

Supporting Information for:

Soluble Narrow Band Gap and Blue Propylenedioxythiophene-Cyanovinylene Polymers
as Multifunctional Materials for Photovoltaic and Electrochromic Applications

Barry C. Thompson,¹ Young-Gi Kim,¹ Tracy D. McCarley,² and

John R. Reynolds^{1}*

¹The George and Josephine Butler Polymer Research Laboratory and the Center for Macromolecular Science and Engineering, Department of Chemistry, University of Florida, Gainesville, FL 32611-7200.

²Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804.

reynolds@chem.ufl.edu

Supporting Information

Experimental Details

General. All chemicals were purchased from commercial sources unless otherwise noted. PCBM was prepared as described in the literature.¹ Reactions were performed under argon or nitrogen using standard Schlenk techniques. Dry THF and ether were obtained from a Fisher keg system and were dried by passing through a column of Al₂O₃. All new monomers were characterized by ¹H NMR (300 MHz, Mercury 300), ¹³C NMR (75 MHz, Mercury 300), high-resolution mass spectroscopy (HRMS) on a Finnigan MAT 95Q mass spectrometer, elemental analysis, and melting point. Polymer ¹H NMR spectra were recorded on a 500 MHz Inova 500.

Polymer GPC was performed on two 300 x 7.5 mm Polymer Laboratories PLGel 5 μM mixed-C columns with Waters Associates liquid chromatography 2996 photodiode array absorption. Polymer solutions were prepared in THF or chloroform and filtered through a 50 μM filter before injection. A constant flow rate of 1 mL/min was used. Molecular weights were obtained relative to polystyrene standards (Polymer Laboratories, S-M2-10 lot 30). Molecular weights were also investigated by matrix assisted laser desorption quadrupole-time-of-flight mass spectrometry (MALDI QqTOF) with an Applied Biosystems QSTAR XL hybrid quadrupole-time-of-flight (QqTOF) mass spectrometer equipped with a vacuum MALDI source (Louisiana State University). HABA (2-(4-hydroxyphenylazo)benzoic acid) or terthiophene matrices were used.

Electrochemical measurements were performed in an argon-filled dry box using an EG&G Princeton Applied Research model 273A potentiostat-galvanostat operated with Corrware II software from Scribner and Associates. Polymer films were drop-cast on a

Pt button electrode from 1% (w/w) solutions of chloroform or toluene or directly electropolymerized onto the electrode surface by repeated potential scans. Measurements were made in a three-electrode setup with a Ag wire pseudo-reference electrode calibrated vs. Fc/Fc^+ and a Pt counter electrode. For electrochemical experiments, acetonitrile was dried over CaH_2 and distilled prior to use. Electrolytes tetrabutylammonium perchlorate (TBAP), tetrabutylammonium hexafluorophosphate (TBAPF_6), and lithium perchlorate (LiClO_4) were purchased, or in the case of TBAP, synthesized from TBABr and HClO_4 .

Spectroelectrochemical experiments were performed using either a Cary 500 UV-Vis-NiR spectrophotometer for bench-top experiments or a Stellarnet diode-array Vis-NiR spectrophotometer equipped with a InGaAs diode array detector with fiber-optic capabilities for dry-box studies. In all cases, a three-electrode cell was utilized, as described above, with indium tin oxide (ITO) coated glass used as the working electrode (Delta Technologies $8\text{-}12 \Omega / \square$). Polymer films were deposited by electropolymerization or by spray coating of the soluble polymer from a 1-2% (w/w) solution of the polymer in dichloromethane using an Iwata HP-BC airbrush. In this experiment, the evolution of the polymer absorption spectra is monitored as a function of applied potential.

Polymer films were also investigated by in-situ colorimetric analysis. In this case polymer films were deposited on ITO as for spectroelectrochemistry. The precise color coordinates were then recorded as a function of potential using a Minolta CS-100 Chroma-Meter and the CIE (Commission Internationale de l'Éclairage) recommended (0/0) illuminating/viewing geometry for transmission measurements. The sample was illuminated from behind with D50 (5000K) light source in a light booth specially

designed to exclude external light. A background measurement was taken using blank ITO in the appropriate electrolyte solution in a quartz cuvette. The Y_{xy} values of the standard illuminant (Y_0, x, y) were thus recorded. CIE 1931 Y_{xy} values were then converted to $L^*a^*b^*$ values which are reported along with the relative luminance ($\%Y = Y/Y_0 \times 100$) as a function of potential. Relative luminance offers an accurate measure of the perceived transmissivity of a material across the entire visible region according to the natural sensitivity of a standard human observer.

Fluorescence and excitation spectra were obtained using a Jobin-Yvon Fluorolog-3PL spectrophotometer. For polymer solutions, emission quantum yields were measured relative to zinc phthalocyanine (Zn-PC) in pyridine² or zinc tetraphenylporphyrin (Zn-TPP) in toluene.³ The optical density of all solutions was kept below $A = 0.1$. Thin film fluorescence data was collected with the same instrument. Polymer thin films and blend films with PCBM (for PL quenching experiments) were deposited on PEDOT-PSS coated glass by spin-coating from dichlorobenzene solution. Molar absorptivities and absorption coefficients were also calculated for all polymers in solution and in thin film form respectively. For thin film measurements, the absorbance of polymer thin films was recorded on PEDOT-PSS coated glass (in order to mimic device conditions) using a Cary 500 UV-Vis-NiR spectrophotometer. In this dual beam instrument, the baseline was measured with two PEDOT-PSS coated glass slides and the reference beam was passed through a PEDOT-PSS coated glass slide during the measurement. The film thickness was then measured using a Dektak 3030 profilometer and the absorption coefficient was calculated using the relationship $A = \alpha x$, where A is the measured absorbance, α is the absorption coefficient, and x is the thickness of the film.

In addition to measuring the thickness of polymer thin films, the surface morphology of the films was investigated using AFM. For both measurements, films were spin-coated on PEDOT-PSS coated glass substrates. Substrate preparation involved cleaning the glass by sonicating with SDS (sodium dodecyl sulfate) in 18 M Ω deionized water, followed by sonicating with successively 18 M Ω deionized water, acetone, and methanol. Substrates were then spin-coated with PEDOT-PSS (Baytron-P) (400 μ L at 4000 rpm for 30s) and annealed in a vacuum oven for 2 hours at 150°C. Polymer films were then coated onto the substrates at a concentration of 30 mg/mL from *o*-dichlorobenzene and spin-coated at 500 rpm for 18 s, followed by 1000 rpm for 60 s. AFM measurements were recorded on a Nanoscope IIIa Dimension 3100 AFM.

Solar cells were fabricated on indium tin oxide (ITO) covered glass substrates (Delta Technologies, $R_s = 8\text{-}12 \Omega/\square$). The ITO/glass substrates were etched by exposure to aqua regia vapor and subsequently cleaned in an ultrasonic bath for 15 min with aqueous sodium dodecyl sulfate (SDS, Fisher scientific), deionized water (Milli-Q), acetone, and isopropanol. The substrates were then treated with oxygen plasma for 15 minutes in a Plasma Cleaner (HARRICK PDC-32G). Aqueous PEDOT-PSS (Bayer Baytron P VP Al 4083) solution was spin coated at 4000 rpm onto a glass substrate and dried under vacuum for 3-4 h at 150 °C. The photoactive layer was then spin-coated and the resulting films were dried under vacuum for 12 h at room temperature. Lithium Fluoride (Li:F, 0.5 nm) and Aluminium (Al, 200 nm) were sequentially deposited by thermal evaporation on the photoactive layer. The devices were then encapsulated with epoxy. The active area of the devices was 0.25 cm². The current–voltage (I–V) characteristics were measured with a Keithley SMU 2400 source measurement unit under

the illumination of simulated AM1.5 light with an incident power density of 100 mW/cm² using a 150 W Xe arc lamp power supply (Oriel instruments) calibrated for each measurement using a power energy meter (Ophir 2A-SH photodiode). No spectral mismatch correction factor was applied.⁴

The external quantum efficiency of the photovoltaic devices was also evaluated by measuring the incident photon to current efficiency (IPCE). In this case device pixels were irradiated with monochromatic light from a 75 W tungsten-halogen lamp. Here, the light from the lamp was passed through a monochromator (Instruments SA Inc., 1200VIS), and the wavelength of light was selected. The power output of the lamp was recorded at 10 nm wavelength intervals between 350 and 750 nm using a UDT instruments S350 Power-Energy Meter equipped with a UDT 221 Silicon Sensor Head. The current response under short circuit conditions was then recorded for each pixel at 10 nm intervals using a Keithley 2400 SMU (positive lead to ITO and negative lead to aluminum).

Synthetic Details.

