0044 g (.0048 mmol) of Pd₂dba₃ and 0.0118 g (0.0388 mmol) of tri(o-tolyl)phosphine. Then the flask was subjected to 6 x vacuum/nitrogen backfill cycles followed by the addition of 20 mL of degassed toluene and 5 mL of chloroform. The mixture was refluxed for ~1 h. Then, 0.2662 g (0.7250 mmol) of Bu₃SnPh was added and the reaction was heated at reflux for approximately 1 h. Then the reaction was poured into 300 mL of MeOH and collected by filtration. Then the polymer was dissolved in 100 mL of CHCl₃ and stirred with an aqueous solution of sodium diethyldithiocarbamate trihydrate (5 g in 100 mL H₂O) overnight. Then the CHCl₃ layer was separated, washed 3 X with water, concentrated and precipitated into 200 mL of methanol. The polymer was then collected by filtration, placed in a thimble and subjected to Soxhlet extraction with methanol, acetone, hexane and CHCl₃ (overnight, ~15-20 h). Then the CHCl₃ solution was concentrated, precipitated into 200 mL of methanol and an orange solid (90 %) was collected by filtration. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 7.89 (br s, 2H), 7.85 (br s, 2H), 3.71 (br, 2H), 1.70 (br, 2H), 1.35-1.25 (br, 26H), 0.87 (br t, *J* = 6.0 Hz, 3H). GPC: $M_n = 8.9 \text{ kg/mol}, M_w = 15 \text{ kg/mol}, PDI = 1.7. TGA (N_2) T_{d99} = 394 \text{°C}, T_{d95} = 488 \text{°C}. DSC:$ No transitions observed.

P3. To a 50 mL 2-neck round bottom flask was added 0.644 g (1.185 mmol) of **5**, 0.486 g (1.185 mmol) of **15**, 0.0108 g (0.0119 mmol) of Pd_2dba_3 and 0.0288 g (0.0948 mmol) of tri(o-tolyl)phosphine. The flask was subjected to 5 x vacuum/nitrogen backfill cycles. Then 20 mL of degassed toluene was added and the flask was placed in a pre-heated oil bath at 88 °C and stirred for 48 h. Then the reaction was cooled and precipitated into 150 mL of methanol and light orange-yellow strands were collected by filtration. Then the polymer was dissolved in 100 mL of CHCl₃ and stirred with an aqueous solution of sodium

diethyldithiocarbamate trihydrate (5 g in 100 mL H₂O) overnight. Then the CHCl₃ layer was separated, washed 3 X with water, concentrated and precipitated into 200 mL of methanol. The polymer was then collected by filtration, placed in a thimble and subjected to Soxhlet extraction with methanol, acetone, hexane and CHCl₃ (overnight, ~15-20 h). Then the CHCl₃ solution was concentrated, precipitated into 200 mL of methanol and light orange-yellow strands (0.5084 g, 92 %) were collected by filtration. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 7.91 (br s, 2H), 7.85 (br s, 2H), 4.26 (br, 1H), 2.11(br, 2H), 1.74 (br, 2H), 1.25 (br, 24H), 0.86 (br t, *J* = 6.8 Hz, 6H). GPC: M_n =40 kg/mol, M_w = 102 kg/mol, PDI = 2.5. TGA (N₂) T_{d99} = 439 °C. DSC: T_m = 255 °C, T_c = 200 °C.

P4. To a 25 mL 2-neck round bottom flask was added 0.3051 g (0.5615 mmol) of 5, 0.2324 g (0.5672 mmol) of **15**, 0.0035 g (0.0057 mmol) of **13**, 0.0052 g (0.0057 mmol) of Pd₂dba₃ and 0.0138 g (0.0454 mmol) of tri(o-tolyl)phosphine. The flask was subjected to 5 x vacuum/nitrogen backfill cycles. Then 9 mL of degassed toluene was added and the flask was placed in a pre-heated oil bath at 88 °C and stirred for 48 h. Then the reaction was cooled and precipitated into 150 mL of methanol and light brown strands were collected by filtration. Then the polymer was dissolved in 100 mL of CHCl₃ and stirred with an aqueous solution of sodium diethyldithiocarbamate trihydrate (5 g in 100 mL H₂O) overnight. Then the CHCl₃ layer was separated, washed 3 X with water, concentrated and precipitated into 200 mL of methanol. The polymer was then collected by filtration, placed in a thimble and subjected to Soxhlet extraction with methanol, acetone, hexane and CHCl₃ (overnight, ~15-20 h). Then the CHCl₃ solution was concentrated, precipitated into 200 mL of methanol and light brown strands (0.2320 g, 88 %) were collected by filtration. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 7.90 (br s, 2H), 7.84 (br s, 2H), 4.25 (br, 1H), 2.08(br, 2H), 1.73 (br, 2H), 1.29-1.24 (br, 24H), 0.85 (br t, J = 6.8 Hz, 6H). GPC: $M_n = 42$ kg/mol, $M_w = 88$ kg/mol, PDI = 2.1. TGA (N₂) $T_{d99} = 431$ °C. DSC: $T_m = 251$ °C, $T_c = 202$ °C.

P5. To a 25 mL 2-neck round bottom flask was added 0.3072 g (0.5654 mmol) of 5, 0.2340 g (0.5711 mmol) of **15**, 0.0052 g (0.0057 mmol) of **14**, 0.0052 g (0.0057 mmol) of Pd₂dba₃ and 0.0139 g (0.0456 mmol) of tri(o-tolyl)phosphine. The flask was subjected to 5 x vacuum/nitrogen backfill cycles. Then 9 mL of degassed toluene was added and the flask was placed in a pre-heated oil bath at 88 °C and stirred for 48 h. Then the reaction was cooled and precipitated into 150 mL of methanol and golden brown strands were collected by filtration. Then the polymer was dissolved in 100 mL of CHCl₃ and stirred with an aqueous solution of sodium diethyldithiocarbamate trihydrate (5 g in 100 mL H₂O) overnight. Then the CHCl₃ layer was separated, washed 3 X with water, concentrated and precipitated into 200 mL of methanol. The polymer was then collected by filtration, placed in a thimble and subjected to Soxhlet extraction with methanol, acetone, hexane and CHCl₃ (overnight, ~15-20 h). Then the CHCl₃ solution was concentrated, precipitated into 200 mL of methanol and golden brown strands (0.2372 g, 88 %) were collected by filtration. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm): 7.91 (br s, 2H), 7.85 (br s, 2H), 4.25 (br, 1H), 2.10 (br, 2H), 1.74 (br, 2H), 1.29-1.24 (br, 24H), 0.86 (br t, J = 6.8 Hz, 6H). GPC: M_n =92 kg/mol, M_w = 396 kg/mol, PDI = 4.3. TGA (N₂) T_{d99} = 434 °C. DSC: T_m = 246 °C, T_c = 197 °C.

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