SUPPORTING INFORMATION

A One-Step Strategy for End-Functionalized Donor-Acceptor Conjugated Polymers

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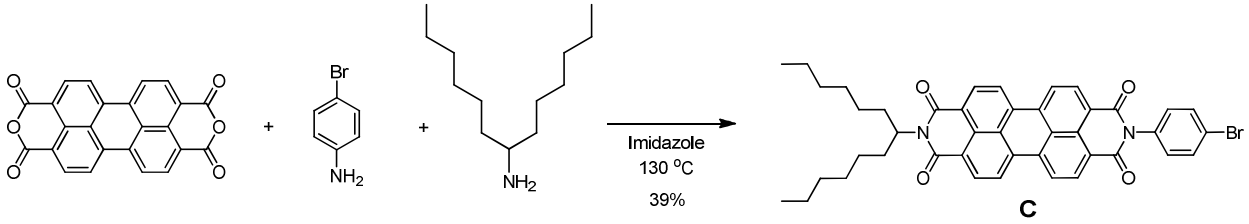
Contents

1. Materials. All reagents from commercial sources were used without further purification unless otherwise stated. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. 2,5-bis(trimethylstannyl)thiophene was prepared according to the literature procedure.[1] 2,5-bis(2-ethylhexyl)-3,6-bis(5-bromofuran-2-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP monomer) was synthesized following a modified procedure[2] with Cs_2CO_3 employed in the alkylation step resulting in a yield of 48%. 1-hexylheptylamine[3] was prepared according to the literature and purified by vacuum distillation prior to use. PDPP2FT homopolymer was prepared following the same procedure as the end-functional polymers with equimolar amounts of AA and BB monomers in the absence of end-capping unit.

2. Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded using a Varian 500 or 600 MHz spectrometer with the solvent signal as internal reference. Gel permeation chromatography (GPC) was performed on a Waters 2690 separation module equipped with Waters 2414 refractive index and 2996 photodiode array detectors using $CHCl_3$ containing 0.25% triethylamine as eluent at a flow rate of 1 mL/min. Molecular weights and molecular weight distributions were calculated relative to linear PS standards. Mass spectrometry was performed on a Micromass QTOF2 quadrupole/time-of-flight tandem mass spectrometer (ESI), a Waters GCT Premier time-of-flight mass spectrometer (EI and FD), or a Bruker Microflex LRF mass spectrometer equipped with a nitrogen laser operating at 337 nm and 60 Hz (MALDI). MALDI MS samples were prepared in chloroform with dithranol as the matrix and analyzed in positive ion reflectron mode with an accelerating voltage of 20 kV. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrometer. UV–Visible spectra were recorded on an Agilent 8453 spectrophotometer. Microwave assisted reactions were performed using a Biotage microwave reactor at a frequency of 2.5 GHz. Cyclic voltammetry was performed in an 80/20 (by volume) solution of *o*-dichlorobenzene/acetonitrile (*o*-DCB/ACN) containing 0.1 M tetrabutylammonium hexafluoroborate as the supporting electrolyte. A 3-electrode setup was used employing platinum working and counter electrodes and a Ag/Ag^{+} reference electrode (containing 0.1 M silver nitrate in 80/20 *o*-DCB/ACN). Potentials were recorded relative to the ferrocene/ferrocenium (Fc/Fc^{+}) redox couple which occurs at a value of +0.099 V under these conditions. LUMO energies were calculated from the onset of the first reduction peak assuming a formal potential of Fc/Fc^{+} of -5.1 eV relative to vacuum level. HOMO energy values were calculated from the optical bandgap measured at the onset of absorption ($E_{HOMO}=E_{LUMO}-E_g$).

3. Synthesis and Characterization of Compounds



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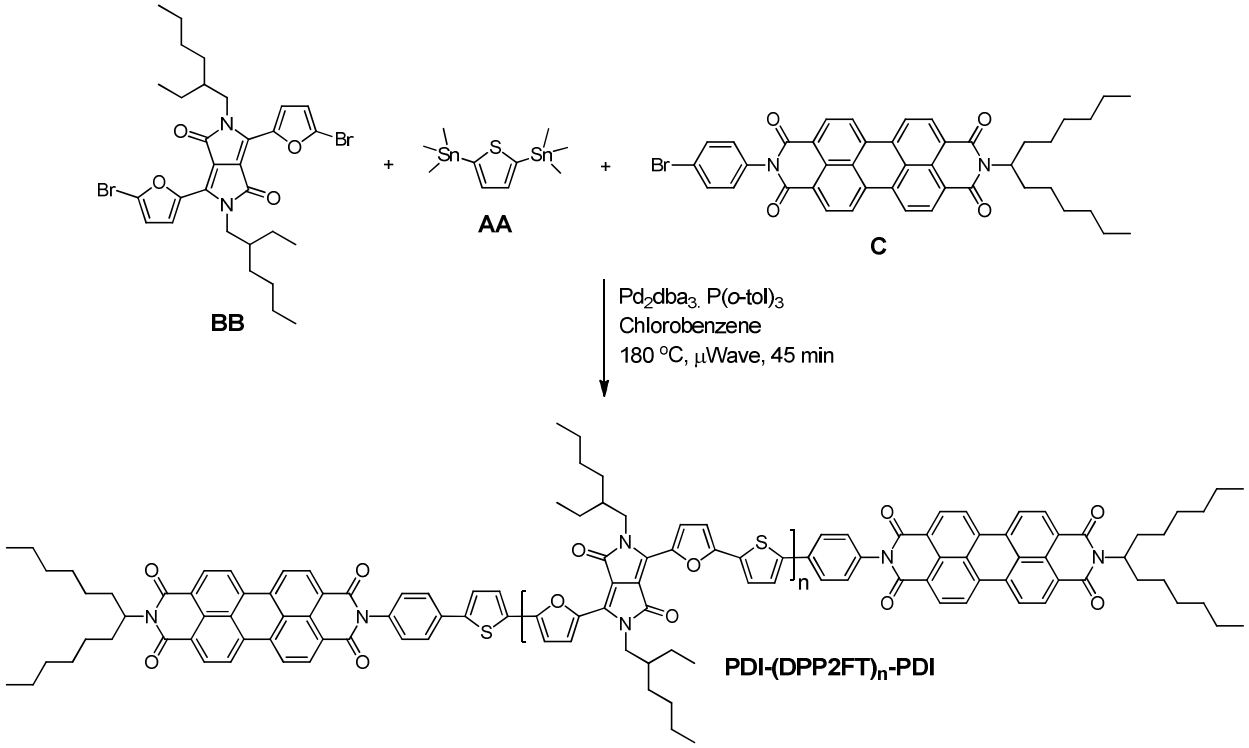
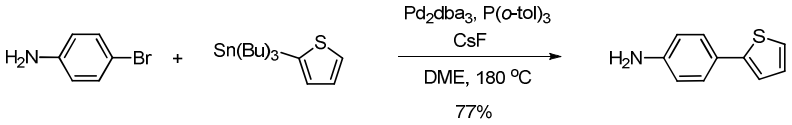
Synthesis of N-(4-bromophenyl)-N'-1-hexylheptyl-3,4,9,10-perylene diimide, PDI End-Capping Unit (C). Perylene-3,4,9,10-tetracarboxylic dianhydride (1.402 g, 3.573 mmol), 4-bromoaniline (0.7356 g, 4.276 mmol), and 1-hexylheptylamine (0.8669 g, 4.348 mmol) were combined with imidazole (19 g) in a 50 mL round bottom flask equipped with a stir bar and sealed with a septum. The flask was purged with argon for approximately 5 min and heated with stirring in an oil bath maintained at 130 °C. After 2 h, the flask was cooled and the contents were taken up in $CHCl_3$ (150 mL). The solution was washed with 2 M HCl (2x100 mL) and the organic layer was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 50 to 100% methylene chloride in hexanes to afford 1.0 g (39%) of the desired product as a red solid after drying under vacuum. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.83 (t, 6H, *J*=7.0 Hz, -C*H*$_3$), 1.17-1.38 (m, 16H, -NCH(CH_2(C*H*$_2$)$_4$$CH_3$)$_2$), 1.82-1.92 (m, 2H, -NCH(C*H*$_2$(CH_2)$_4$$CH_3$)$_2$), 2.20-2.30 (m, 2H, -NCH(C*H*$_2$(CH_2)$_4$$CH_3$)$_2$), 5.19 (tt, 1H, *J*=9.4, 5.8 Hz, -NC*H*-), 7.23-7.26 (m, 2H, -N*Ph*Br), 7.69-7.72 (m, 2H, -N*Ph*Br), and 8.63-8.76 (m, 8H, *Ar*) ppm. ^{13}C NMR (150