1,4-bis(bromomethyl)-2,5-bis(dodecyloxy)benzene. To a solution consisting of 30 mL of 33% HBr in acetic acid and 110 mL of glacial acetic acid, 13.8 g (31 mmol, 1 equiv) of 1,4-bis(dodecyloxy)benzene⁵ and 2.80 g of paraformaldehyde (93 mmol, 3 equiv) were added. The white slurry was heated to 70-75°C, resulting in the dissolution of all solids. After a few minutes at this temperature, a white precipitate began to form and stirring was continued for 2 h. The reaction mixture was then cooled to 0°C, poured into cold water, and filtered. The crude off-white product was then recrystallized from hexane followed by recrystallization from dichloromethane-methanol to yield 12.02 g

(61%) of the product as a white solid. mp 92-93°C (Lit.⁶ 96-97°C). ¹H NMR (300 MHz, CDCl₃) δ 6.85 (s, 2H), 4.52 (s, 4H), 3.98 (t, 4H), 1.81 (m, 4H), 1.5-1.2 (br 36H), 0.88 (t, 6H).

1,4-bis(cyanomethyl)-2,5-bis(dodecyloxy)benzene (Route A) (1). Sodium cyanide (2.41 g, 49 mmol, 2.5 equiv) and 1,4-bis(bromomethyl)-2,5-bis(dodecyloxy)benzene (12.0 g, 19 mmol, 1 equiv) were dissolved in 250 mL of dry DMF and the solution was heated to 110°C. The reaction was stirred for two days, during which time the reaction turned dark orange and a precipitate was observed to form. The reaction was then cooled to room temperature and poured into 750 mL of cold water that was 0.5 M in sodium hydroxide. The crude solid was isolated by filtration and then taken up in chloroform and washed with water. The organic layer was then dried with MgSO₄. The crude solid was then purified by column chromatography on silica (1:1 hexanes and dichloromethane) followed by recrystallization from ethanol and chloroform (2:3) to give 5.12 g (51%) of the product as a white solid. mp 98-100°C. ¹H NMR (300 MHz, CDCl₃) δ 6.91 (s, 2H), 3.97 (t, 4H), 3.70 (s, 4H), 1.79 (m, 4H), 1.5-1.2 (br, 36H), 0.88 (t, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 150.27, 119.35, 118.05, 112.89, 69.27, 32.13, 29.88, 29.85, 29.82, 29.78, 29.59, 29.48, 26.82, 25.05, 22.90, 18.86, 14.33. IR (KBr cm⁻¹) 2961, 2870, 2849, 2917, 2246, 1514, 1466, 1427, 1392, 1341, 1222, 1209, 1070, 999, 846, 720, 686. HRMS calcd for C₃₄H₅₆N₂O₂ (M⁺), 524.4342; found 524.4341. Anal. calcd for C₃₄H₅₆N₂O₂: C, 77.81; H, 10.76; N, 5.34; O, 6.10. Found: C, 77.85; H, 11.07; N, 5.18.

1,4-bis(cyanomethyl)-2,5-bis(dodecyloxy)benzene (Route B) (1). In a Schlenk flask under Argon, 3.66 g (32.7 mmol, 4.1 equiv) of potassium *t*-butoxide was dissolved in 15 mL of dry DME. The solution was then cooled to -45°C. At this time, a solution of

3.26 g (16.7 mmol, 2.1 equiv) tosylmethyl isocyanide (TosMIC) in 15 mL DME was added dropwise. The resulting brown-orange solution was then cooled to -62°C . Then a solution of 2,5-bis(dodecyloxy)terephthalaldehyde (**2**) (4.00 g, 8.0 mmol, 1 equiv) in 100 mL of DME and 500 mL dichloromethane was added dropwise. The resulting orange solution was heated to 40°C and then 50 mL of dry methanol was added dropwise. The solution was then heated at 40°C for 1 h and then cooled to room temperature and poured into water which had been acidified with a few drops of acetic acid. The mixture was extracted with dichloromethane, after which the organic layer was washed with saturated sodium bicarbonate, followed by water. The organic layer was then dried with MgSO_4 . The crude product was purified by column chromatography on silica (1:1 hexanes and dichloromethane) to give 1.03 g (25%) of product. ^1H NMR (300 MHz, CDCl_3) δ 6.91 (s, 2H), 3.97 (t, 4H), 3.70 (s, 4H), 1.79 (m, 4H), 1.5-1.2 (br, 36H), 0.88 (t, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 150.27, 119.35, 118.05, 112.89, 69.27, 32.13, 29.88, 29.85, 29.82, 29.78, 29.59, 29.48, 26.82, 25.05, 22.90, 18.86, 14.33.

2,5-bis(dodecyloxy)terephthalaldehyde (2). In 600 mL of dry ether, 88.9 g (147 mmol, 1 equiv) of 1,4-dibromo-2,5-bis(dodecyloxy)benzene⁵ was dissolved and cooled to 0°C . Then 142 mL (369 mmol, 2.5 equiv) of 2.6 M *n*-butyllithium was added dropwise. After addition was complete, 90 mL of DMF (1160 mmol, 7.9 equiv) was added rapidly and the solution was stirred and warmed to room temperature overnight. The solution was then poured into water, which had been acidified with a few drops of HCl. The mixture was then extracted with dichloromethane and the organic layer was dried with MgSO_4 . Column chromatography on silica (1:1 hexanes and toluene) followed by recrystallization from hexanes gave the product as long yellow needles (21.16 g, 29%). mp $81-83^{\circ}\text{C}$. ^1H

NMR (300 MHz, CDCl₃) δ 10.52 (s, 2H), 7.43 (s, 2H), 4.08 (t, 4H), 1.83 (m, 4H), 1.5-1.2 (br, 36H), 0.88 (t, 6H). ¹³C NMR (300 MHz, CDCl₃) δ 189.68, 155.48, 129.54, 111.87, 9.50, 32.13, 29.86, 29.84, 29.79, 29.77, 29.56, 29.54, 29.28, 26.24, 22.91, 14.33. IR (KBr cm⁻¹) 2870, 2850, 1680, 1490, 1471, 1429, 1390, 1284, 1215, 1126, 996, 884, 717, 696. HRMS calcd for C₃₂H₅₄O₄ (M⁺), 502.4022; found 502.4028. Anal. calcd for C₃₂H₅₄O₄: C, 76.45; H, 10.83; O, 12.73. Found: C, 76.58; H, 11.19.

3-dodecylthiophene-2,5-dicarbaldehyde (3). At -78°C, 38 mL of 2.3 M *n*butyllithium (87 mmol, 2.2 equiv) was added dropwise to a solution of 9.838 g (39.0 mmol, 1 equiv) of 3-dodecylthiophene (Aldrich) in 200 mL dry THF. The solution was then stirred at this temperature for 45 minutes, after which 24 mL (310 mmol) of dry DMF was added rapidly via syringe. The resulting solution was warmed to room temperature and stirred for 1 h. The reaction was then poured into 2M HCl (300 mL) and extracted with dichloromethane. The organic layer was then washed with saturated NaHCO₃ and dried with MgSO₄. Upon removal of solvent by rotary evaporation, 10.8 g of crude product were obtained. The crude product consisted of a 9:1 mixture of 4-dodecylthiophene-2-carbaldehyde and 3-dodecylthiophene-2-carbaldehyde. The crude mixture (10.8 g, 39 mmol) was dissolved in 200 mL benzene with 0.145 g *p*toluenesulfonic acid (0.8 mmol) and 4 mL of ethylene glycol (70 mmol) and refluxed for 24 h with a Dean-Stark trap to remove water. The solution was cooled, poured into 20 mL of 10% (w/w) NaHCO₃/water and washed three times with 10 mL of the same solution. The organic layer was then dried with MgSO₄ and the solvent was removed by rotary evaporation and the product (brown solid) was dried under vacuum. The dried product was then dissolved in 250 mL of dry THF and cooled to -40°C, at which point

18 mL of 2.4 M *n*-butyllithium (43 mmol) was added dropwise and the solution was stirred for 30 minutes at the same temperature. Then 20 mL of dry DMF (260 mmol) was added rapidly via cannula and the reaction was warmed to room temperature and stirred for 1 h before pouring into 300 mL 2 M HCl. The mixture was then extracted with ether and the organic layer was washed with saturated NaHCO₃, followed by water before drying with MgSO₄. The crude product was then stirred with 100 mL of 3M H₂SO₄ at room temperature and then worked up again as described above. Column chromatography with 9:1 hexanes and ethyl acetate to give 3.27 g (27% from 3-dodecylthiophene) of the product as a white solid. mp 28-29°C. ¹H NMR (300 MHz, CDCl₃) δ 10.14 (s, 1H), 9.97 (s, 1H), 7.65 (s, 1H), 2.44 (t, 2H), 1.70 (m, 2H), 1.4-1.2 (br, 18H), 0.88 (t, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 183.57, 183.20, 152.21, 148.09, 143.52, 137.34, 32.12, 31.43, 29.84, 29.82, 29.80, 29.69, 29.55, 29.54, 29.43, 28.73, 22.90, 14.33. IR (KBr cm⁻¹) 2923, 2850, 1671, 1529, 1463, 1219, 1163, 863, 780, 685, 582, 481. HRMS calcd for C₁₈H₂₈O₂S (M⁺), 308.1810; found 308.1810. Anal. calcd for C₁₈H₂₈O₂S: C, 70.08; H, 9.15; O, 10.37; S, 10.39. Found: C, 70.54; H, 9.43.

