

Influence of Simultaneous Tuning of Molecular Weights and Alkyl Substituents of Poly(thienoisoindigo-*alt*-naphthalene)s on Morphology and Charge Transport Properties

Hye Jin Cho,^{†,§} Seok-Ju Kang,^{‡,§} Sang Myeon Lee,[†] Mingyu Jeong,[†] Gyoungsik Kim,^{†,1} Yong-Young Noh,^{‡,} and Changduk Yang^{†,*}*

[†]Department of Energy Engineering, School of Energy and Chemical Engineering, Low Dimensional Carbon Materials Center, Perovtronics Research Center, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulju-gun, Ulsan 44919, Republic of Korea

[‡]Department of Energy and Materials Engineering, Dongguk University, 30 Pildong-ro 1-gil, Jung-gu, Seoul 04620, Republic of Korea

¹Current address: Photo-Electronic Hybrids Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea

[§]These authors contributed equally to this work.

Corresponding Authors

*E-mail: yynoh@dongguk.edu and yang@unist.ac.kr

Experimental Section

General Procedures and Method: All the chemicals and reagents were purchased from Sigma-Aldrich, Alfa Aesar Chemical Company, and Tokyo Chemical Industry Co., Ltd. and used without any further purification. All solvents are ACS and anhydrous grade by distillation. The intermediates (1-iodo-2-decyltetradecane, 2-(2-decyltetradecyl)isoindoline-1,3-dione, 2-decyltetradecan-1-amine, *N*-(2-decyltetradecyl)thiophen-3-amine, *N*-(2-decyltetradecyl)thiophen-3-amine, *N*-(2-decyltetradecyl)thiophen-3-amine, (*E*)-2,2'-dibromo-4,4'-bis(2-hexyldecyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione, (*E*)-2,2'-dibromo-4,4'-bis(2-octyldecyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione, and 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene) were synthesized according to literature procedures.¹⁻⁷ ¹H NMR spectra were recorded on an Agilent 400 MHz spectrometer using deuterated chloroform (CDCl₃) as solvent and tetramethylsilane (TMS) as an internal standard. Elementary analyses were carried out with a Flash 2000 element analyzer (Thermo Scientific, Netherlands) and Matrix-Assisted Laser Desorption Ionization Mass Spectrometry (MALDI-TOF MS) spectra were obtained by Ultraflex III (Bruker, Germany). UV-Vis spectra in solution and in thin films were taken on a Cary 5000 (Varian USA) spectrophotometer. Number of average, weight of average molecular weight, and polydispersity index (PDI) of the polymers were determined by gel-permeation chromatography (GPC) with Agilent 1200 HPLC Chemstation using a series of mono disperse polystyrene as standards in tetrahydrofuran (THF) (HPLC grade) as eluent at 40 °C. Cyclic voltammetry (CV) measurements were performed on AMETEK Versa STAT 3 with a three-electrode cell system in a nitrogen bubbled 0.1 M tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu₄NPF₆) solution in acetonitrile at a scan rate of 100 mV/s at room temperature. Ag/Ag⁺ electrode, platinum wire, and a glass carbon disk were used as the reference electrode, counter electrode, and working electrode, respectively. The Ag/Ag⁺

reference electrode was calibrated using a ferrocene/ferrocenium redox couple as an external standard, whose oxidation potential is set at -5.1 eV with respect to a zero vacuum level. The highest occupied molecular orbital (HOMO) energy levels were obtained from the equation E_{HOMO} (eV) = $-(E_{(\text{ox})}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}} + 5.1)$. The lowest unoccupied molecular orbital (LUMO) levels were obtained from the equation E_{LUMO} (eV) = $-(E_{(\text{red})}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}} + 5.1)$.⁸

Synthesis of 4-(2-decyltetradecyl)-4H-thieno[3,2-b]pyrrole-5,6-dione (2): Isolated yield = 24 %. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.98 (d, 1H, $J = 4.3$ Hz), 6.75 (d, 1H, $J = 4.3$ Hz), 3.55 (d, 2H, $J = 7.0$ Hz), 1.77 (m, 1H), 1.30–1.25 (m, 40H), 0.90–0.86 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.31, 165.85, 162.07, 144.05, 113.45, 111.38, 46.80, 37.32, 32.25, 32.23, 31.73, 30.24, 30.00, 29.97, 29.94, 29.88, 29.69, 29.66, 29.64, 26.70, 23.02, 14.44, 14.43. MALDI-TOF MS (m/z) calcd: 489.36. Found: 489.92 (MH⁺).

Synthesis of (E)-4,4'-bis(2-decyltetradecyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'(4H,4'H)-dione: Compound 2 (1 equiv.) and Lawesson's reagent (0.5 equiv.) in *o*-xylene was put in the two-neck round flask and stirred at 60 °C for 2 h (color changed into violet blue). After cooling down to the room temperature, the solvent was concentrated by evaporation. The crude was purified by column chromatography on silica gel with hexane:dichloromethane to obtain the product. Isolated yield = 42 %. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.51 (d, 2H, $J = 4.9$ Hz), 6.77 (d, 2H, $J = 4.9$ Hz), 3.68 (d, 4H, $J = 7.1$ Hz), 1.89 (m, 2H), 1.31–1.22 (m, 80H), 0.88–0.85 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 171.65, 151.88, 134.53, 121.40, 114.58, 111.67, 46.49, 37.49, 32.28, 32.26, 31.81, 30.30, 30.02, 30.00, 29.97, 29.91, 29.71, 29.68, 26.76, 23.04, 14.47. Elemental Analysis: Anal. Calcd for C₆₀H₁₀₂N₂O₂S₂: C, 76.05; H, 10.85; N, 2.96; S, 6.77 Found: C, 75.56; H, 10.87; N, 2.98; S, 6.69. MALDI-TOF MS (m/z) calcd: 946.74. Found: 946.70 (MH⁺).

Synthesis of (E)-2,2'-Dibromo-4,4'-bis(2-decyltetradecyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5' (4H,4'H)-dione: To a solution of TIIG in THF in a two-neck round flask with an ice bath, add *N*-bromosuccinimide (NBS) dropwise over 30 min. After TLC check, the reaction was quenched by addition of water. The crude was taken up in 200 ml of dichloromethane, washed three times with water and once with brine. After drying by MgSO₄, the crude was purified by column chromatography on silica gel with hexane:dichloromethane. Isolated yield = 53 %. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.82 (s, 2H), 3.62 (d, 4H, *J* = 7.3 Hz), 1.83 (m, 2H), 1.28–1.24 (m, 80H), 0.89–0.86 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 170.66, 150.49, 123.41, 119.96, 115.28, 115.02, 46.51, 37.53, 32.28, 32.27, 31.74, 30.30, 30.04, 30.02, 30.01, 29.99, 29.91, 29.72, 29.69, 26.71, 23.04, 14.47. Elemental Analysis: Anal. Calcd for C₆₀H₁₀₀Br₂N₂O₂S₂: C, 65.19; H, 9.12; N, 2.53; S, 5.80 Found: C, 65.47; H, 9.33; N, 2.54; S, 5.78. MALDI-TOF MS (*m/z*) calcd: 1102.56. Found: 1102.76 (MH⁺).

Typical Synthesis Procedure of PTIIG-N_p by Suzuki Polymerization: In a Schlenk flask, dibromide TIIG and diboronic ester naphthalene were dissolved in anhydrous toluene (5 mL), a solution of K₃PO₄, P(*o*-tolyl)₃, and deionized water (3 mL) with Aliquat 336 was added. The mixture was vigorously stirred at room temperature under argon. After 30 min, Pd₂(dba)₃ was added to the reaction mixture. The crude product was poured into a mixture of methanol and ammonia (4:1 v/v, 250 mL). The resulting solid was filtered off and subjected to sequential Soxhlet extraction with methanol (1 d), acetone (1 d), and hexane (1 d) to remove impurities of the materials. The residue was extracted with chloroform to produce a dark-green product after precipitating again from methanol and drying in *vacuo*.