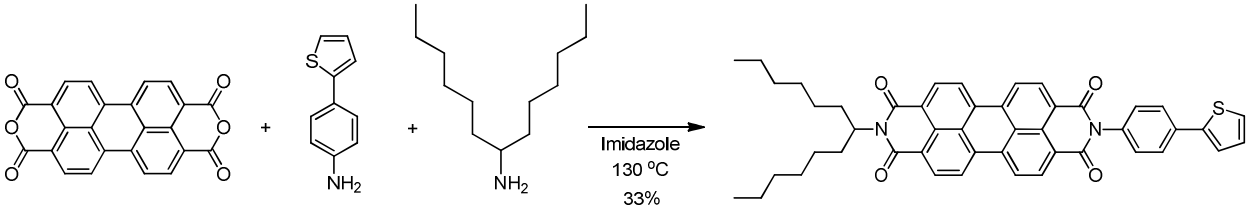
MHz, $CDCl_3$): δ 14.27, 22.81, 27.20, 29.43, 31.98, 32.57, 55.12, 123.14, 123.15, 123.17, 123.47, 126.39, 126.66, 129.58, 129.84, 130.62, 131.15, 131.92, 132.88, 134.16, 134.20, 135.27, and 163.44 ppm. MS (ESI): m/z $[M + Na]^+$ calcd for $[C_{43}H_{39}BrN_2O_4 + Na]^+$, 749.199; found, 749.198.



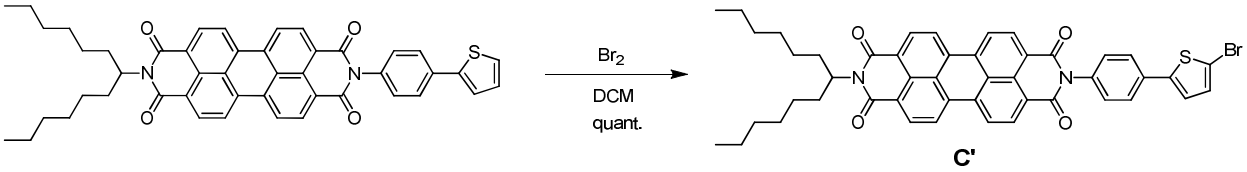
General Synthesis of End-Functional Conjugated Polymers. A detailed procedure of the synthesis of $[PDI\text{-}(DPP2FT)_{16}]_2$ (r=0.961) is provided. DPP monomer **BB** (150 mg, 0.231 mmol), 2,5-bis(trimethylstannyl)thiophene **AA** (98.4 mg, 0.240 mmol), end-capping unit **C** (14.0 mg, 0.0192 mmol), Pd_2dba_3 (2 mol %, 4.5 mg, 0.0049 mmol), and P(*o*-tol)$_3$ (8 mol %, 5.6 mg, 0.018 mmol) were accurately weighed into a 10 mL Biotage microwave vial equipped with a PTFE stir bar. The reaction vial was taken into an argon-filled glovebox and dry chlorobenzene (5.0 mL) was added, the vial was securely sealed and removed from the glovebox, and the contents were mixed using a magnetic stirrer. The vial was placed into a microwave reactor and heated with stirring for 45 min at 180 °C. After cooling, the solution was added dropwise to stirring methanol (200 mL), the precipitate was collected by filtration, and the solid was washed repeatedly with methanol, acetone, and hexanes. The polymer was quickly dried, dissolved in a small amount of chloroform, and eluted through a short pad of silica gel with chloroform. The eluate was partially concentrated and added to methanol (200 mL). The precipitated polymer was collected by filtration using a 0.45 μm nylon membrane, washed with methanol and acetone, and dried under vacuum to afford 89.3 mg (62%) of a dark blue solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.61-1.05 (br m), 1.07-1.62 (br m), 1.68-2.00 (br m,), 2.20-2.32 (br m), 3.00-4.70 (br m, DPP-NCH_2-), 5.00-5.26 (br m, PDI-NC*H*-), 6.31-7.53 (br m), and 8.10-8.92 (br m) ppm; DPP2FT:PDI=16; M_n=19.6 kg/mol. GPC ($CHCl_3$): M_n=45.1 kg/mol; M_w/M_n=2.19.