3,3-dihexyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-dicarbaldehyde (ProDOT-Hx₂-(CHO)₂) (4). To 120 mL of dry THF containing 9.69g (29.9 mmol) of ProDOT-Hx₂⁷ at -78°C, was added 33 mL of 2.1 M *n*-butyllithium (69 mmol, 2.3 equiv). The solution was warmed to 0°C for 30 minutes and then cooled back to -78°C. Then 8.5 mL of dry DMF (110 mmol, 3.7 equiv) was added rapidly via syringe and the solution was then warmed to room temperature and stirred for 1 h. After this, the solution was poured into 3 M HCl and extracted with dichloromethane. The organic layer was washed with saturated NaHCO₃ and then dried with MgSO₄. After removing the solvent by rotary

evaporation, the crude product was purified by column chromatography with 2:1 dichloromethane and hexanes to yield 8.92 g (79%) of product as a white solid. mp 75-77°C. ¹H NMR (300 MHz, CDCl₃) δ 10.04 (s, 2H), 4.11 (s, 4H), 1.4-1.2 (m, 20H), 0.90 (t, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 182.25, 155.19, 127.96, 78.57, 44.03, 32.41, 31.89, 30.21, 23.03, 22.83, 14.27. IR (KBr cm⁻¹) 2954, 2930, 2860, 1670, 1652, 1492, 1463, 1385, 1248, 1198, 1109, 1091, 1072, 727, 690. HRMS calcd for C₂₁H₃₂O₄S (M⁺), 380.2021; found 380.2020. Anal. calcd for C₂₁H₃₂O₄S: C, 66.28; H, 8.48; O, 16.82; S, 8.43. Found: C, 66.32; H, 8.59; S, 8.38.

2-(3,3-dihexyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)acetonitrile (ProDOT-Hx2-ACN) (5). In 150 mL of dry THF, ProDOT-Hx₂ (13.71 g, 42.3 mmol, 1 equiv) was dissolved and cooled to -78°C. Then 18 mL of 2.5 M *n*-butyllithium (45 mmol, 1.1 equiv) was added and the reaction was stirred at -78°C for 1 h. Then the solution was transferred via cannula to an addition funnel and subsequently added to a solution consisting of 50 mL of THF and 45 mL 1.0 M ZnCl₂ (45 mmol) at 0°C. The resulting solution was stirred at 0°C for 2 h. This solution was then transferred via cannula to a solution consisting of 5.18 g bromoacetonitrile (43.2 mmol), 1.14 g cyclohexyldiphenylphosphine (4.3 mmol), and 1.17 g Ni(acac)₂ (4.6 mmol) in THF. The resulting brown solution was heated to 70°C overnight. After cooling to room temperature, the reaction was then poured into 500 mL of 1 M HCl. After extraction, the organic layer was washed with 0.2 M HCl and then dried over MgSO₄. Column chromatography on silica gel eluting with hexanes and ethyl acetate (10:1) gave the product (4.35 g, 28%) as a viscous yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 6.38 (s, 1H), 3.88 (s, 2H), 3.83 (s, 2H), 3.70 (s, 2H), 1.4-1.2 (br, 20H), 0.89 (t, 6H). ¹³C NMR (75

MHz, CDCl₃) δ 149.56, 147.87, 117.09, 108.97, 103.28, 77.99, 77.90, 44.19, 31.97, 31.91, 30.31, 22.93, 22.83, 15.44, 14.27. HRMS calcd for C₂₁H₃₃O₂NS (M⁺), 363.2232; found 363.2248.

3,3-dihexyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6-carbaldehyde (ProDOT-Hx₂-CHO) (6). In 40 mL of dry THF, ProDOT-Hx₂ (3.394 g, 10.5 mmol) was dissolved and cooled to -78°C . Then 4.6 mL of 2.5 M *n*-butyllithium (11.5 mmol, 1.1 equiv) was added dropwise. The solution was then warmed to 0°C and was stirred at this temperature for 20 minutes. The solution was again cooled to -78°C and 5 mL (65 mmol, 6.2 equiv) of dry DMF was added rapidly via syringe. The solution was then warmed to room temperature and stirred for 1 h, after which it was poured into ice-water acidified with HCl. The solution was then extracted with THF and the organic layer was dried with MgSO₄. After rotary evaporation, the crude oil was purified by column chromatography on silica gel eluting with 10:1 hexanes and ethyl acetate (followed by filtering through activated carbon to remove persistent colored impurities) to give 2.15 g (58%) of the product as a faint-yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 9.91 (s, 1H), 6.85 (s, 1H), 4.06 (s, 2H), 3.90 (s, 2H), 1.4-1.2 (m, 20 H), 0.89 (t, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 181.13, 156.30, 148.39, 122.01, 115.09, 77.91, 77.73, 43.74, 32.15, 31.68, 30.04, 22.80, 22.62, 14.05. HRMS calcd for C₂₀H₃₂O₃S (M⁺), 352.2072; found 352.2055. Anal. calcd for C₂₀H₃₂O₃S: C, 68.14; H, 9.15; O, 13.62; S, 9.10. Found: C, 68.06; H, 9.10; S, 9.02.

2,3-bis(3,3-dihexyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)acrylonitrile (BProDOT-Hx₂:CNV) (7). In 100 mL of absolute ethanol, ProDOT-Hx₂-ACN (5) (3.45 g, 9.50 mmol) and ProDOT-Hx₂-CHO (6) (3.37 g, 9.57 mmol) were dissolved and 1.41 g (12.6 mmol) of potassium *t*-butoxide was added. The solution

immediately darkened on addition of the base and was then heated to reflux for 3 h. The reaction mixture was then cooled to room temperature and poured into water to give a red precipitate, which was isolated by filtration. The precipitate was redissolved in dichloromethane, washed with water and dried with MgSO₄. Chromatography on silica gel with hexanes and dichloromethane (1:1) gave the product (5.75 g, 87 %) as an orange solid. mp 68-74°C. ¹H NMR (300 MHz, CDCl₃) δ 7.65 (s, 1H), 7.64 (s, 0.2 H), 6.63 (s, 1H), 6.59 (s, 0.2 H), 6.53 (s, 0.2 H), 6.41 (s, 1H), 3.96 (s, 4H), 3.87 (s, 4H), 1.4-1.2 (br, 0H), 0.88 (t, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 151.52, 150.41, 149.37, 147.31, 30.94, 117.81, 117.45, 117.23, 109.01, 103.73, 98.05, 78.28, 78.09, 78.01, 44.06, 43.95, 2.31, 32.13, 31.95, 31.93, 30.36, 30.32, 23.02, 22.85, 14.28. HRMS calcd for ₄₁H₆₃NO₄S₂ (M⁺), 697.4198; found 697.4196. Anal. calcd for C₄₁H₆₃NO₄S₂: C, 70.54; H, 9.10; N, 2.01; O, 9.17; S, 9.19. Found: C, 70.57; H, 9.43; N, 1.85; S, 9.16.

2,3-bis(8-bromo-3,3-dihexyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)acrylonitrile (BProDOT-Hx₂:CNV-Br₂) (8). In 125 mL DMF BProDOT-Hx₂-CNV (7) (2.294 g, 3.29 mmol) was dissolved and the solution was cooled to 0°C. Then 1.23 g of freshly recrystallized NBS was added in one portion and the solution was then allowed to warm gradually to room temperature. After two hours the solution had changed from bright red to a dark black. At this point the reaction mixture was poured into 300 mL of brine and extracted with ether. The ether layer was washed with brine and then dried with MgSO₄. Chromatography on silica eluting with 18:1 petroleum ether and ether gave the product as a dark red, highly viscous oil (2.11 g, 75 %). ¹H NMR (300 MHz, CDCl₃) δ 7.47 (s, 1H), 3.96-3.94 (m, 8H), 1.4-1.2 (br, 40H), 0.88 (t, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 150.34, 148.21, 147.20, 146.50, 146.22, 132.92, 129.60, 129.09, 117.04,

116.84, 116.43, 99.75, 92.86, 85.61, 78.46, 78.39, 78.36, 78.23, 43.95, 43.81, 31.70, 30.09, 30.04, 22.75, 22.64, 14.07. HRMS calcd for $C_{41}H_{61}Br_2NO_4S_2$ (M^+), 853.2406; found 853.2440. Anal. calcd for $C_{41}H_{61}Br_2NO_4S_2$: C, 57.54; H, 7.18; Br, 18.67; N, 1.64; O, 7.48; S, 7.49. Found: C, 57.69; H, 7.22; N, 1.55.