For Low-M_n Polymer Cases: The dibromide TIIG (79.4 mmol, 1.0 equiv.), diboronic ester naphthalene (103.29 mmol, 1.3 equiv.), Pd₂(dba)₃ (1.45 mg, 2 mol%), P(*o*-tolyl)₃ (84.3 mg,

8 mol %), and K_3PO_4 (84.3 mg, 5 equiv.) were placed in Schlenk flask, and kept at 90 °C for 3 hour-reaction time.

L-PTIIGHD-Np: Isolated yield = 72%. GPC analysis (THF as eluent); M_n = 24.6 kDa, M_w = 50.4 kDa and PDI = 2.05. 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.33-6.96 (br, 8H), 3.76-3.69 (br, 4H) 2.02-2.00 (br, 2H), 1.25-1.23 (br, 48H), 0.84 (br, 12H).

L-PTIIGOD-Np: Isolated yield = 68 %. GPC analysis (THF as eluent); M_n = 34.3 kDa, M_w = 96.5 kDa and PDI = 2.81. 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.33-6.96 (br, 8H), 3.76-3.69 (br, 4H) 2.02-2.00 (br, 2H), 1.25-1.23 (br, 64H), 0.84 (br, 12H).

L-PTIIGDT-Np: Isolated yield = 73 %. GPC analysis (THF as eluent); M_n = 50.6 kDa, M_w = 130.4 kDa and PDI = 2.57. 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.33-6.96 (br, 8H), 3.76-3.69 (br, 4H) 2.02-2.00 (br, 2H), 1.25-1.23 (br, 80H), 0.84 (br, 12H).

For High- M_n Polymer Cases: The dibromide TIIG (79.4 mmol, 1.0 equiv.), diboronic ester naphthalene (79.4 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (1.45 mg, 2 mol%), $P(o\text{-tolyl})_3$ (84.3 mg, 8 mol %), and K_3PO_4 (84.3 mg, 5 equiv.) were placed in Schlenk flask, and kept at 90 °C for 24 hour-reaction time.

H-PIIGHD-Np: Isolated yield = 86 %. GPC analysis (THF as eluent); M_n = 61.3 kDa, M_w = 129.5 kDa and PDI = 2.11.

H-PTIIGOD-Np: Isolated yield = 68%. GPC analysis (THF as eluent); M_n = 63.8 kDa, M_w = 204.0 kDa and PDI = 3.19.

H-PTIIGDT-Np: Isolated yield = 83 %. GPC analysis (THF as eluent); M_n = 108.7 kDa, M_w = 412.0 kDa and PDI = 3.79.

OFET Device Fabrication and Characterization: TG-BC devices were fabricated and tested with the polymers in nitrogen atmosphere. The polymer films were spin-cast from 1,2,4-trichlorobenzene solutions ($\sim 5 \text{ mg mL}^{-1}$) on glass substrates with lithographically patterned Ni/Au source-drain electrodes (3 nm/12 nm), and subsequently dried at room temperature for 2 h before a thermal annealing at to 300 °C for 30 min and then allowed to cool down slowly. The patterned channel width/length was 1.0 mm/20 μm . PMMA (Sigma-Aldrich, M_n : 120 kDa) was spin-coated at 2000 rpm from a 80 mg ml⁻¹ solution in *n*-butyl acetate on top of the active layer to form a dielectric layer ($\sim 500 \text{ nm}$ thick), and subsequently baked at 80 °C for 30 min. Finally, Al gate electrodes were thermally evaporated on top of PMMA layers as gate electrodes to complete top-gate transistors. The devices were characterized through a Keithley 4200 parameter analyzer on a probe station in nitrogen atmosphere. The charge-carrier mobility was calculated from the data measured in the saturated regime of transistor operation according to the following equation:

$$I_{DS} = \frac{\mu C_{diel} W}{2L} (V_{GS} - V_{th})^2$$

Where W and L are the channel width and length, C_{diel} is the gate dielectric layer capacitance value per unit area, and V_{GS} and V_{th} are the gate voltage and threshold voltage.

GIXD Characterization: Grazing incidence X-ray diffraction (GIXD) measurements were conducted at PLS-II 6D UNIST-PAL and 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. The used X-ray energy was 11.6 keV (wavelength $\lambda = 1.069 \text{ \AA}$) for 6D and 11.17 keV (wavelength $\lambda = 1.1099 \text{ \AA}$) for 9A beamline. The thin film sample was kept in vacuum chamber ($10^{-2} - 10^{-3} \text{ torr}$) during the measurement and incidence angle of X-ray beam was set to 0.12° for PTIIG-Np polymers. The critical angle of the film was experimentally determined to be about 0.118° by using the well-known phenomena that, for $\alpha_i = \alpha_c$, X-rays

are in phase so the intensity of the evanescent (transmitted) wave is four times that of the incident beam under no absorption ($\beta = \lambda\mu/4\pi = 0$, where λ and μ is the wavelength and absorption coefficient). That is, GIXD intensity is abruptly increased when α_i reaches α_c of the film. GIXD patterns were recorded with a 2D CCD detector (Rayonix MX 225-HS for 6D and SX165 for 9A) and diffraction angles were calibrated using a sucrose standard (Monoclinic, P21, $a = 10.8631 \text{ \AA}$, $b = 8.7044 \text{ \AA}$, $c = 7.7624 \text{ \AA}$, $\beta = 102.938^\circ$). The pole figure was obtained using GIXS images according to following steps. First, the (100) lamellar crystalline peaks were extracted from the line cut data along the radius line at 2.5° , 5° , 7.5° ,... 87.5° of azimuth angle. Then, the integral area of each (100) crystalline peak (per cutting line) was plotted for every 2.5° angle to complete the pole figure. To compare the orientation distribution of the polymer crystals for the polymer films, the relative portions of edge-on and face-on crystallites were determined by the integral values of each section in the pole figure. In detail, the range of χ of $0-45^\circ$ and $45-90^\circ$ with respect to the surface normal were assumed to be edge-on and face-on orientation, respectively.

AFM Characterization: Agilent 5500 scanning probe microscope (SPM) running with a Nanoscope V controller was used to obtain AFM images of polymer thin films. AFM images were recorded in high-resolution tapping mode under ambient conditions. Premium silicon cantilevers (TESP) were used with a rotated tip to provide more symmetric representation of features over 200 nm.

N-(2-decyltetradecyl)thiophen-3-amine

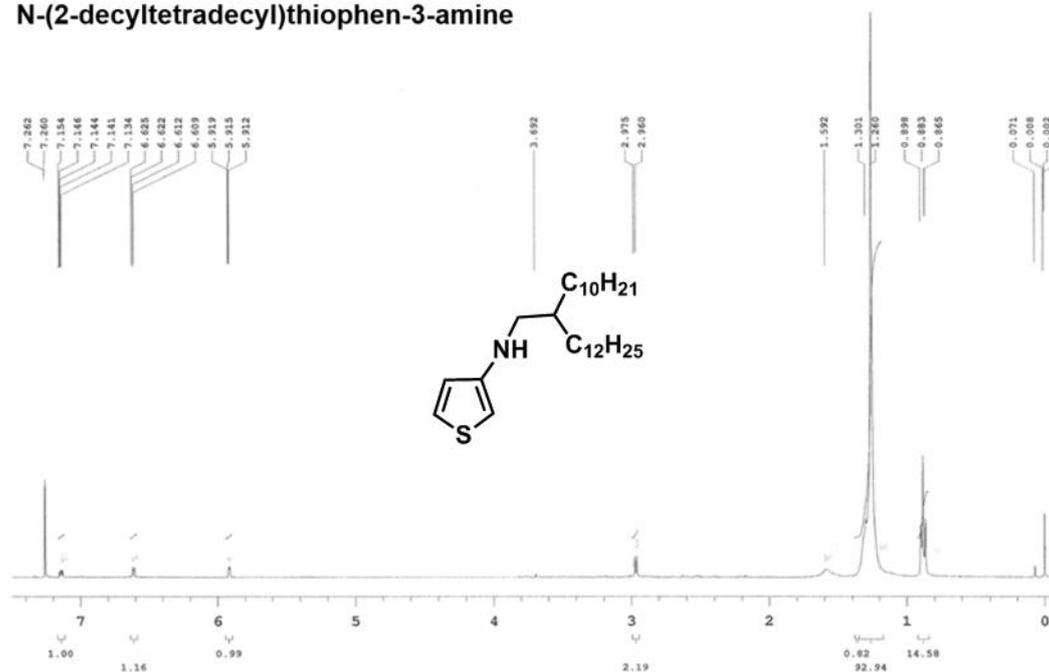


Figure S1. ¹H-NMR spectra of *N*-(2-decyltetradecyl)thiophene-3-amine in CDCl₃.