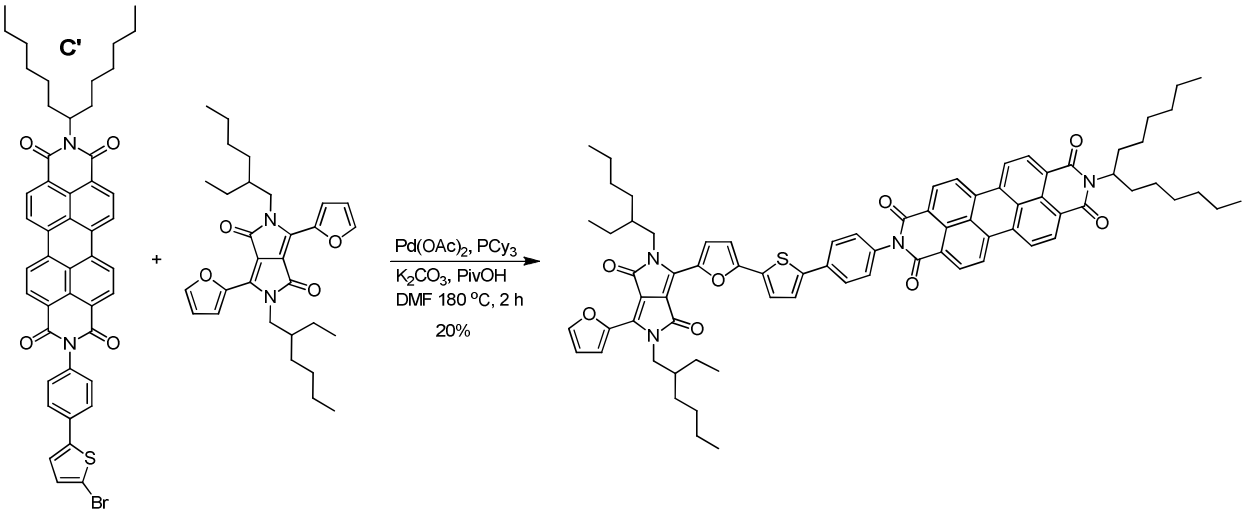
Synthesis of 4-(thiophen-2-yl)aniline. 4-bromoaniline (1.60 g, 9.30 mmol), Pd_2dba_3 (166 mg, 0.181 mmol), P(*o*-tol)$_3$ (226 mg, 0.743 mmol), and cesium fluoride (3.38 g, 22.3 mmol) were added to a 20 mL Biotage microwave reaction vial equipped with a stir bar and the vial was securely sealed with a septum cap. The vial was evacuated/backfilled with argon (4x) followed by the addition of 2-(tributylstannyl)thiophene (3.6 mL, 11 mmol) and 1,2-dimethoxyethane (9.0 mL) *via* syringe. The vial was placed into a microwave reactor and heated with stirring for 2 h at 180 °C. After cooling, the crude reaction solution was eluted through a short pad of silica gel using ethyl acetate (250 mL) and the eluate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 6 to 50% ethyl acetate in hexanes to afford 1.25 g (77%) of the desired product as a slightly yellow solid after drying under vacuum. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.73 (br s, 2H, -N*H*$_2$), 6.64-6.75 (m, 2H, -*Ph*-), 7.03 (dd, 1H, *J*=5.1, 3.5 Hz, -*Th*), 7.11-7.21 (m, 2H, -*Th*), and 7.37-7.47 (m, 2H, -*Ph*-) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 115.46, 121.43, 123.24, 125.31, 127.32, 127.99, 145.18, and 146.17 ppm. MS (EI): m/z $[M]^+$ calcd for $[C_{10}H_9NS]^+$, 175.05; found, 175.04.



Synthesis of N-(4-(thiophene-2-yl)phenyl)-N'-1-hexylheptyl-3,4,9,10-perylene diimide. Perylene-3,4,9,10-tetracarboxylic dianhydride (2.128 g, 5.424 mmol), 4-(thiophen-2-yl)aniline (1.044 g, 5.957 mmol), and 1-hexylheptylamine (0.1190 g, 5.969 mmol) were combined with imidazole (29 g) in a 100 mL round bottom flask equipped with a stir bar and sealed with a septum. The flask was purged with argon for approximately 5 min and heated with stirring in an oil bath maintained at 130 °C. After 4 h, the flask was cooled and the contents were taken up in $CHCl_3$ (200 mL). The solution was washed with 2 M HCl (2x100 mL) and the organic layer was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 60 to 100% methylene chloride in hexanes to afford 1.32 g (33%) of the desired product as an orange-red solid after drying under vacuum. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.83 (t, 6H, *J*=6.9 Hz, -C*H*$_3$), 1.17-1.40 (m, 16H, -NCH(CH$_2$(C*H*$_2$)$_4$CH$_3$)$_2$), 1.82-1.93 (m, 2H, -NCH(C*H*$_2$(CH$_2$)$_4$CH$_3$)$_2$), 2.20-2.30 (m, 2H, -NCH(C*H*$_2$(CH$_2$)$_4$CH$_3$)$_2$), 5.19 (tt, 1H, *J*=9.4, 5.8 Hz, -NC*H*-), 7.12 (dd, 1H, *J*=5.2, 3.5 Hz, -*Th*), 7.34 (d, 1H, *J*=5.2 Hz, -*Th*) 7.35-7.41 (m, 3H, -*Ar*), 7.76-7.84 (m, 2H, -*Ph*-), and 8.59-8.81 (m, 8H, -*Ar*-) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.27, 22.81, 27.16, 29.44, 31.98, 32.60, 55.06, 123.32, 123.47, 123.59, 124.12, 125.69, 126.69, 126.96, 127.24, 128.35, 129.30, 129.79, 130.11, 131.38, 132.16, 134.33, 134.54, 135.34, 135.46, 143.70, and 163.82 ppm. MS (ESI): m/z $[M + Na]^+$ calcd for $[C_{47}H_{42}N_2O_4S + Na]^+$, 753.276; found, 753.273.