Bis-ProDOT-Hx₂-CNV-1,4-(2,5-didodecyloxybenzene) (BProDOT-Hx₂:CN-PPV) (9). In 60 mL of THF and 60 mL of *t*-butanol, ProDOT-Hx₂-CHO (**6**) (0.964 g, 2.73 mmol) and 0.709 g (1.35 mmol) of 2,5-didodecyloxy-1,4-phenylene-diacetonitrile (**1**) were dissolved and the solution was heated until all solids were dissolved (~50°C). Then 0.65 g (5.8 mmol) of *t*-butoxide was added and the reaction was heated to 70°C for 3 h. The reaction was then cooled and poured into water and extracted with ether. The organic layer was then dried with MgSO₄. After chromatography on silica gel (1:1 heaxanes and dichloromethane) the product was dissolved in dichloromethane and precipitated by dripping into cold methanol. Filtration gave the product as a yellow-brown solid (0.138 g, 9%). mp 106-107°C. ¹H NMR (300 MHz, CDCl₃) δ 8.25 (s, 2H), 7.09 (s, 2H), 6.69 (s, 2H), 4.04 (t, 4H), 3.96 (s, 4H), 3.89 (s, 4H), 1.85 (m, 4H), 1.4-1.2 (br, 76H), 0.89 (m, 18H). ¹³C NMR (75 MHz, CDCl₃)δ 152.03, 149.39, 135.81, 134.76, 124.18, 116.11, 114.39, 109.59, 99.81, 86.05, 78.52, 76.65, 69.87, 43.95, 32.34, 32.15, 31.96, 30.35, 29.90, 29.71, 29.59, 27.51, 26.27, 23.06, 22.87, 14.28. . HRMS calcd for $C_{74}H_{116}N_2O_6S_2$ (M^+), 1192.8275; found 1192.8247. Anal.calcd for $C_{74}H_{116}N_2O_6S_2$: C, 74.45; H, 9.79; N, 2.35; O, 8.04; S, 5.37. Found: C, 72.95; H, 10.41; N, 2.27.

1,4-phenylene-diacetonitrile (10). In a flask under argon was placed 3.06 g (15.7 mmol) of TosMIC. In a separate flask, 3.45 g (30.8 mmol) of *t*BuOK was added and both flasks were charged with 15 mL of dry DME. In a third flask, 1.008 g of

terephthalaldehyde (7.5 mmol) was dissolved in 25 mL of DME. The *t*BuOK solution was then cooled to -45°C and the TosMIC solution was slowly dripped into the flask. After addition was complete, the combined solution was cooled to -62°C and then the solution of terephthalaldehyde was added dropwise. The reaction was then stirred for a full hour at -62°C before 40 mL of anhydrous methanol were added and the reaction was subsequently heated to reflux for 15 minutes. The reaction was then cooled to room temperature and the solvent was removed. Water acidified with a few drops of acetic acid was then added and the mixture was extracted with dichloromethane. The organic layer was dried with MgSO_4 and after removal of the solvent, the crude product was purified by chromatography on silica (dichloromethane) to give 0.380 g (33%) of the product as a white solid. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.37 (s, 4H), 3.77 (s, 4H) (matched authentic sample, Aldrich). HRMS calcd for $\text{C}_{10}\text{H}_8\text{N}_2$ (M^+), 156.0687; found 156.0685.

2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5-carbaldehyde (EDOT-CHO) (11).⁸ In 100 mL of dry THF, 6.65 g (46.8 mmol, 1.0 equiv) of EDOT was dissolved and the solution was cooled to -78°C . Then 21 mL of 2.5 M *n*-butyllithium (53 mmol, 1.1 equiv) was added dropwise. The solution was then warmed to 0°C and was stirred at this temperature for 20 minutes. The solution was again cooled to -78°C and 6.8 mL (88 mmol, 1.9 equiv) of anhydrous DMF was added rapidly via syringe. The solution was then warmed to room temperature and stirred for one hour, after which it was poured into ice-water acidified with HCl. The resulting precipitate was isolated by filtration and washed with water. After recrystallization from methanol, the product was obtained (4.82 g, 61%) as yellow plates. mp $127\text{-}129^{\circ}\text{C}$ (Lit. 142°C). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 9.91 (s, 1H), 6.80 (s, 1H), 4.37 (m, 2H), 4.28 (m, 2H).

BEDOT:CN-PPV (12). In a solution consisting of 30 mL of 3:1 *t*-butanol and THF, 0.534 g (3.1 mmol) of EDOT-CHO (**11**) and 0.255 g (1.6 mmol) of 1,4-phenylenediacetonitrile (**10**) were dissolved by heating to 50°C. Then 0.035 g (0.31 mmol, 0.1 equiv) of potassium *t*-butoxide and 0.3 mL of 0.1 M tetrabutylammonium hydroxide (0.3 mmol, 0.1 equiv) was added, resulting in the immediate darkening of the solution. The solution was then heated to 50°C for 2 h. At this time the reaction was cooled to room temperature and poured into water yielding a sticky black precipitate. The precipitate was redissolved in chloroform and washed with water. Upon removal of the solvent, 0.468 g (65%) of a dark red solid was isolated. mp dec. > 220 °C. ¹H NMR (300 MHz, DMSO-d₆) δ 7.88 (s, 2H), 7.72 (s, 4H), 7.10 (s, 2H), 4.40 (m, 4H), 4.29 (m, 4H). HRMS calcd for C₂₄H₁₆N₂O₄S₂ (M⁺), 460.0551; found 460.0550. Anal. calcd for C₂₄H₁₆N₂O₄S₂: C, 62.59; H, 3.50; N, 6.08; O, 13.90; S, 13.93. Found: C, 62.03; H, 3.59; N, 5.99.

CN-PPV. In a solution consisting of 17 mL THF and 17 mL *t*-butanol, 0.200 g (0.40 mmol) 2,5-bis(dodecyloxy)terephthalaldehyde (**2**) and 0.208 g (0.40 mmol) 1,4-bis(cyanomethyl)-2,5-bis(dodecyloxy)benzene (**1**) were dissolved at room temperature. Then 0.090 g (0.80 mmol) potassium *t*-butoxide was added and the solution was heated to 70°C for 2 h. The reaction mixture was then cooled to room temperature and poured into 600 mL of ice-cold methanol acidified with 1 mL of acetic acid. The precipitate was then isolated by filtration and dried under vacuum. The solid was then reprecipitated from chloroform into methanol to give 0.351 g (92%) of the polymer as a dark red solid. ¹H NMR (300 MHz, CDCl₃) δ 8.14 (b, 2H), 7.95 (b, 2H), 7.12 (b, 2H), 4.11 (b, 8H), 1.86 (b, 8H), 1.5-1.2 (bm, 72 H), 0.87 (b, 12H). IR (neat cm⁻¹): 2955, 2924, 2853, 2211, 1725,

1604, 1505, 1466, 1422, 1377, 1261, 1217, 1095, 1022, 919, 866, 800, 710, 668. Anal. calcd: C, 79.78; H, 10.96; N, 2.82. Found: 79.29; H, 11.75; N, 2.55. GPC Analysis (THF vs. PS): $M_n = 13,700$ g/mol; $M_w = 29,900$ g/mol; PDI = 2.17.

Th-CN-PPV. In a solution consisting of 40 mL THF and 40 mL *t*-butanol, 0.291 g (0.945 mmol) 3-dodecylthiophene-2,5-dicarbaldehyde (**3**) and 0.495 g (0.945 mmol) 1,4-bis(cyanomethyl)-2,5-bis(dodecyloxy)benzene (**1**) were dissolved at room temperature. Then 0.28 g (2.5 mmol) potassium *t*-butoxide was added and the solution was heated to 70°C for 2 h. The reaction mixture was then cooled to room temperature and poured into 500 mL of ice-cold methanol acidified with 1 mL of acetic acid. The precipitate was then isolated by filtration and dried under vacuum. The solid was then Soxhlet extracted with methanol for 24 h followed by hexanes for 24 h. The polymer was then isolated by Soxhlet extraction with chloroform to give 0.342 g (43%) of a deep red-purple solid. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.29 (b, 2H), 7.89 (b, 1H), 7.13 (b, 2H), 4.07 (bm, 4H), 2.77 (b, 2H), 1.9-1.2 (bm, 60H), 0.87 (bm, 9H). IR (neat cm^{-1}): 2953, 2921, 2851, 2209, 1725, 1502, 1455, 1376, 1261, 1218, 1095, 1025, 870, 801. Anal. calcd: C, 78.14; H, 10.34; N, 3.50; S, 4.01. Found: C, 77.43; H, 9.07; N, 3.13; S, 4.31. GPC Analysis (THF vs. PS): $M_n = 25,500$ g/mol; $M_w = 102,500$ g/mol; PDI = 4.02.

PBProDOT-H_x:CNV. In 100 mL of anhydrous DMF, 2.07 g of BProDOTH_x-CNV-Br₂ (**8**) was dissolved and the solution was bubbled with argon for 30 minutes and heated to 60°C. Then a solution of 0.803 g (2.9 mmol) of Ni(COD)₂ and 0.463 g (3.0 mmol) of 2,2'-bipyridine and 0.30 mL (2.4 mmol) of freshly degassed cyclooctadiene in 25 mL of DMF was stirred at 60°C for 30 minutes and added to the monomer solution dropwise via cannula. The reaction mixture was then stirred at 60°C for 24 h, cooled to

room temperature and poured into 1 L of ice-cold methanol. The resulting precipitate was isolated by filtration into a Soxhlet thimble and then extracted with methanol for 24 h followed by hexane for 24 h. The polymer was then taken up in dichloromethane and reprecipitated into methanol and washed successively with 200 mL of hot 0.01 M EDTA solution (pH = 3-4), 200 mL of hot 0.01 M EDTA solution (pH = 8-9), and 200 mL of water. The polymer was then dried under vacuum to give 0.487 g (29%) of a dark blue solid. ^1H NMR (300 MHz, CDCl_3) δ 7.77-7.71 (m, 1H), 3.99 (m, 8H), 1.5-1.2 (m, 40H), 0.89 (bs, 12H). IR (neat cm^{-1}): 2961, 2926, 2868, 2206, 1725, 1547, 1454, 1375, 1261, 1094, 1020, 866, 800, 709, 662. Anal. calcd (assuming that all bromines have reacted): C, 70.54; H, 9.10; N, 2.01; S, 9.19. Found: C, 42.41; H, 7.75; N, 0.40; S, 2.81; Br, 0.37; Ni, 0.02. GPC Analysis: $M_n = 14,300$ g/mol; $M_w = 40,000$ g/mol; PDI = 2.80.