4-(2-decyltetradecyl)-4H-thieno[3,2-b]pyrrole-5,6-dione

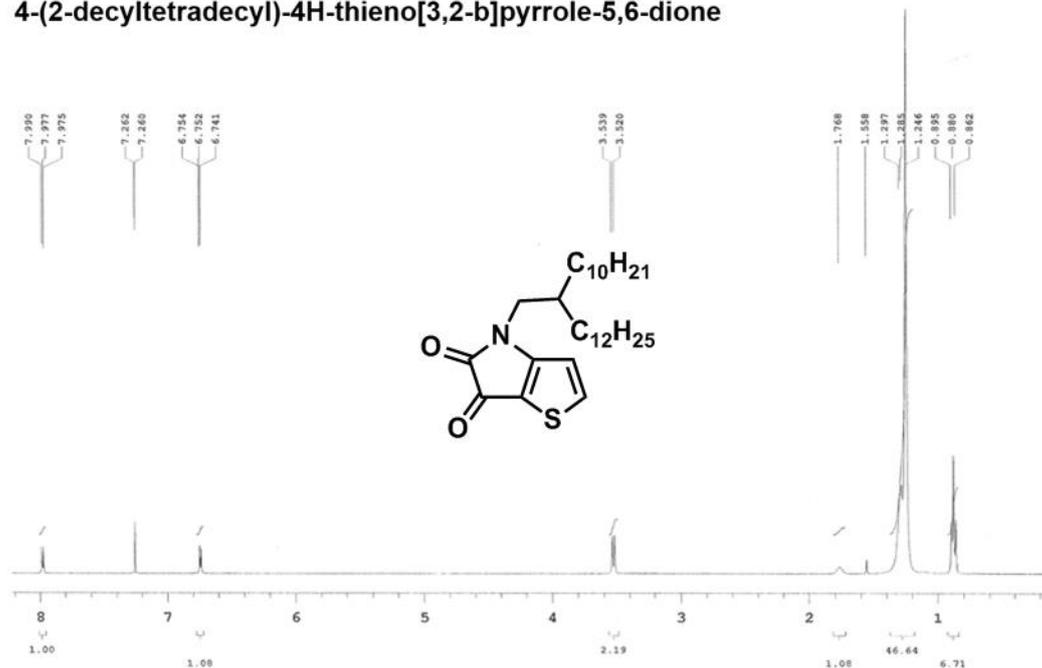


Figure S2. ¹H-NMR spectra of 4-(2-decyltetradecyl)-4H-thieno[3,2-b]pyrrole-5,6-dione in CDCl₃.

(E)-4,4'-bis(2-decyltetradecyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'(4H,4'H)-dione

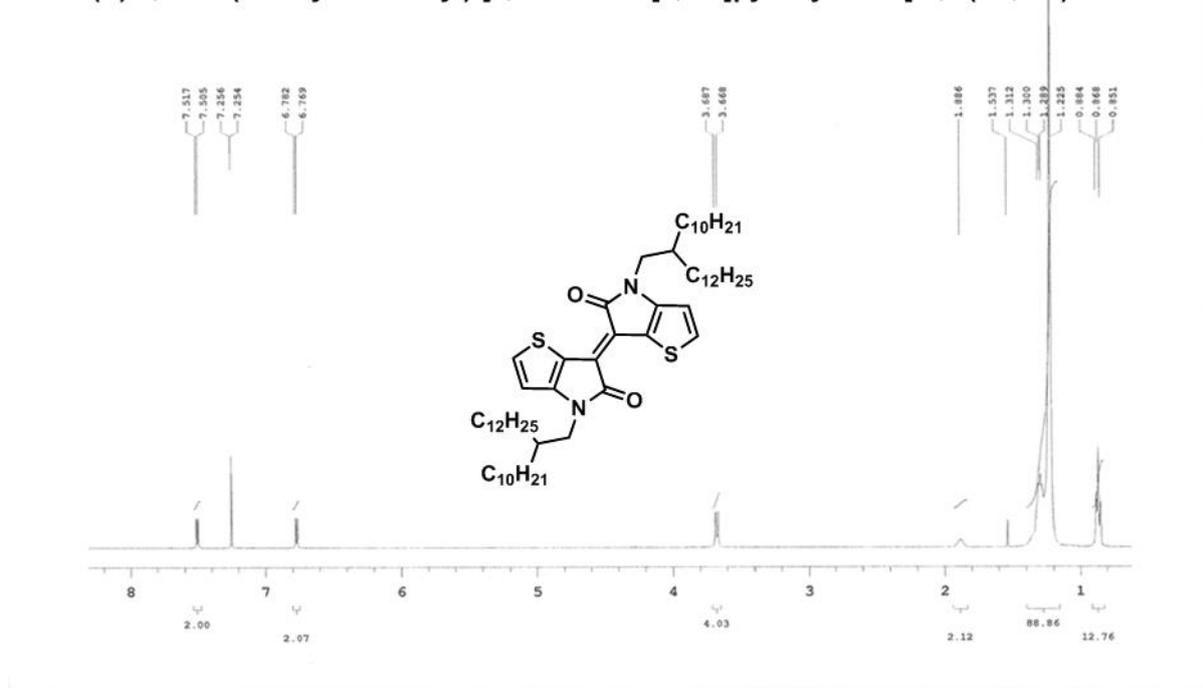


Figure S3. ¹H-NMR spectra of (E)-4,4'-bis(2-decyltetradecyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'(4H,4'H)-dione in CDCl₃.