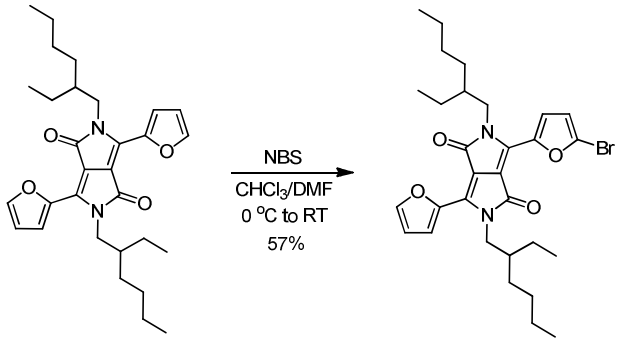


Synthesis of N-(4-(5-bromothiophene-2-yl)phenyl)-N'-1-hexylheptyl-3,4,9,10-perylene diimide, PDI End-Capping Unit (C'). *N*-(4-(thiophene-2-yl)phenyl)-*N'*-1-hexylheptyl-perylene diimide (0.8712 g, 1.192 mmol) was dissolved in methylene chloride (250 mL) in a 500 mL round bottom flask equipped with a stir bar, sealed with a septum, and protected from light with aluminum foil. A 0.5 M stock solution of bromine (3.1 mL, 1.6 mmol) was added *via* syringe and the reaction was stirred at room temperature. After 1.5 h, the reaction solution was concentrated under reduced pressure and the crude solid was washed with methanol and dried under vacuum to afford 0.963 g (quant.) of the desired product as an orange-red, shimmery solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.83 (t, 6H, *J*=6.9 Hz, -C*H*$_3$), 1.17-1.40 (m, 16H, -NCH(CH$_2$(C*H*$_2$)$_4$CH$_3$)$_2$), 1.83-1.92 (m, 2H, -NCH(C*H*$_2$(CH$_2$)$_4$CH$_3$)$_2$), 2.20-2.30 (m, 2H, -NCH(C*H*$_2$(CH$_2$)$_4$CH$_3$)$_2$), 5.19 (tt, 1H, *J*=9.4, 5.8 Hz, -NC*H*-), 7.07 (d, 1H, *J*=3.8 Hz, -*Th*), 7.13 (d, 1H, *J*=3.8 Hz, -*Th*), 7.35-7.41 (m, 2H, -*Ph*-), 7.68-7.74 (m, 2H, -*Ph*-), and 8.65-8.78 (m, 8H, -*Ar*-) ppm. MS (ESI): m/z [M + Na]$^+$ calcd for [$C_{47}H_{41}BrN_2O_4S$ + Na]$^+$, 831.187; found, 831.184.



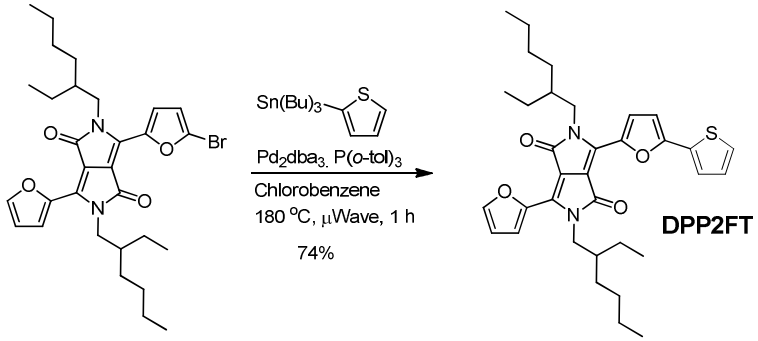
Synthesis of Model Compound. The model compound was synthesized *via* a direct arylation reaction between *N*-2-ethylhexyl substituted, non-brominated DPP monomer and end-capping unit **C'** following a modified literature procedure.[4] DPP monomer (89.6 mg, 0.182 mmol), end-capping unit **C'** (75.2 mg, 0.0929 mmol), $Pd(OAc)_2$ (1.4 mg, 0.0021 mmol), $P(Cy)_3$ (1.2 mg, 0.0043 mmol), pivalic acid (3.6 mg, 0.035 mmol), and K_2CO_3 (22.6 mg, 0.164 mmol) were weighed into a 10 mL Biotage microwave vial equipped with a stir bar and the vial was securely sealed with a septum cap. The vial was evacuated/backfilled with argon (4x) followed by the addition of dry dimethylformamide (3.0 mL) *via* syringe. The vial was placed into a microwave reactor and heated with stirring for 1 h at 180 °C. After cooling, the purple

solution was triturated with methanol and the purple solid was collected by filtration using a 0.45 µm nylon membrane. The crude product was purified by column chromatography on silica gel using a gradient of 0 to 10% ethyl acetate in methylene chloride followed by size exclusion chromatography on Bio-Beads® S-X1 Beads using tetrahydrofuran as eluent. The second band corresponding to the low molecular weight fraction was concentrated under reduce pressure and the solid was triturated with methanol and collected by filtration to afford 23 mg (20%) of the desired product as a dark purple solid after drying under vacuum. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.80-0.96 (m, 18H, -C*H*$_3$), 1.19-1.51 (m, 32H, -C*H*$_2$-), 1.72-1.80 (m, 1H, -NCH$_2$C*H*-), 1.83-1.92 (m, 2H, -NCH(C*H*$_2$(CH$_2$)$_4$CH$_3$)$_2$), 1.92-1.98 (m, 1H, -NCH$_2$C*H*-), 2.21-2.30 (m, 2H, -NCH(C*H*$_2$(CH$_2$)$_4$CH$_3$)$_2$), 4.00-4.07 (m, 2H, -NC*H*$_2$-), 4.15 (d, 2H, *J*=7.7 Hz, -NC*H*$_2$-), 5.19 (tt, 1H, *J*=9.4, 5.8 Hz, -NC*H*-), 6.69 (dd, 1H, *J*=3.7, 1.7 Hz, -*Ar*), 6.86 (d, 1H, *J*=3.8 Hz, -*Ar*), 7.38-7.44 (m, 4H, -*Ar*-), 7.61 (d, 1H, *J*=1.0 Hz, -*Ar*), 7.79-7.84 (m, 2H, -*Ph*-), 8.32 (d, 1H, *J*=3.6 Hz, -*Ar*), 8.49 (d, 1H, *J*=3.9 Hz, -*Ar*-), and 8.61-8.81 (m, 8H, -*Ar*-) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.71, 10.90, 14.21, 22.76, 23.18, 23.37, 23.62, 23.64, 24.01, 27.16, 28.61, 28.62, 28.81, 29.40, 30.36, 30.67, 31.93, 32.53, 39.50, 40.04, 46.23, 46.72, 54.99, 106.76, 106.82, 109.39, 113.62, 120.14, 123.07, 123.16, 123.29, 123.39, 125.15, 126.03, 126.38, 126.64, 126.82, 129.54, 129.56, 129.82, 131.12, 131.86, 131.89, 133.01, 133.16, 134.21, 134.25, 134.89, 135.20, 143.64, 144.61, 144.77, 144.93, 152.11, 160.92, 161.10, and 163.52 ppm. MS (FD): m/z [M]$^+$ calcd for [$C_{77}H_{80}N_4O_8S$]$^+$, 1220.6; found, 1220.5.