PProDOT-Hx₂:CN-PPV.⁹ In a solution consisting of 37 mL THF and 37 mL *t*-butanol, 0.339 g (0.89 mmol) ProDOT-Hx₂-(CHO)₂ (**4**) and 0.467 g (0.89 mmol) 1,4-bis(cyanomethyl)-2,5-bis(dodecyloxy)benzene (**1**) were dissolved at room temperature. Then 0.20 g (1.8 mmol) potassium *t*-butoxide was added and the solution was heated to 70°C for 2 h. The reaction mixture was then cooled to room temperature and poured into 600 mL of ice-cold methanol acidified with 1 mL of acetic acid. The precipitate was then isolated by filtration and dried under vacuum. The solid was then reprecipitated from chloroform into methanol to give 0.472 g (67%) of the polymer as a black solid. ^1H NMR (300 MHz, CDCl_3) δ 8.75 (b, 2H), 6.92 (b, 2H), 4.22 (b, 2H), 3.96 (bm, 4H), 1.99 (b, 4H), 1.5-1.2 (bm, 56H), 0.88 (bm, 12H). IR (neat cm^{-1}): 2925, 2854, 2205, 1572, 1512, 1479, 1450, 1384, 1338, 1285, 1218, 1058, 917, 858, 814. Anal. calcd: C, 75.81, H, 9.95,

N, 3.21, S, 3.68. Found: C, 75.49, H, 10.51, N, 2.96, S, 3.17. GPC Analysis (THF vs. PS): $M_n = 17,400$ g/mol; $M_w = 26,300$ g/mol; PDI = 1.51.

Spectral Data.

MALDI.

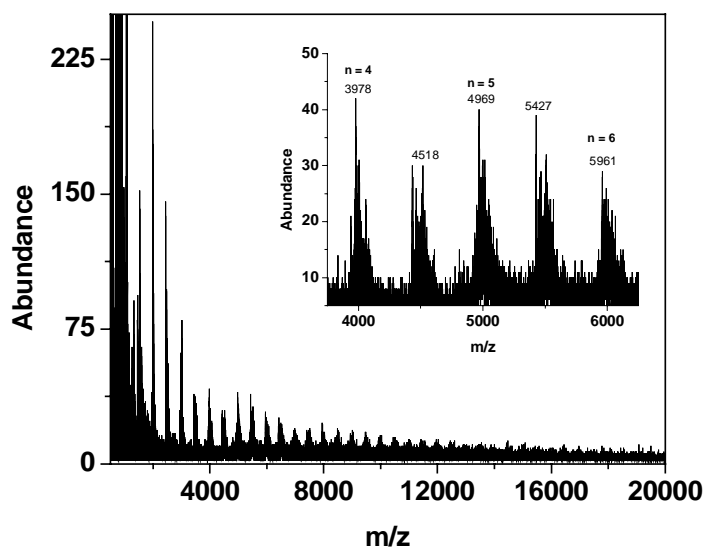


Figure S-1. MALDI-MS of CN-PPV. HABA was used as the matrix.

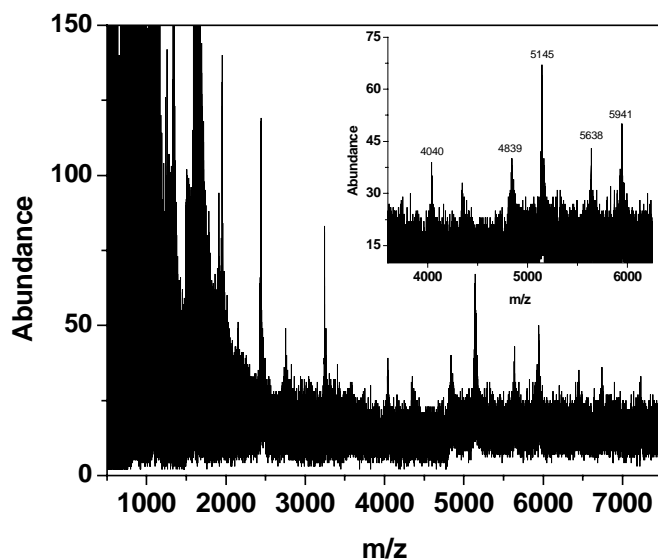


Figure S-2. MALDI-MS of Th-CN-PPV. HABA was used as the matrix.

GPC-Photodiode Array

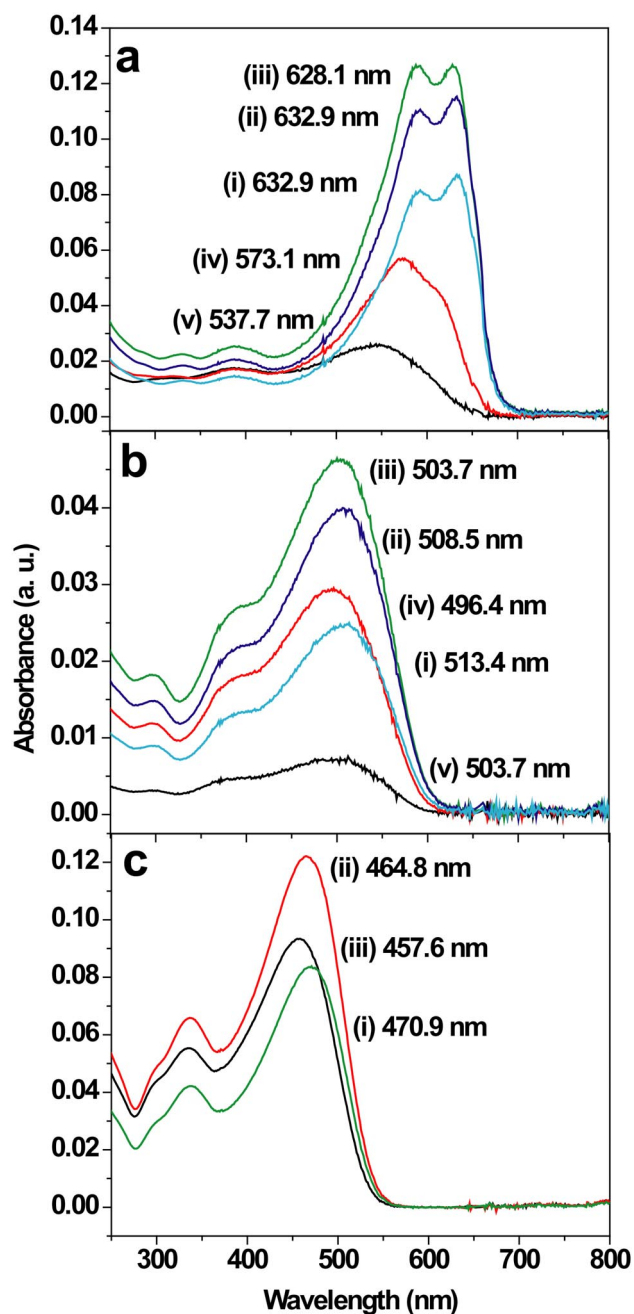


Figure S-3. Absorption spectra for molecular weight fractions of Knoevenagel polymers. Molecular weights are reported in g/mol vs. polystyrene. (a) **PProDOT-H_x₂:CN-PPV**: (i) 37,500, (ii) 25,000, (iii) 16,500, (iv) 6,000, (v) 3,800. (b) **Th-CN-PPV**: (i) 93,000, (ii) 39,500, (iii) 14,900, (iv) 6,400, (v) 2,300. (c) **CN-PPV**: (i) 41,300, (ii) 15,500, (iii) 6,200.

Solution Absorption Spectra.

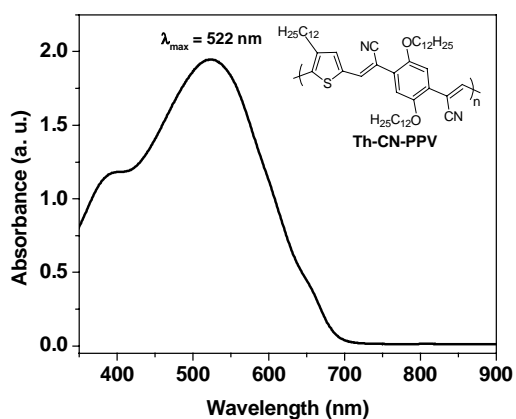


Figure S-4. Solution absorbance spectrum of **Th-CN-PPV** in toluene.

Fluorescence spectroscopy.