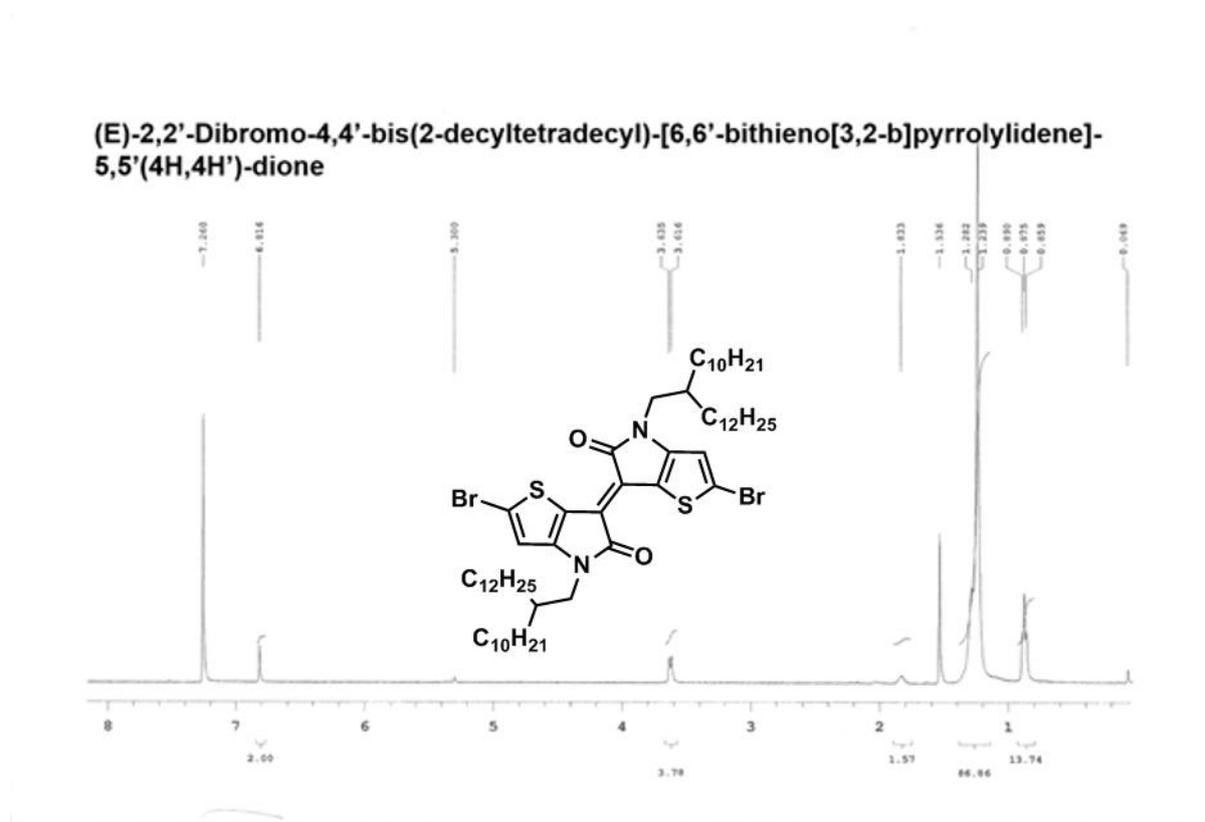


Figure S4. ¹H-NMR spectra of (*E*)-2,2'-Dibromo-4,4'-bis(2-decyltetradecyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5' (4H,4H')-dione in CDCl₃.

L-PTIIGHD-Np (Tetrahydrofuran)

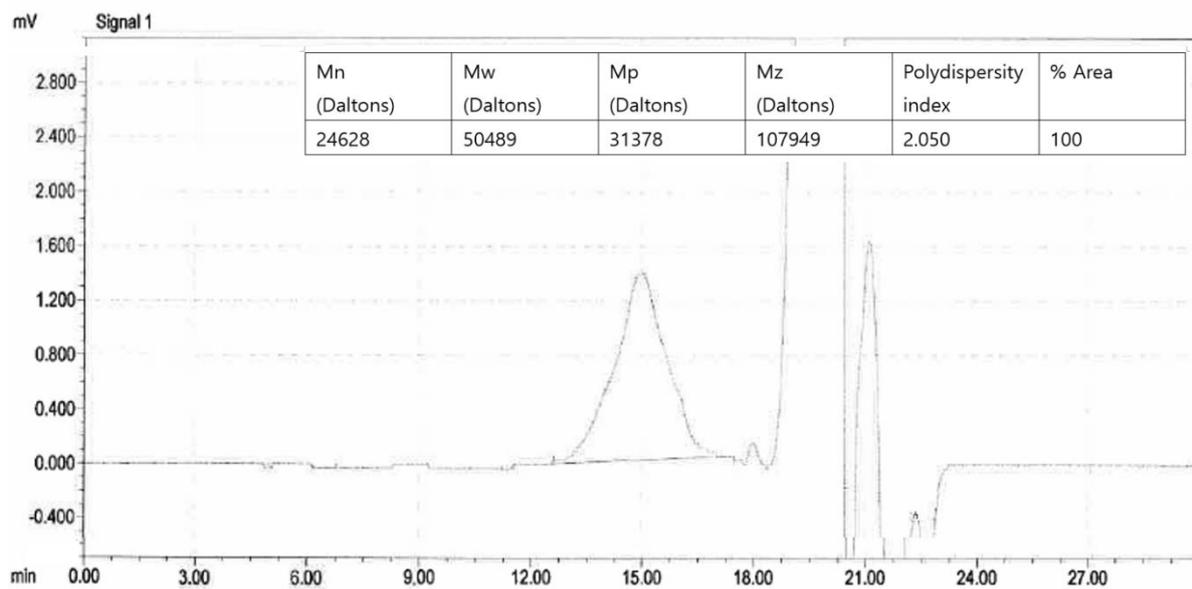


Figure S5. GPC chromatograms of L-PTIIGHD-Np measured in THF at 40 °C.

H-PTIIGHD-Np (Tetrahydrofuran)

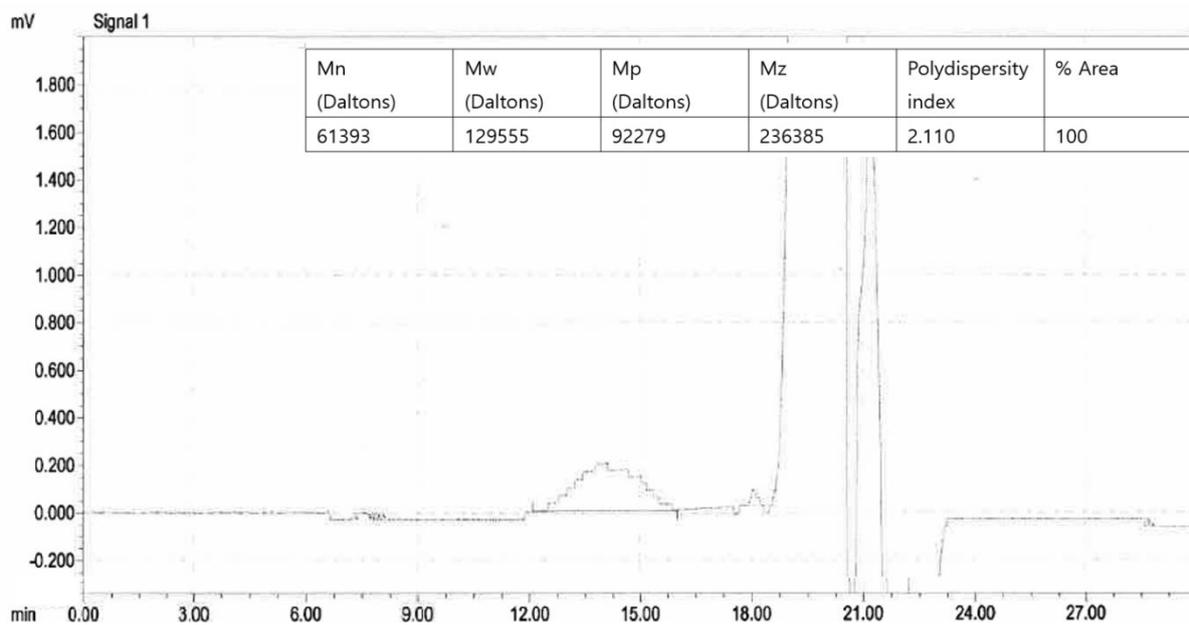


Figure S6. GPC chromatograms of H-PTIIGHD-Np measured in THF at 40 °C.