***Synthesis of 3-(5-bromofuran-2-yl)-2,5-bis(2-ethylhexyl)-6-(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione, mono-brominated DPP monomer*.** Non-brominated DPP monomer (1.00 g, 3.02 mmol) was dissolved in chloroform (100 mL) in a 250 mL round bottom flask equipped with a stir bar. The solution was protected from light with aluminum foil, cooled in an ice bath, and a solution of N-bromosuccinimide (0.361 g, 2.03 mmol, 0.34 M) in DMF was added at a rate of 1 mL/h *via* syringe pump. After slowly warming to room temperature and stirring overnight the solution was concentrated, diluted with diethyl ether (150 mL), and washed with water (2x100 mL), brine (100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 1 to 10% ethyl acetate in hexanes to afford 0.656 g (57%) of the desired product as a red solid after drying under vacuum. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.84-0.95 (m, 12H, -C*H*$_3$), 1.22-1.42 (m, 16H, -C*H*$_2$-), 1.70-1.78 (m, 2H, -NCH$_2$C*H*-), 3.95-4.06 (m, 4H, -NC*H*$_2$-), 6.62 (d, 1H, *J*=3.7 Hz, -*Ar*), 6.69 (d, 1H, *J*=3.7 Hz, -*Ar*), 7.62 (d, 1H, *J*=1.7 Hz, -*Ar*), 8.29 (d, 1H, *J*=3.7 Hz, -*Ar*), and 8.34 (d, 1H, *J*=3.7 Hz, -*Ar*). ^{13}C NMR (150 MHz, $CDCl_3$): δ 10.91, 10.96, 14.28, 14.30, 23.26, 23.41, 23.97, 24.08, 28.88, 28.96, 30.74,

30.76, 40.14, 40.28, 46.41, 106.50, 106.65, 113.76, 115.64, 120.74, 122.16, 126.22, 132.64, 134.47, 144.79, 145.24, and 146.46 ppm. MS (EI): m/z $[M]^+$ calcd for $[C_{30}H_{39}BrN_2O_4]^+$, 570.209; found, 570.208.



***Synthesis of 2,5-bis(2-ethylhexyl)-3-(furan-2-yl)-6-(5-(thiophen-2-yl)furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione, DPP2FT*.** Mono-brominated DPP monomer (93.8 mg, 0.190 mmol), Pd_2dba_3 (4.6 mg, 0.0050 mmol), and P(*o*-tol)$_3$ (6.0 mg, 0.020 mmol) were added to a 10 mL Biotage microwave reaction vial equipped with a stir bar and the vial was securely sealed with a septum cap. The vial was evacuated/backfilled with argon (4x) followed by the addition of 2-(tributylstannyl)thiophene (0.12 mL, 0.38 mmol) and chlorobenzene (2.0 mL) *via* syringe. The vial was placed into a microwave reactor and heated with stirring for 1 h at 180 °C. After cooling, the reaction solution was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel using a gradient of 20 to 50% methylene chloride in hexanes to afford 81 mg (74%) of the desired product as a purple solid after drying under vacuum. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.79-0.94 (m, 12H, -C*H*$_3$), 1.18-1.48 (m, 16H, -C*H*$_2$-), 1.72-1.79 (m, 1H, -NCH$_2$C*H*-), 1.88-1.96 (m, 1H, -NCH$_2$C*H*-), 4.00-4.08 (m, 2H, -NC*H*$_2$-), 4.13 (d, 2H, *J*=7.8 Hz, -NC*H*$_2$-), 6.68 (dd, 1H, *J*=3.6, 1.7 Hz, -*Ar*), 6.79 (d, 1H, *J*=3.8 Hz, -*Ar*-), 7.10 (dd, 1H, *J*=5.0, 3.7 Hz, -*Ar*), 7.36 (dd, 1H, *J*=1.1 Hz, -*Ar*), 7.41 (dd, 1H, *J*=3.7, 1.1 Hz, -*Ar*), 7.60 (d, 1H, *J*=1.6 Hz, -*Ar*), 8.32 (d, 1H, *J*=3.6 Hz, -*Ar*), and 8.46 (d, 1H, *J*=3.8 Hz, -*Ar*-) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.65, 10.90, 23.17, 23.29, 23.58, 24.02, 28.63, 28.81, 30.31, 30.70, 39.49, 40.06, 46.29, 46.75, 106.72, 106.86, 109.03, 113.55, 120.03, 123.12, 124.86, 126.45, 128.29, 132.39, 133.31, 133.40, 143.57, 144.83, 144.85, 152.33, 161.15, and 161.31 ppm. MS (EI): m/z $[M]^+$ calcd for $[C_{34}H_{42}N_2O_4S]^+$, 574.287; found, 574.285.

(1) Seitz, D. E.; Lee, S.-H.; Hanson, R. N.; Bottaro, J. C. *Synthetic Commun.* **1983**, *13*, 121–128.
(2) Woo, C. H.; Beaujuge, P. M.; Holcombe, T. W.; Lee, O. P.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2010**, *132*, 15547–15549.
(3) Holman, M. W.; Liu, R.; Adams, D. M. *J. Am. Chem. Soc.* **2003**, *125*, 12649–12654.
(4) Baghbanzadeh, M.; Pilger, C.; Kappe, C. O. *J. Org. Chem.* **2011**, *76*, 8138–8142.

4. ^{1}H NMR Spectra of End-Functional Conjugated Polymers (Determination of DPP2FT:PDI Ratios)