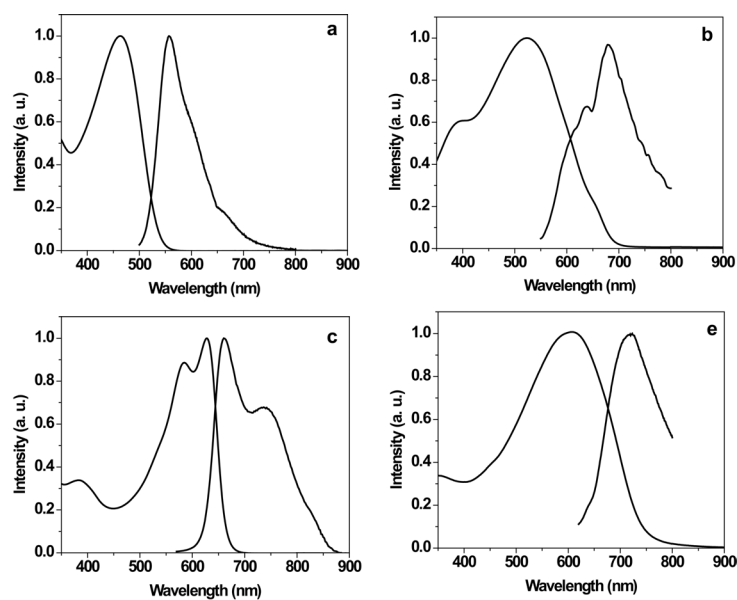


Figure S-5. Absorbance and photoluminescence spectra of CN-PPV analogues in toluene solution. (a) **CN-PPV**, (b) **Th-CN-PPV**, (c) **PProDOTHx₂:CN-PPV**, (d) **PBProDOT-Hx₂:CNV**.

Electrochemical Data.

Figure S-6 shows the CV and DPV for electrodeposited films of **PBEDOT:CN-PPV** and **PBProDOT-Hx₂:CN-PPV**. Both polymers were deposited by repeated oxidative cycling in solutions that were 0.005 M in monomer and 0.1 M in supporting electrolyte (TBAPF₆) in either dichloromethane (**BEDOT:CN-PPV**) or a 50/50 mixture of dichloromethane and acetonitrile (**BProDOT-Hx₂:CN-PPV**). The peak monomer oxidation potentials were found to be +0.83 V and +0.69 V respectively for **PBEDOT:CN-PPV** and **PBProDOT-Hx₂:CN-PPV** measured vs. Fc/Fc⁺.

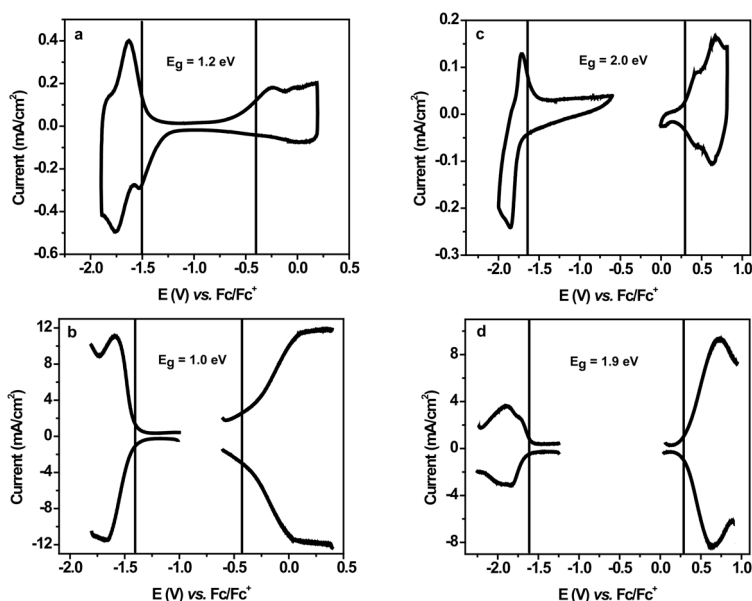


Figure S-6. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) for electropolymerized compounds. (a) CV of **PBEDOT:CN-PPV**, (b) DPV of **PBEDOT:CN-PPV**, (c) CV of **PBProDOT-Hx₂:CN-PPV**, (d) DPV of **PBProDOT-Hx₂:CN-PPV**. Measurements were performed on a 0.02 cm² Pt button working electrode in 0.1 M TBAPF₆ / acetonitrile with a Pt wire counter electrode and a silver wire pseudo reference electrode calibrated vs. Fc/Fc⁺.

Figure S-7 shows the CV and DPV for a solution cast film of **PBProDOT-Hx₂:CNV** and an electrodeposited film **PBProDOT-Hx₂:CNV**. The solution cast film was deposited by drop casting from a 1% (w / w) solution in dichloromethane, while the

electrodeposited film was formed by repeated oxidative cycling from a 0.005 M solution in monomer in 0.1 M TBAPF₆ / acetonitrile. The peak of monomer oxidation was found to be +0.72 V vs. Fc/Fc⁺.

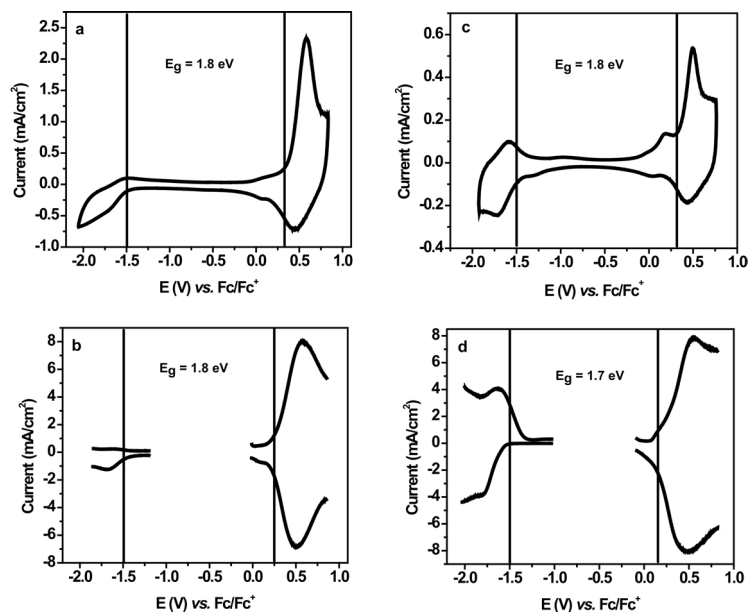


Figure S-7. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) for **PBProDOT-Hx₂:CNV**. (a) CV of solution cast film, (b) DPV of solution cast film, (c) CV of electrodeposited film, (d) DPV of electrodeposited film. Measurements were performed on a 0.02 cm² Pt button working electrode in 0.1 M TBAPF₆ / acetonitrile with a Pt wire counter electrode and a silver wire pseudo reference electrode calibrated vs. Fc/Fc⁺.

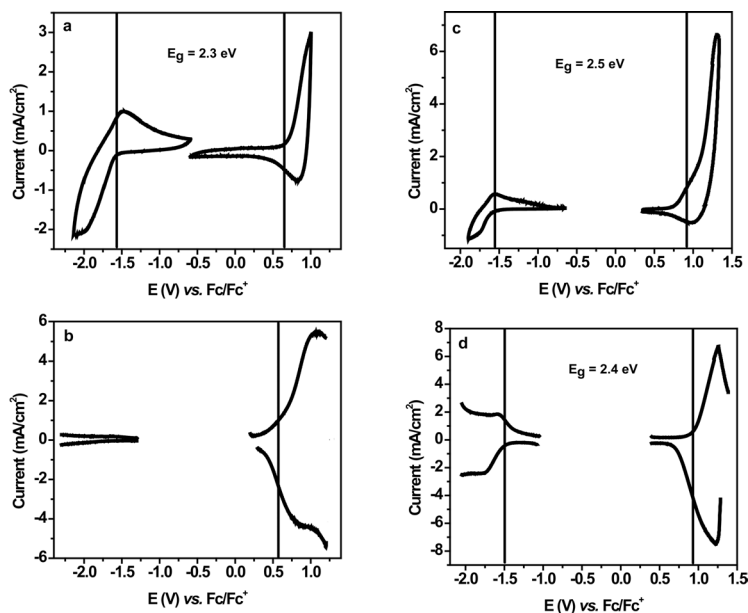


Figure S-8. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) for **PProDOT-Hx₂:CN-PPV** and **Th-CN-PPV**. Films were drop cast from dichloromethane solution (1 wt %). (a) CV of **PProDOT-Hx₂:CN-PPV**, (b) DPV of **PProDOT-Hx₂:CN-PPV**, (c) CV of **Th-CN-PPV**, (d) DPV of **Th-CN-PPV**. Measurements were performed on a 0.02 cm² Pt button working electrode in 0.1 M TBAPF₆ / acetonitrile with a Pt wire counter electrode and a silver wire pseudo reference electrode calibrated vs. Fc/Fc⁺.