L-PTIIGOD-Np (Tetrahydrofuran)

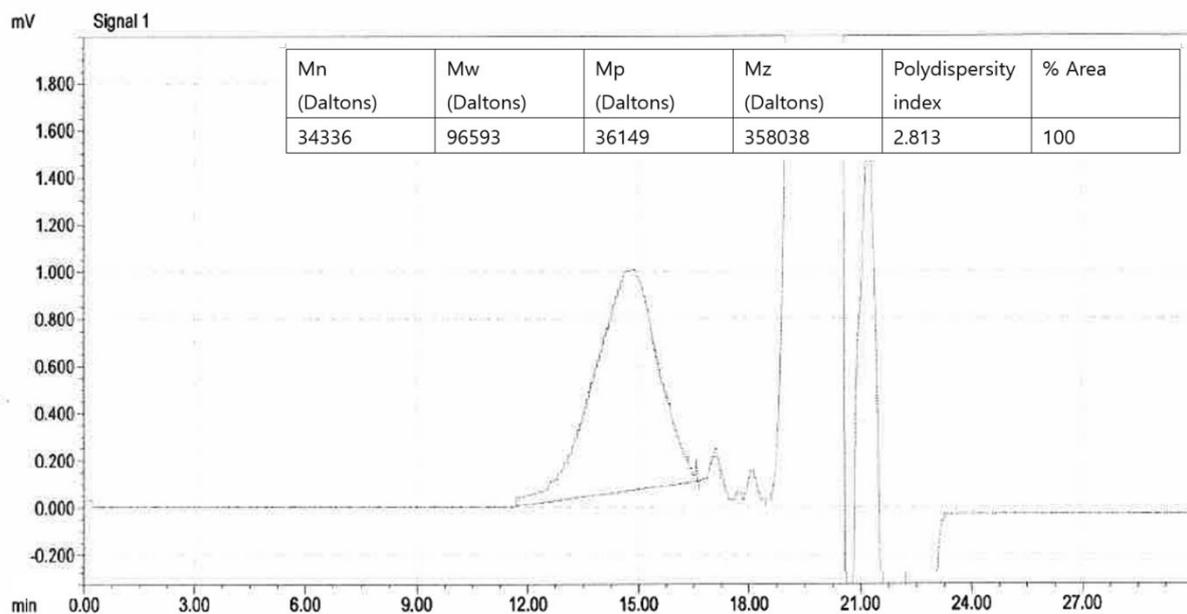


Figure S7. GPC chromatograms of L-PTIIGOD-Np measured in THF at 40 °C.

H-PTIIGOD-Np (Tetrahydrofuran)

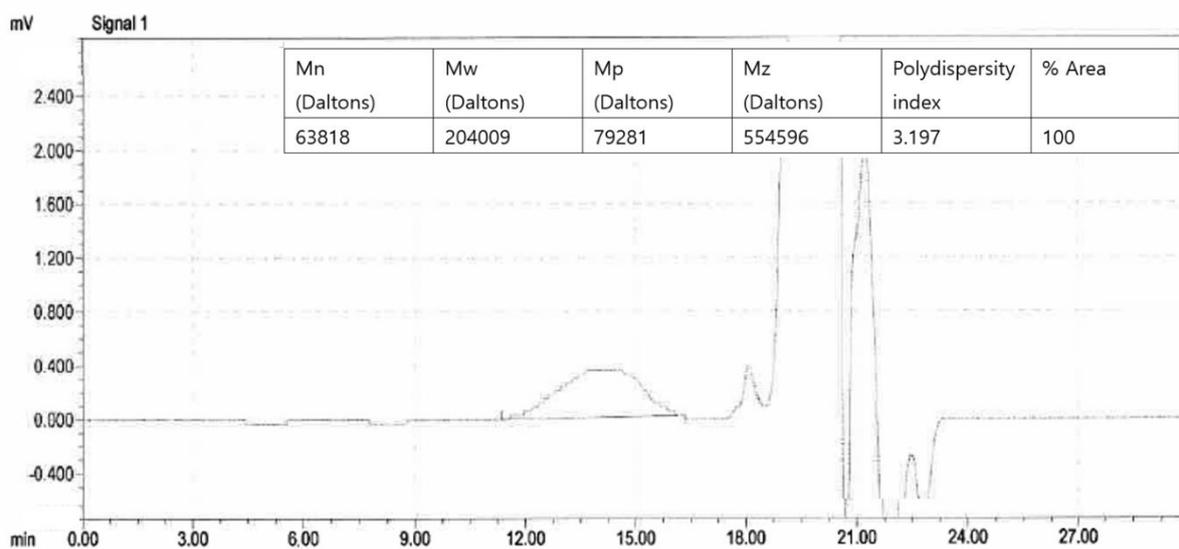


Figure S8. GPC chromatograms of H-PTIIGOD-Np measured in THF at 40 °C.

L-PTIIGDT-Np (Tetrahydrofuran)

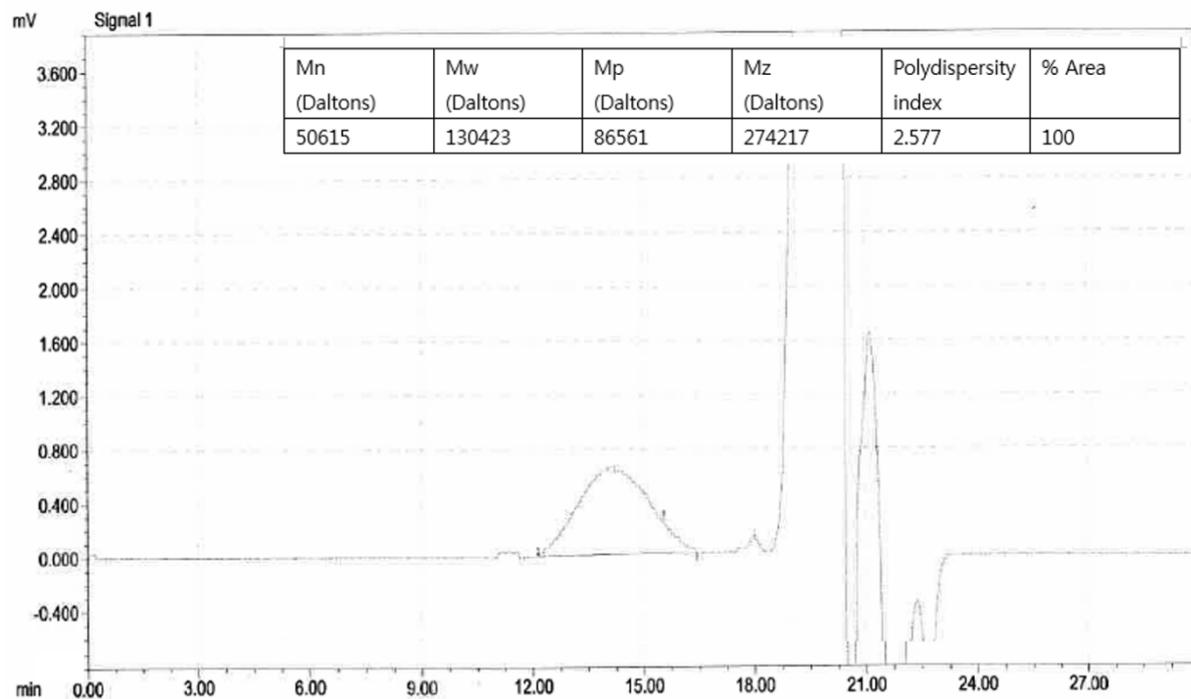


Figure S9. GPC chromatograms of L-PTIIGDT-Np measured in THF at 40 °C.