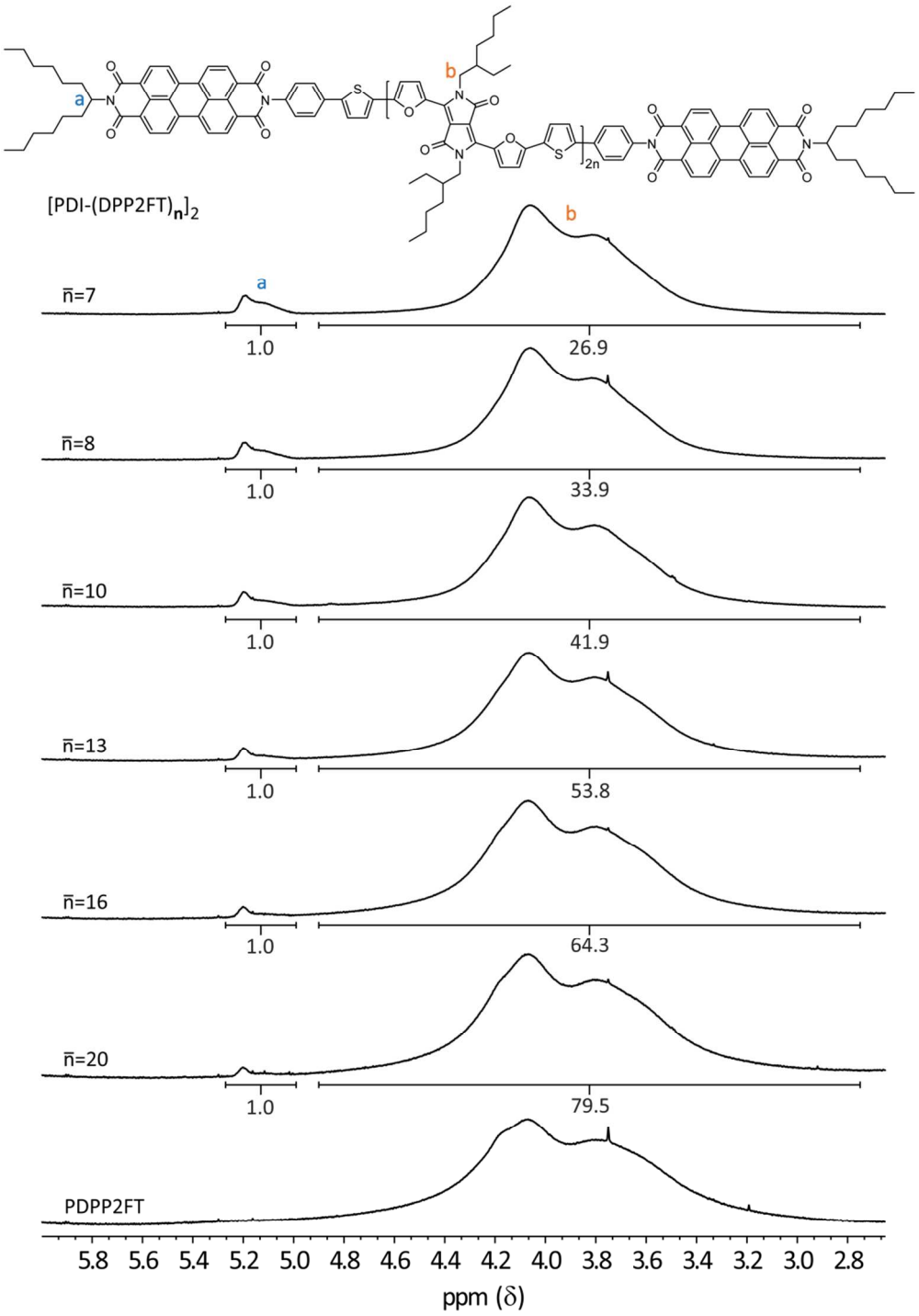


Figure S1. ^{1}H NMR spectra of end-functional conjugated polymers and PDPP2FT homopolymer showing resonances corresponding to the methylene and methine protons alpha to the nitrogen atoms on the DPP (3.9 ppm) and PDI (5.1 ppm) units, respectively.

5. GPC Chromatograms of End-Functional Conjugated Polymers Monitored Using a UV-Visible Photodiode Array Detector

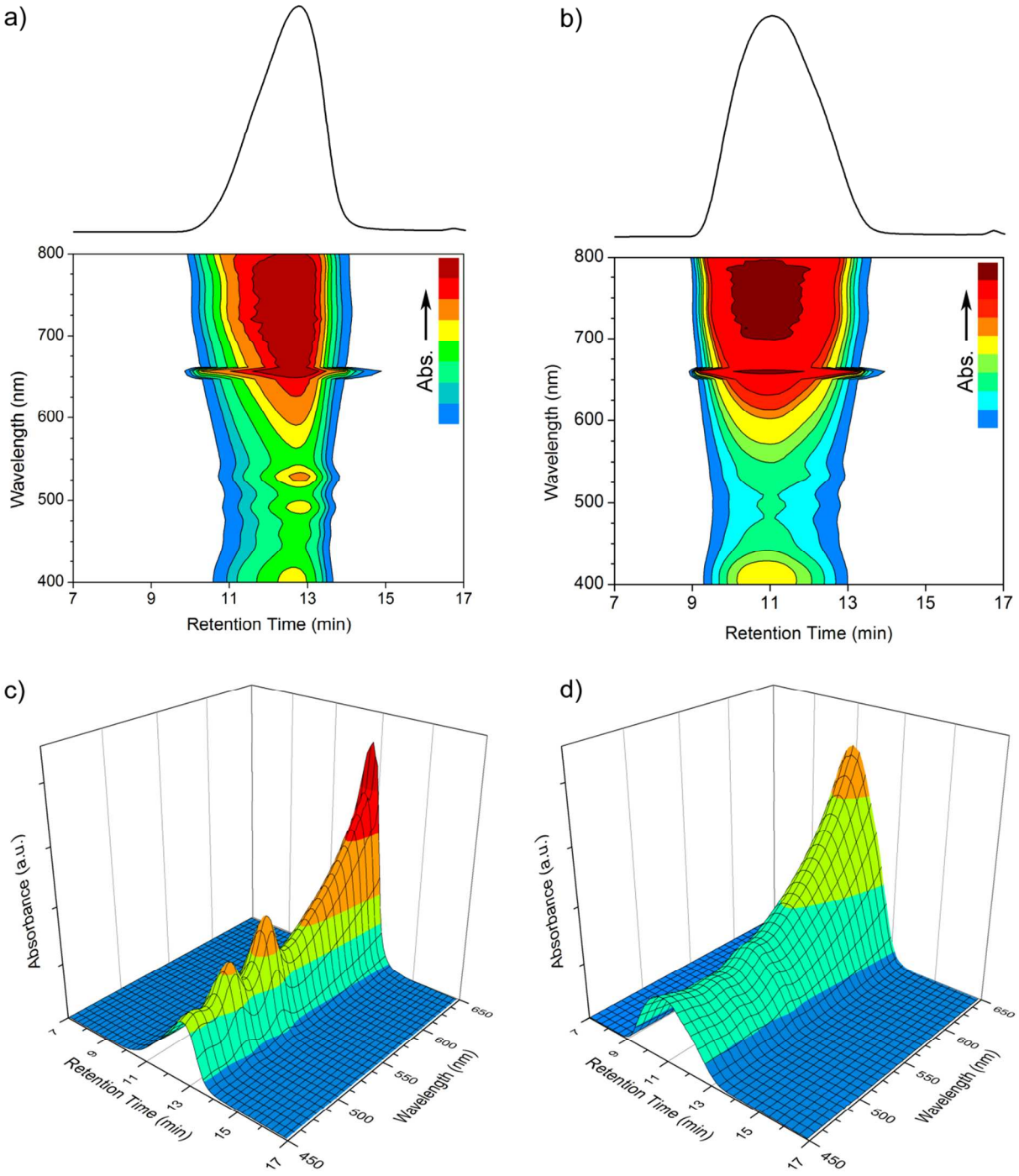


Figure S2. Representative GPC chromatograms monitored using a UV-visible photodiode array detector of end-functional conjugated polymers $[PDI\text{-}(PDPP2FT)_n]_2$ with (a,c) $\bar{n}$=7 and (b,d) $\bar{n}$=20.

6. UV-Visible Spectra of Model Compound, PDI (C), and DPP2FT

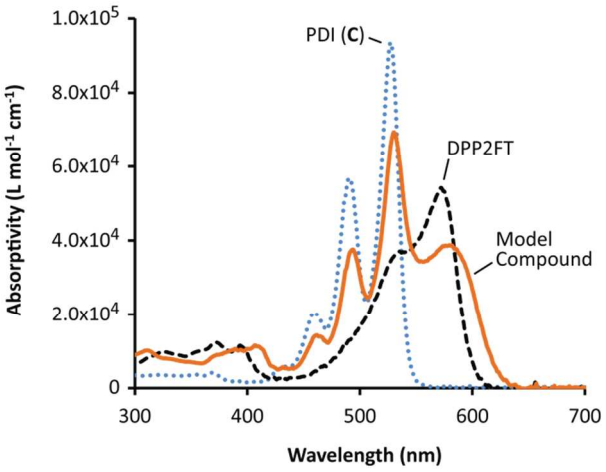


Figure S3. UV-Visible spectra of model compound, DPP2FT (λ_{max}=572 nm), and PDI **C** (λ_{max}=527 nm) in $CHCl_3$.