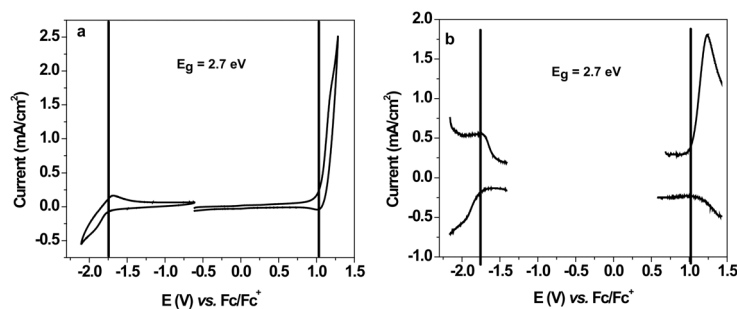


Figure S-9. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) for **CN-PPV**. Films were drop cast from dichloromethane solution (1 wt%). (a) CV of **CN-PPV**, (b) DPV of **CN-PPV**. Measurements were performed on a 0.02 cm² Pt button working electrode in 0.1 M TBAPF₆ / acetonitrile with a Pt wire counter electrode and a silver wire pseudo reference electrode calibrated vs. Fc/Fc⁺.

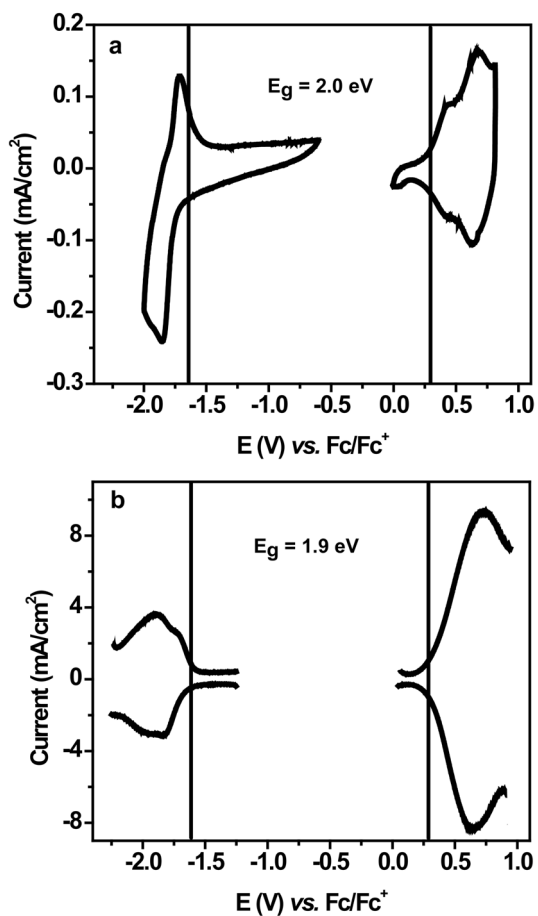


Figure S-10. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) for electropolymerized polymer films in 0.1M TBAPF₆/acetonitrile on a Pt button working electrode with a Ag wire reference electrode calibrated vs. Fc/Fc⁺. (a) CV of PBProDOT-Hx₂:CN-PPV, (b) DPV of PBProDOT-Hx₂:CN-PPV.

Photoluminescence Quenching.

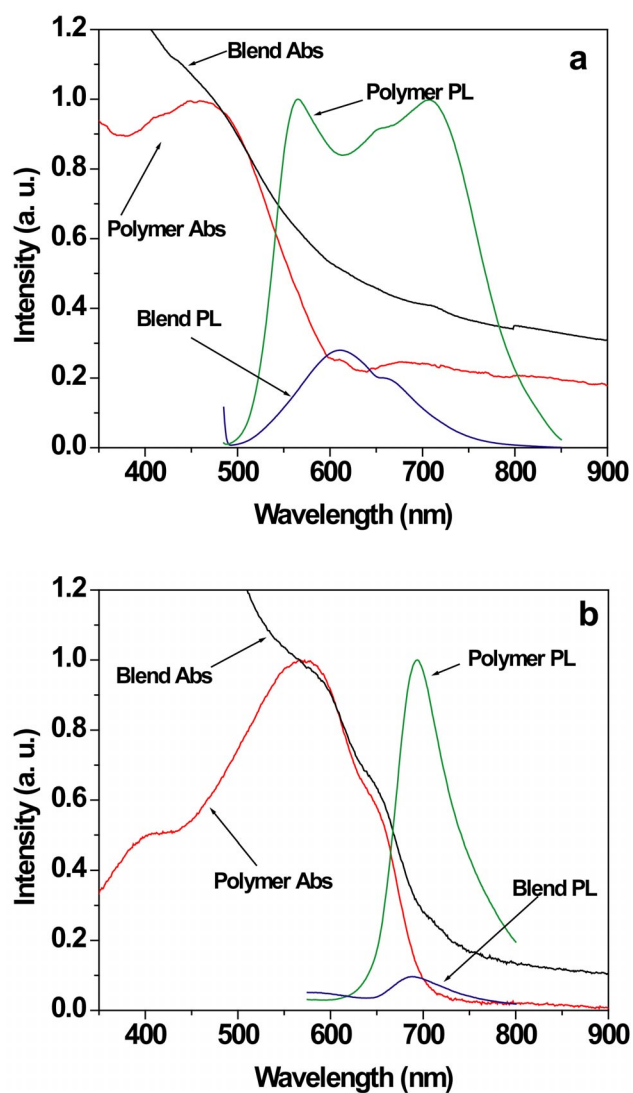


Figure S-11. Photoluminescence quenching of **CN-PPV** and **Th-CN-PPV** with PCBM. (a) **CN-PPV** with excitation wavelength of 465 nm for pristine polymer and blend. (b) **Th-CN-PPV** with excitation wavelength of 540 nm for pristine polymer and blend. Red lines show the normalized absorption of the pristine polymer film and black lines show the normalized absorption of the polymer/PCBM (1/4) blend film on PEDOT-PSS coated glass. Green lines show the normalized emission of the pristine polymers and blue lines show the photoluminescence of the blend films.

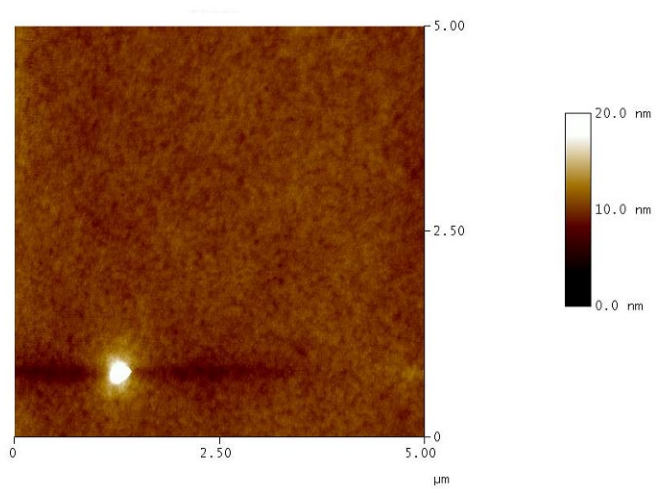
Atomic Force Microscopy.

Figure S-12. AFM height image of **PProDOT-Hx₂:CN-PPV / PCBM** blend (1/4).

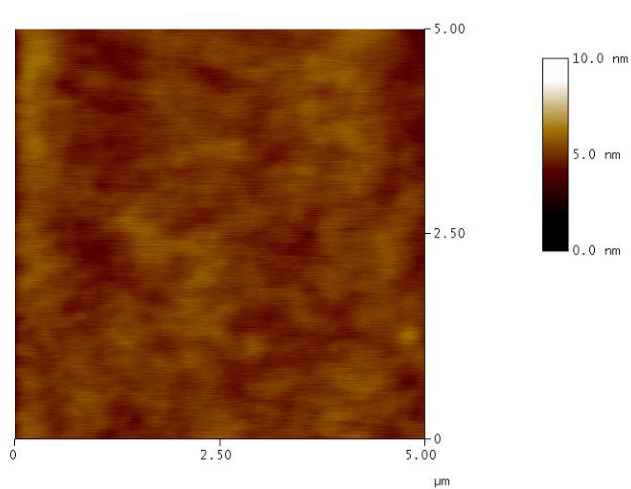


Figure S-13. AFM height image of a **PBProDOT-Hx₂:CNV / PCBM** blend (1/4).

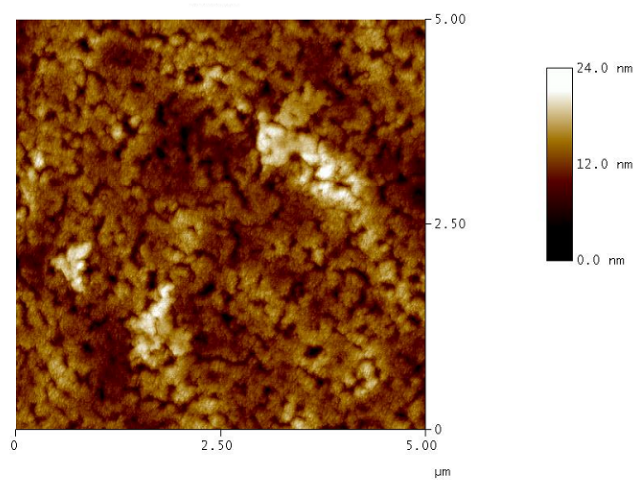


Figure S-14. AFM height image of **Th-CN-PPV** / PCBM blend (1/4).