H-PTIIGDT-Np (Tetrahydrofuran)

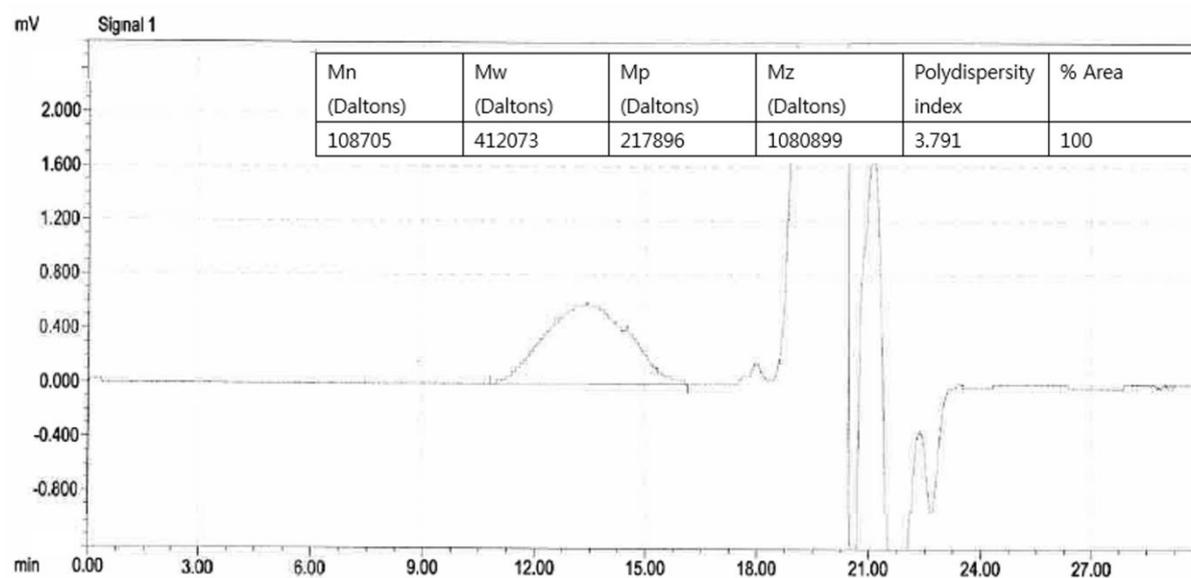


Figure S10. GPC chromatograms of H-PTIIGDT-Np measured in THF at 40 °C.

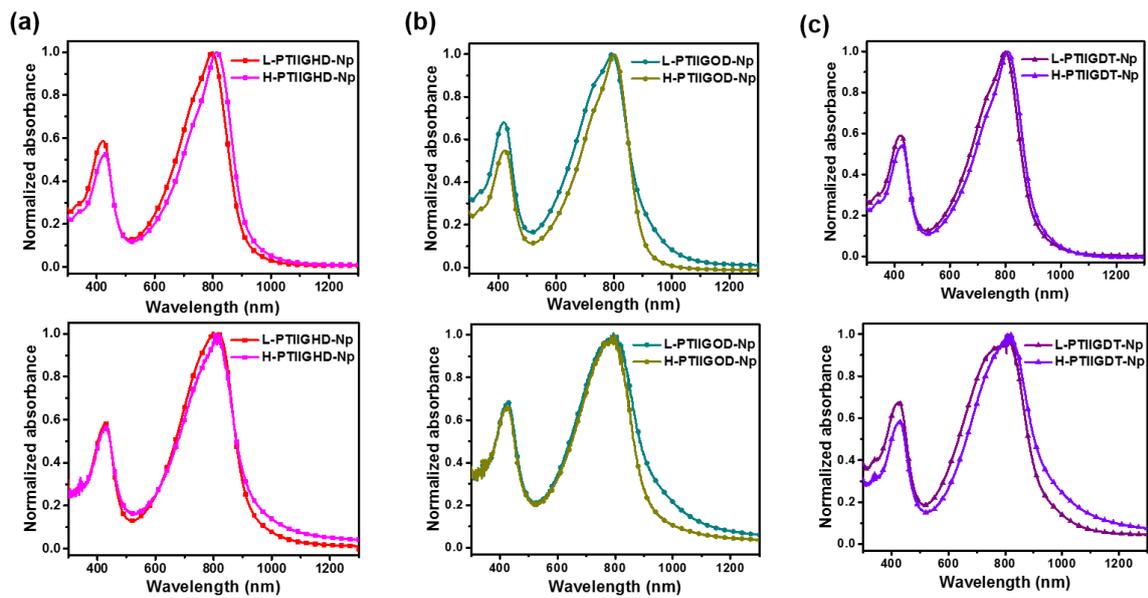
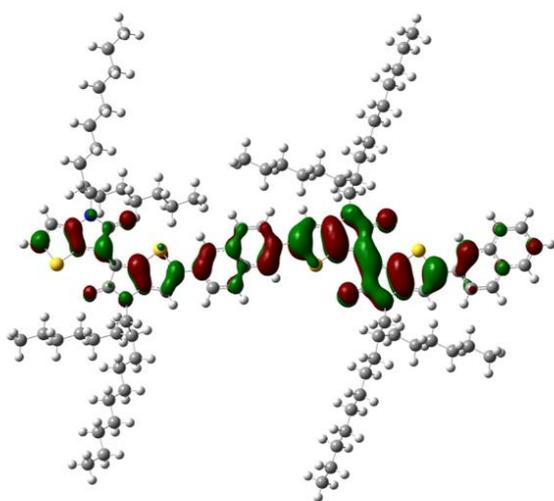
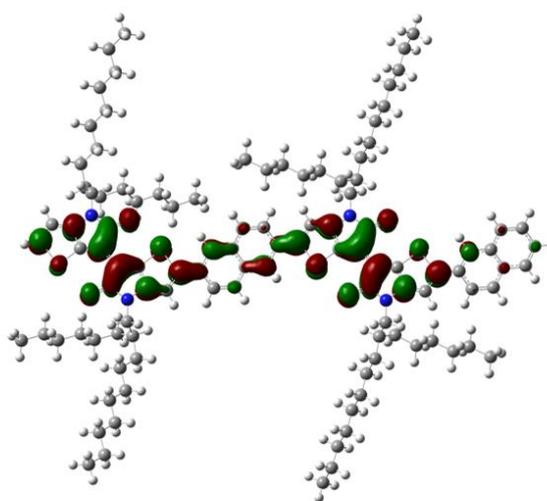


Figure S11. Normalized UV-vis absorption spectra of PTIIG-Np polymers for PTIIGHD-Np (a), for PTIIGOD-Np (b), and for PTIIGDT-Np (c) in CHCl_3 (upper line) and film (bottom line), respectively.

PTIIGHD-Np



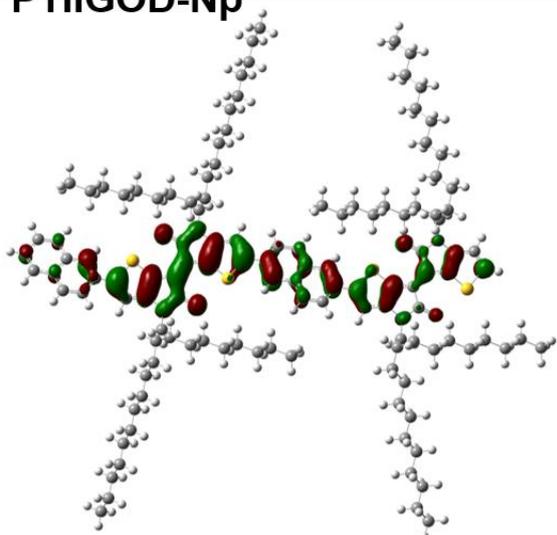
HOMO = - 4.73



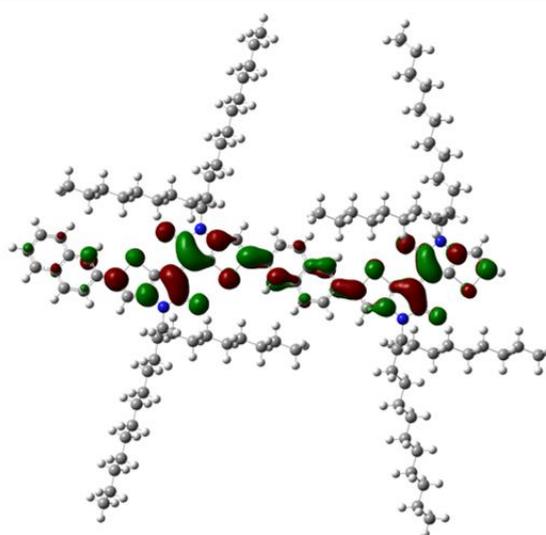
LUMO = - 2.94

Figure S12. Optimized frontier molecular geometries of simulated HOMO (left) and LUMO (right) for the PTIIG-Np based dimers with 2-hexyldecyl alkyl substituents (-HD).