7. MALDI Mass Spectrum of End-Functional Conjugated Polymer

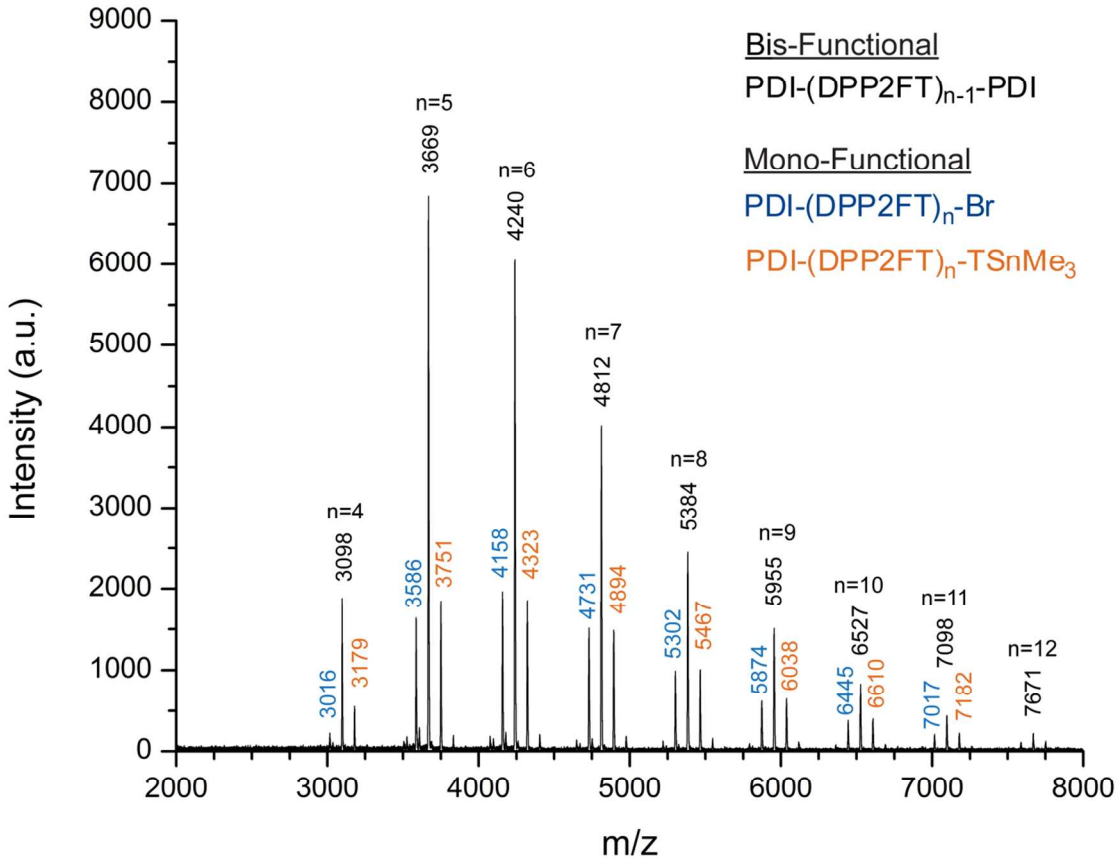


Figure S4. MALDI mass spectrum of end-functional conjugated polymer $[PDI\text{-}(PDPP2FT)_n]_2$ ($\bar{n}$=7). The major series of peaks corresponds to the bis-functional polymer bearing a PDI group at both chain-ends while two additional series of peaks with lower intensity are observed corresponding to polymer species bearing one PDI group and either a furyl bromide (blue labels) or a thienyl trimethylstannane group (orange labels) at the opposite chain-end.

8. Photoluminescence Spectra of Model Compound, PDI (C), and DPP2FT

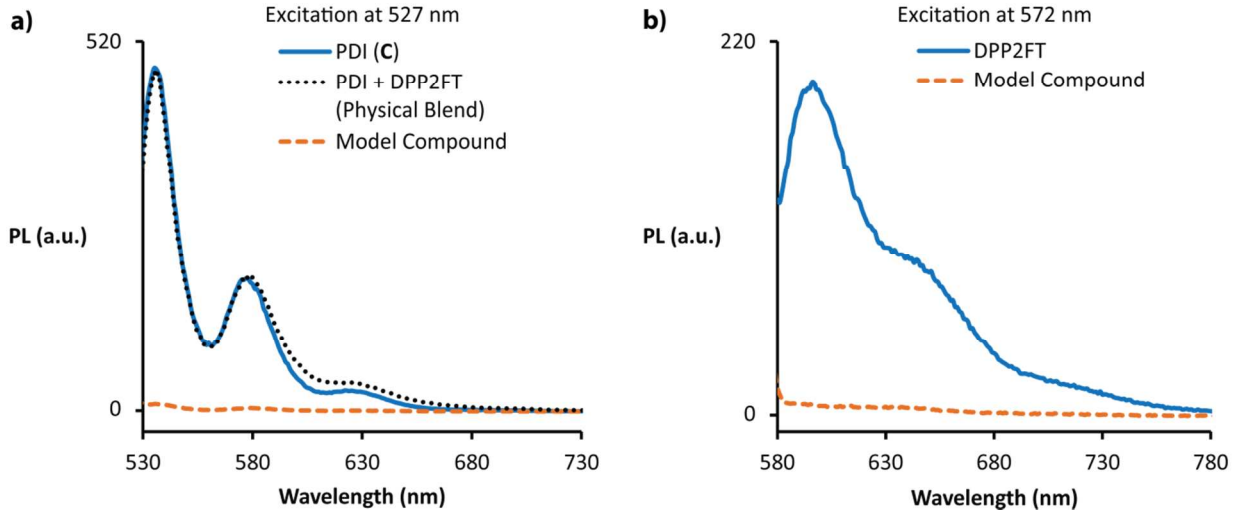


Figure S5. Photoluminescence spectra in $CHCl_3$ ($7x10^{-7}$ M) of (a) PDI **C**, a physical blend of PDI **C** + DPP2FT, and model compound after excitation at 527 nm ($\lambda_{max,\ PDI}$), and (b) DPP2FT and model compound after excitation at 572 nm ($\lambda_{max,\ DPP2FT}$). Fluorescence quenching is observed in each case only for the model compound; the results indicate efficient intramolecular charge transfer.