Spectroelectrochemistry and Colorimetry.

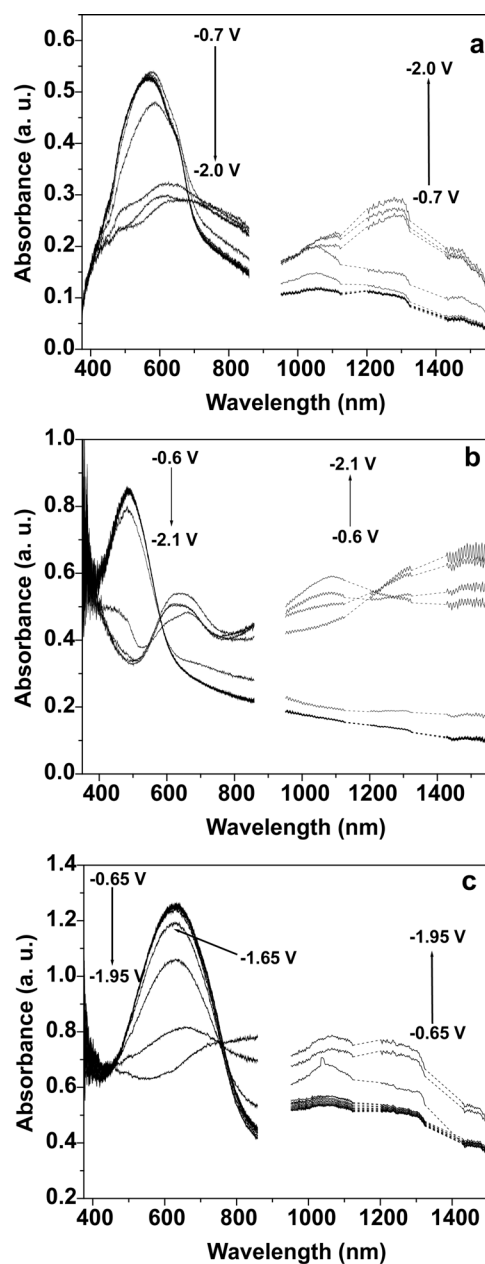


Figure S-15. Reductive spectroelectrochemistry of (a) **Th-CN-PPV**, (b) **CN-PPV**, and (c) **PBEDOT:CN-PPV**. No data is shown between 860 nm and 950 nm as the detectors do not cover this wavelength range. Potentials were increased in 100 mV steps and all potentials are reported vs. Fc/Fc^+ . The supporting electrolyte consisted of 0.1 M $\text{TBAPF}_6/\text{acetonitrile}$. Note that the data between 1125-1200 nm as well as 1325-1425 nm (dashed lines) has been removed due to overtones that appear to be attributed to acetonitrile, which appear when using a fiber optic spectrometer.

Table S-1. Colorimetric data for CN-PPV analogues.

Polymer	State	E (V) ^a	L*	a*	b*	Observed color
PProDOT-Hx₂:CN-PPV	N	-0.6	76	-8	-14	blue
PProDOT-Hx₂:CN-PPV	Ox	1.0	85	-2	-3	gray-blue
PProDOT-Hx₂:CN-PPV	Red	-1.9	----	----	----	gray-blue
PBProDOT-Hx₂:CNV	N	-0.6	81	0	-9	blue
PBProDOT-Hx₂:CNV	Ox	0.7	90	-1	1	colorless
PBProDOT-Hx₂:CNV	Red	-2.1	----	----	----	gray-blue
Th-CN-PPV	N	-0.6	61	12	-12	purple
Th-CN-PPV	Ox	1.3	80	5	9	gray
Th-CN-PPV	Red	-2.0	----	----	----	gray-blue
CN-PPV	N	-0.6	82	25	29	orange
CN-PPV	Ox	1.5	90	5	13	light yellow
CN-PPV	Red	-2.1	----	----	----	gray-blue
PBEDOT:CN-PPV	N	-1.0	54	-1	-27	blue
PBEDOT:CN-PPV	Ox	0.6	67	-2	-13	blue-gray
PBEDOT:CN-PPV	Red	-2.0	----	----	----	gray-blue

N = neutral, Ox = oxidized, and Red = reduced. ^aE(V) vs. Fc/Fc⁺

Photovoltaic Properties.

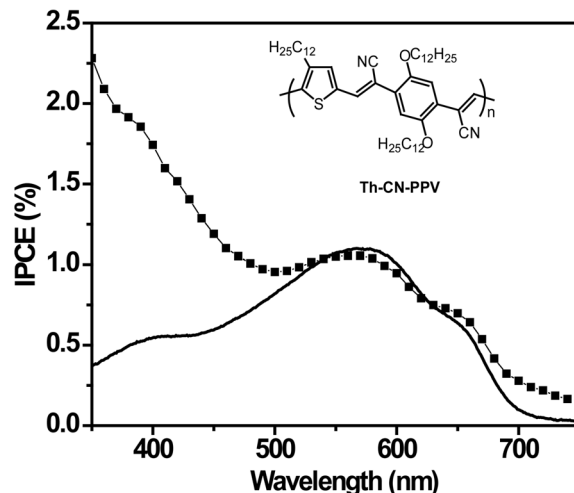


Figure S-16. Photocurrent action spectra for **Th-CN-PPV** / PCBM solar cells based on a 1:4 blend (w:w) of polymer relative to PCBM. Black squares represent the IPCE value at the given wavelength and the solid curve is the absorption spectra of a pristine polymer film shown as reference.

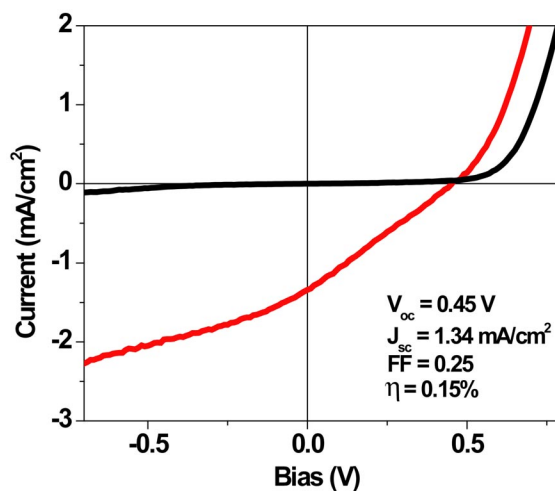


Figure S-17. Photovoltaic properties of **PProDOT-Hx₂:CN-PPV** / PCBM solar cells based on a 1:4 blend (w:w) of polymer and PCBM. (a) Current voltage characteristic of a representative device as evaluated under simulated AM1.5 conditions (100 mW/cm²). Black curve shows the dark current and the red curve shows the current upon illumination. (b) Photocurrent action spectra for the device. Black squares represent the IPCE value at the given wavelength. The solid curve is the absorption spectra of a pristine polymer film shown as reference.

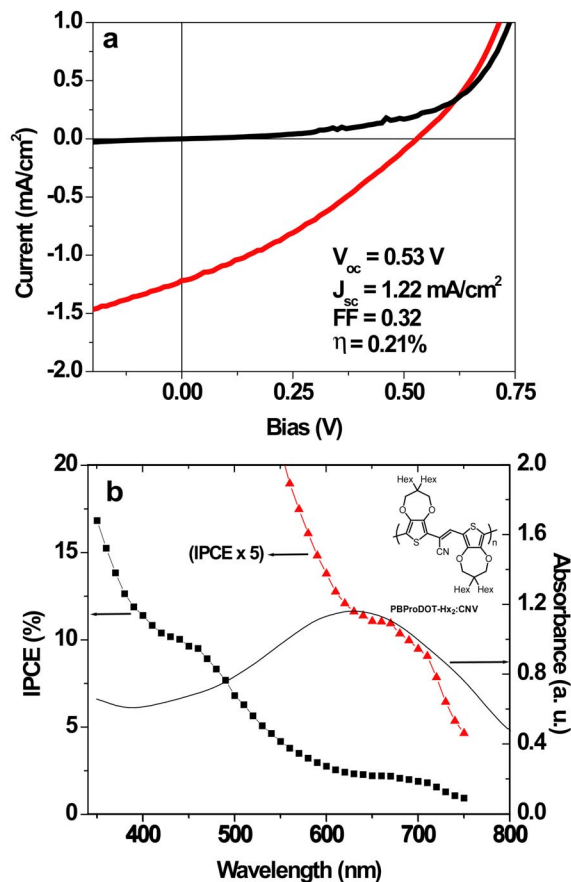


Figure S-18. Photovoltaic properties of **PBProDOT-Hx₂:CNV** / PCBM solar cells based on a 1:4 blend (w:w) of polymer and PCBM. (a) Current voltage characteristic of a representative device as evaluated under simulated AM1.5 conditions ($100 \text{ mW}/\text{cm}^2$). (b) Photocurrent action spectra for the device. Black squares represent the IPCE value at the give wavelength. The solid curve is the absorption spectra of a pristine polymer film shown as reference. Red triangles represent the IPCE of the device multiplied by a factor of 5 to show the relationship to the polymer absorption spectrum.

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