PTIIGOD-Np



HOMO = - 4.76



LUMO = - 2.95

Figure S13. Optimized frontier molecular geometries of simulated HOMO (left) and LUMO (right) for the PTIIG-Np based dimers with 2-octyldecyl alkyl substituents (-OD).

PTIIGDT-Np

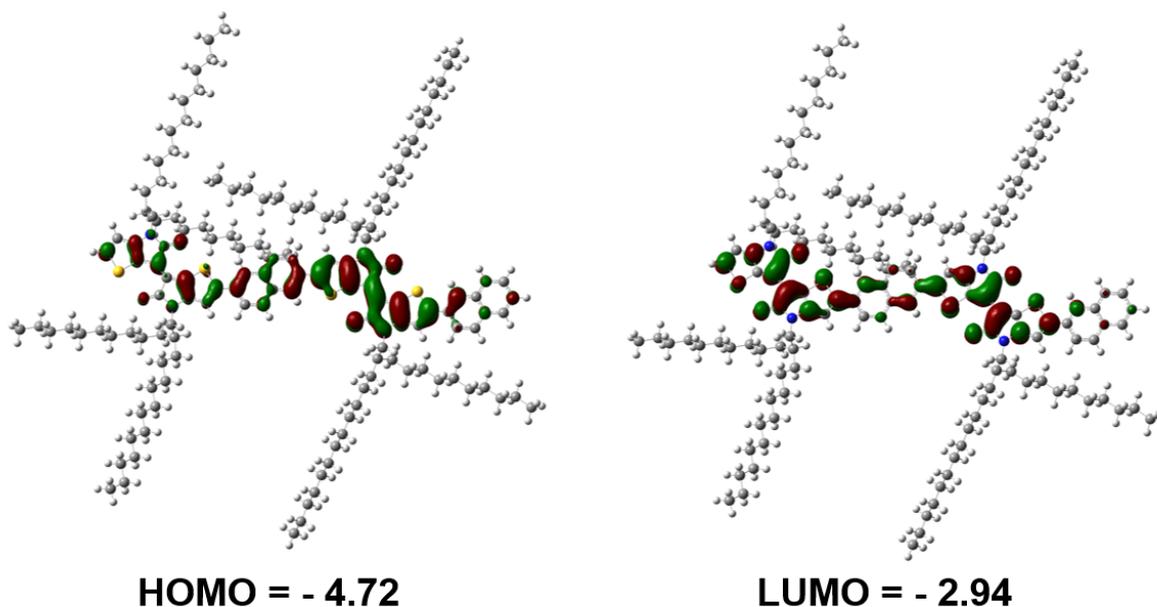


Figure S14. Optimized frontier molecular geometries of simulated HOMO (left) and LUMO (right) for the PTIIG-Np based dimers with 2-decyltetradecyl alkyl substituents (-DT).

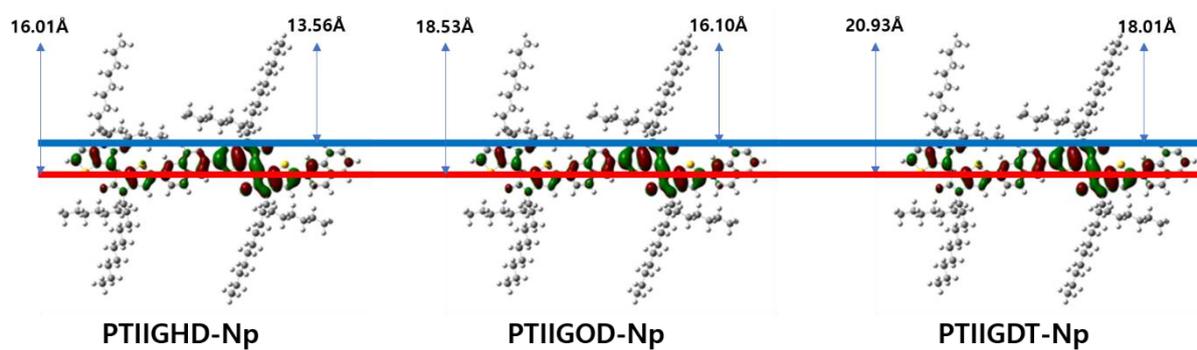


Figure S15. Theoretical lengths of different alkyl substituents (-HD, -OD, -DT) from the TIIG core obtained by Density functional theory (DFT) calculations.

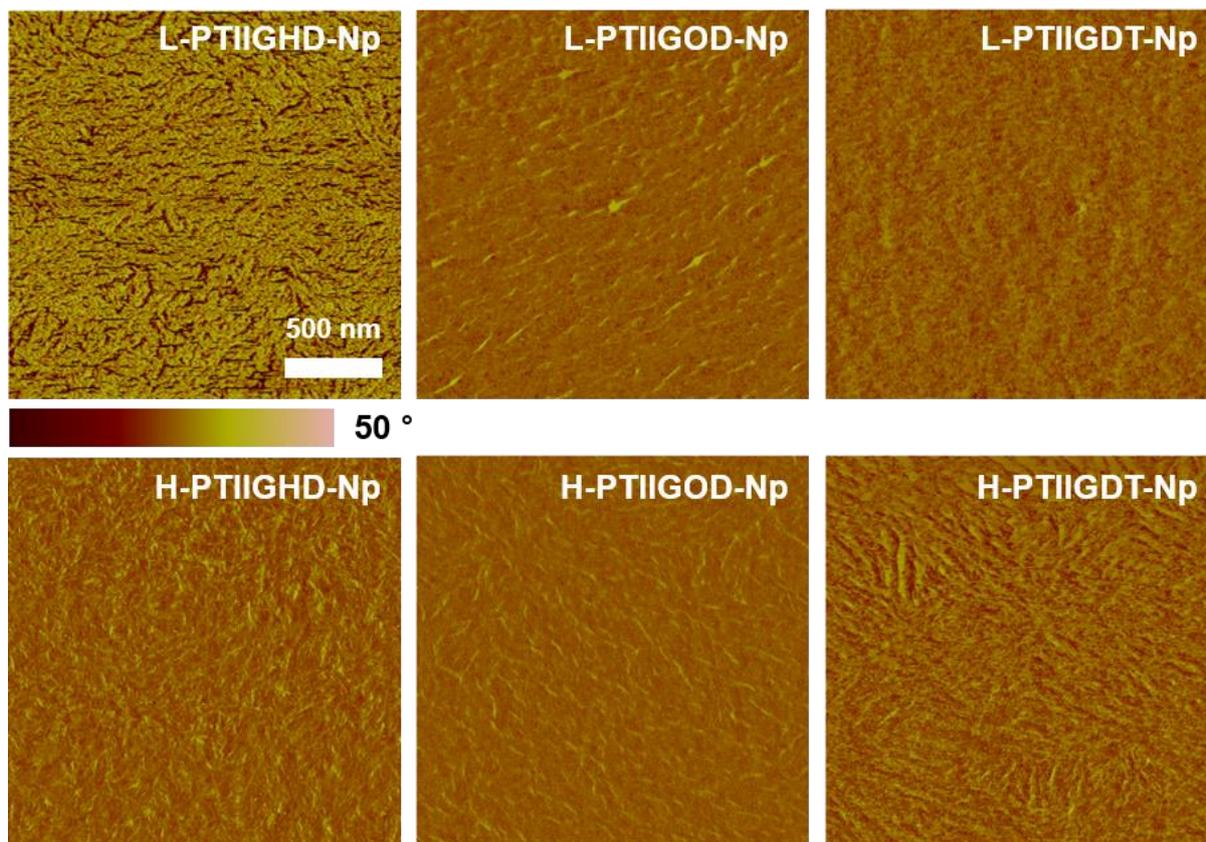


Figure S16. AFM phase images of the PTIIG-Np polymers depending on the length of alkyl substituents (-HD, -OD, -DT) and molecular weight (L-, H-), where scale bar is 500 nm.