9. GPC Chromatograms of End-Functional Conjugated Polymers

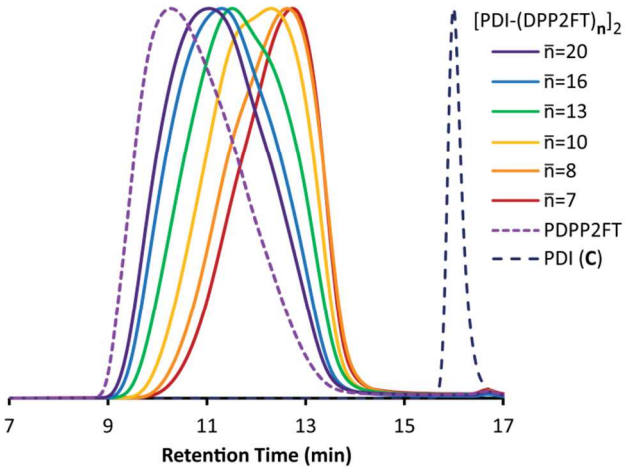


Figure S6. GPC chromatograms (RI) of end-functional conjugated polymers, PDPP2FT homopolymer, and PDI end-capping unit **C**.

10. ^{1}H NMR Spectrum of Model Compound with Assignments

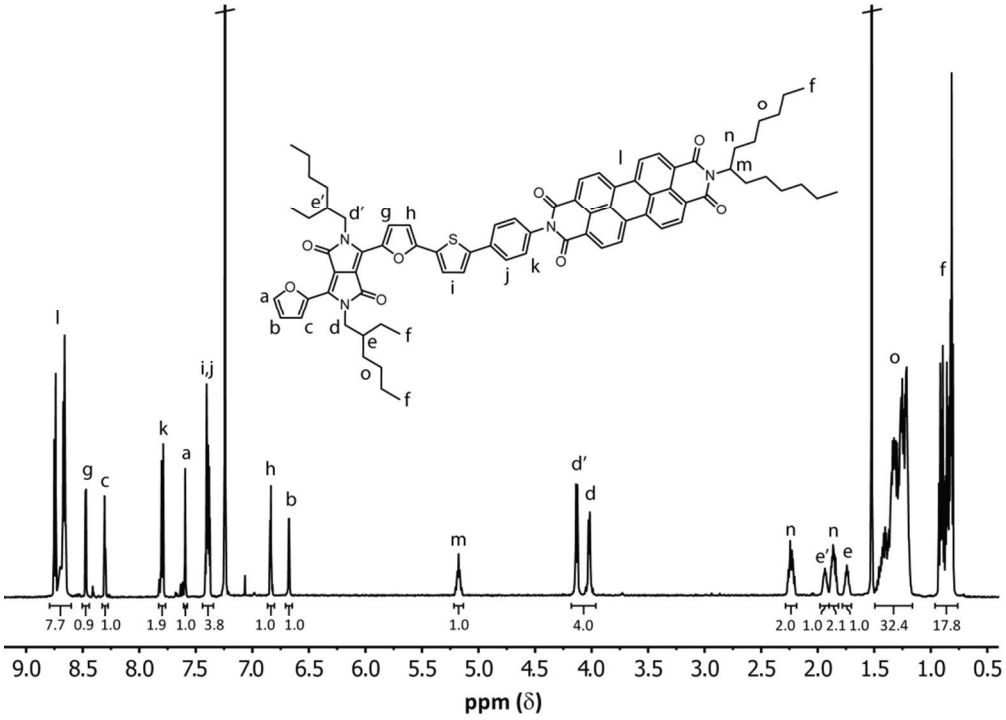


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) and structure of model compound.

11. ^{1}H NMR Spectrum of End-Functional Conjugated Polymer

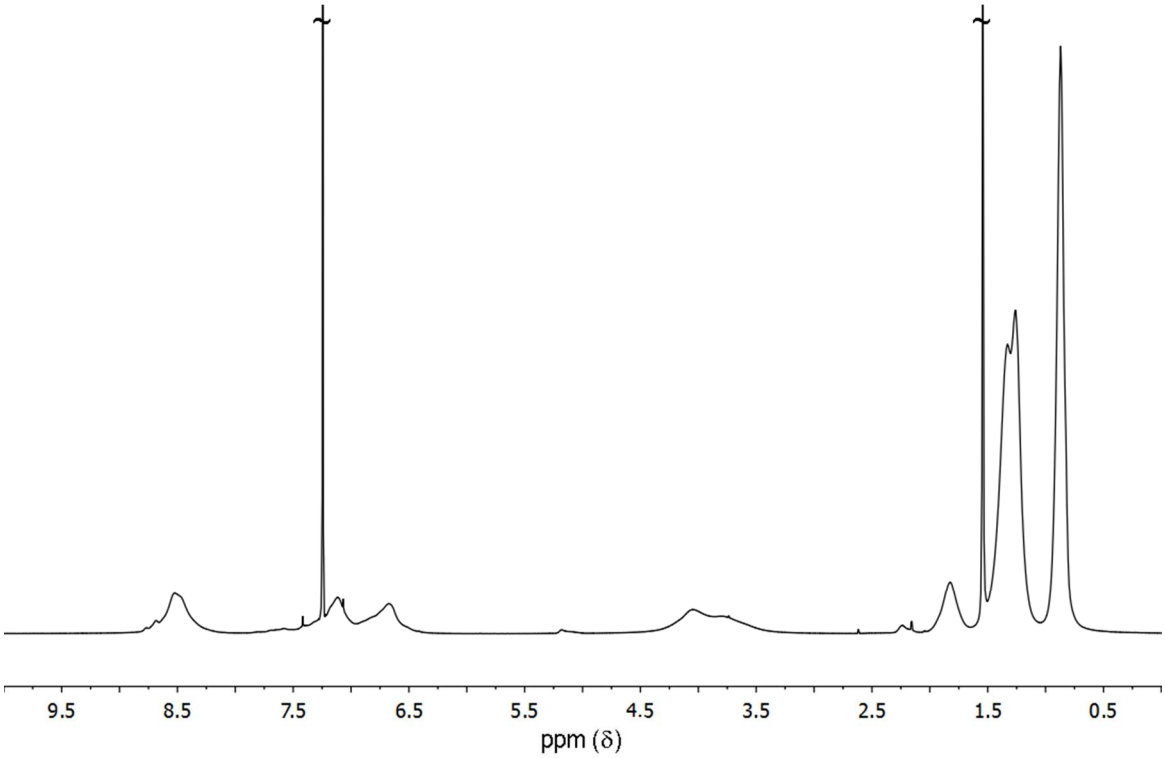


Figure S8. Representative ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of end-functional conjugated polymer [PDI-(PDPP2FT)$_n$]$_2$ ($\bar{n}$=10).