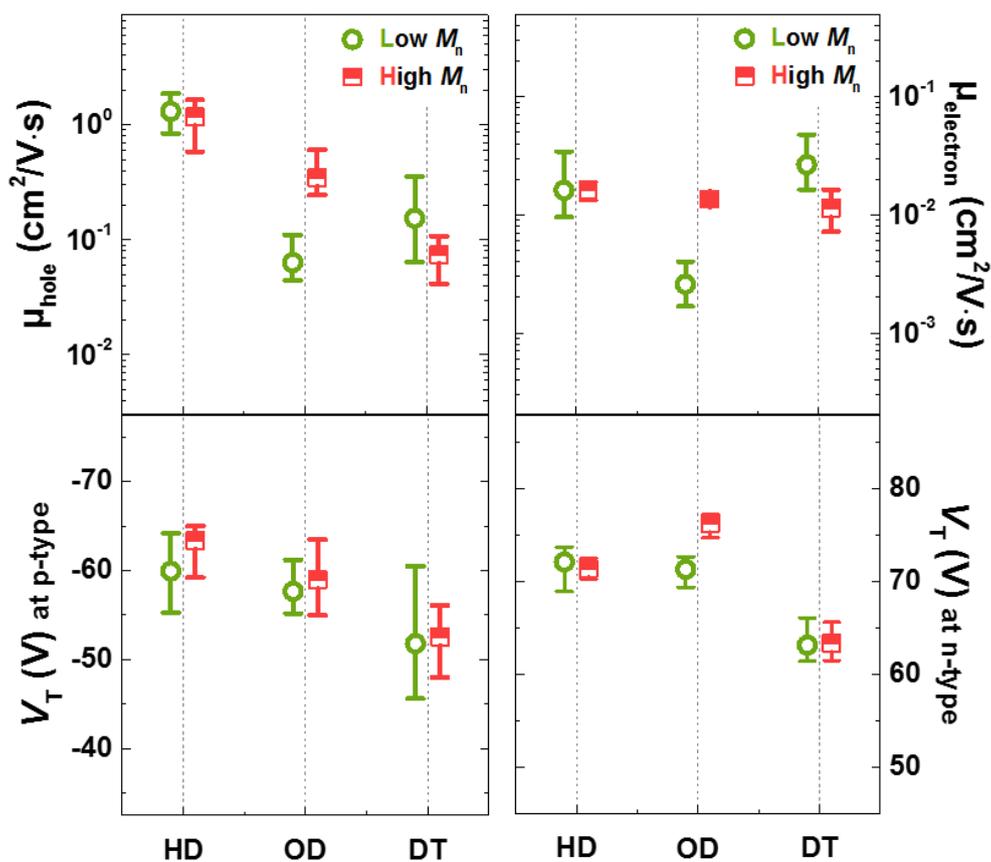


Figure S17. The distributions of charge carrier mobilities (μ) and threshold voltages (V_T) resulted from OFETs using PTIIG-Np based polymers (PTIIGHD-Np, PTIIGOD-Np, and PTIIGDT-Np) [left panel: p-type (at $V_{DS} = -100$ V), right panel: n-type (at $V_{DS} = 100$ V) characteristic]

Table S1. Crystallography parameters of PTIIG-Np polymers with different alkyl substituents (-HD, -OD, -DT) and molecular weight (L-, H-).

		In-plane				Out-of-plane			
		q_{xy} (\AA^{-1})	d-spacing (\AA)	FWHM (\AA^{-1})	Coherence length (\AA)	q_z (\AA^{-1})	d-spacing (\AA)	FWHM (\AA^{-1})	Coherence length (\AA)
L-PTIIGHD-Np	(100)	0.2918	21.5	-	-	0.2922	21.5	-	-
	(010)	1.7116	3.7	0.2140	26.4	1.7097	3.7	0.1800	31.4
H-PTIIGHD-Np	(100)	0.2881	21.8	-	-	0.2941	21.4	-	-
	(010)	1.7032	3.7	0.2017	28.0	1.7227	3.7	0.1954	28.9
L-PTIIGOD-Np	(100)	0.2601	24.2			0.2569	24.5	-	-
	(010)	1.6930	3.7	0.1518	37.3	1.6999	3.7	0.1729	32.7
H-PTIIGOD-Np	(100)	0.2583	24.3			0.2569	24.5	-	-
	(010)	1.7049	3.7			1.6999	3.7	0.1698	33.3
L-PTIIGDT-Np	(100)	0.2434	25.8			0.2271	27.7	-	-
	(010)	1.7066	3.7	0.2647	21.4	1.7162	3.7	0.2139	26.4
H-PTIIGDT-Np	(100)	0.2413	26.0	-	-	0.2308	27.2	-	-
	(010)	1.7028	3.7	0.1154	49.0	1.6901	3.7	0.1154	49.0

Table S2. Relative ratios of face-on to edge-on π - π stacking crystallites.

	Population of face-on crystallites
	A_{xy}/A_z ratio value
L-PTIIGHD-Np	0.16
H-PTIIGHD-Np	0.07
L-PTIIGOD-Np	0.17
H-PTIIGOD-Np	0.04
L-PTIIGDT-Np	0.12
H-PTIIGDT-Np	0.05

References

- (1) Ashraf, R. S.; Kronemeijer, A. J.; James, D. I.; Sirringhaus, H.; McCulloch, I., A New Thiophene Substituted Isoindigo Based Copolymer for High Performance Ambipolar Transistors. *Chem. Commun.* **2012**, *48*, 3939-3941.
- (2) Dutta, G. K.; Han, A. R.; Lee, J.; Kim, Y.; Oh, J. H.; Yang, C., Visible-Near Infrared Absorbing Polymers Containing Thienoisindigo and Electron-Rich Units for Organic Transistors with Tunable Polarity. *Adv. Funct. Mater.* **2013**, *23*, 5317-5325.
- (3) Guo, X.; Watson, M. D., Conjugated Polymers from Naphthalene Bisimide. *Org. Lett.* **2008**, *10*, 5333-5336.
- (4) Kim, G.; Kang, S.-J.; Dutta, G. K.; Han, Y.-K.; Shin, T. J.; Noh, Y.-Y.; Yang, C., A Thienoisindigo-Naphthalene Polymer with Ultrahigh Mobility of 14.4 cm²/V·s That Substantially Exceeds Benchmark Values for Amorphous Silicon Semiconductors. *J. Am. Chem. Soc.* **2014**, *136*, 9477-9483.
- (5) Kim, G.; Kim, H.; Jang, M.; Jung, Y. K.; Oh, J. H.; Yang, C., Ultra-Narrow-Bandgap Thienoisindigo Polymers: Structure-Property Correlations in Field-Effect Transistors. *J. Mater. Chem. C* **2016**, *4*, 9554-9560.
- (6) Shin, J.; Park, G. E.; Lee, D. H.; Um, H. A.; Lee, T. W.; Cho, M. J.; Choi, D. H., Bis(thienothiophenyl) Diketopyrrolopyrrole-Based Conjugated Polymers with Various Branched Alkyl Side Chains and Their Applications in Thin-Film Transistors and Polymer Solar Cells. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3280-3288.
- (7) Van Pruissen, G. W. P.; Gholamrezaie, F.; Wienk, M. M.; Janssen, R. A. J., Synthesis and Properties of Small Band Gap Thienoisindigo Based Conjugated Polymers. *J. Mater. Chem.* **2012**, *22*, 20387-20393.

(8) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C., Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. *Adv. Mater.* **2011**, *23*, 2367-2371.