Supplementary information for:

Impact of aromatic to quinoidal transformation on the degradation kinetics of imine-based semiconducting polymers

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Author Contributions

⁋Naoya Nozaki and Azalea Uva contributed equally.

Contents

General

Materials

All chemicals and solvents were of reagent grade purchased from Derthon Optoelectronic Materials Co., Kanto Chemical Co., Inc., Tokyo Kasei Chemical Industries, Wako Pure Chemical Industries, and Sigma Aldrich and used without further purification.

Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECZ400S FT-NMR at 400 MHz at room temperature for small molecules and 120°C for polymers. Chemical shifts for ^{1}H-NMR spectra were reported in parts per million and were referenced to residual protonated solvent ($CDCl_3$: δ 7.25, DMSO-d_6: δ 3.33, 1,1,2,2-tetrachloroethane-d_2: δ 5.96-5.97, dichloromethane-d_2: δ 5.29), and that for ^{13}C-NMR spectra were reported in parts per million and were referenced to solvent ($CDCl_3$: δ 77.1, DMSO-d_6: δ 40.0, dichloromethane-d_2: δ 54.1-53.0).

High resolution mass spectroscopy

The exact mass for all reported small molecules was detected by using a Bruker micrOTOF II with electrospray ionization.

Gel permeation chromatography

Number average molecular weight (Mn), weight average molecular weight (Mw), and dispersity ($Đ$) were characterized by gel permeation chromatography (GPC) on a Tosoh EcoSEC instrument (model HLC®-8321GPC/HT) equipped with two Tosoh TSKgel GMH_{HR}-H(S)-HT2 columns and a dual-flow refractive-index detector. HPLC grade 1,2,4-trichlorobenzene containing butyl butylated hydroxytoluene (BHT, 0.015%. 500 mg in 4 L) was filtered through basic alumina (Sigma-Aldrich) and used as the eluent at 135 °C with a flow rate of 0.5 mL/min. The system was calibrated against monodisperse polystyrene standards (Tosoh oligomer kit A2500-F128) and data processing was performed using the EcoSEC Data Analysis software (version 1.14).

All samples were prepared with concentrations of ~0.30 mg/mL using the same solvent as the system (HPLC grade 1,2,4-trichlorobenzene containing 0.015% BHT). The samples were left on a shaker for 18 hours at 330 rpm, followed by heating at 135°C for 5 minutes to fully dissolve the polymers. All samples were filtered using a 0.22 μm PTFE filter before transferring into the GPC vials.

Thermogravimetry

Thermogravimetry analysis (TGA) curves were measured using a Rigaku Thermo plus EVO TG

8120 thermal analyzer under N_2 atmosphere, heated from room temperature to 500°C with a 10°C/min of heating rate.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was collected by a HITACHI DSC7000X Thermal Analysis System with 5°C/min of heating and cooling rate under N_2 atmosphere. The scanning was conducted at a temperature area from -50°C to 300°C with two scanning cycles for both samples.

Ultraviolet-visible-near-infrared absorption spectroscopy

JASCO V-670 was used to collect UV-vis-NIR spectra. For solution measurements, a quartz cell with a 10 mm light path was used. For film measurements, a quartz plate was used.

Cyclic voltammetry

For cyclic voltammetry (CV) measurements, a Solartron SI 1287 electrochemical interface was used. The reference electrode was $Ag/AgNO_3$, the working electrode was glassy carbon with polymer films, and the counter electrode was Pt. 0.1 M tetrabutylammonium hexafluorophosphate (TBA PF_6) / acetonitrile solution was used as an electrolyte and ferrocene was used as a standard calibration. The scanning rate was 50 mV/sec.

Density functional theory (DFT) calculation

All computations were performed at the theoretical level of B3LYP-D3/6-31G** level.[1]

Grazing incidence wide-angle X-ray scattering (GIWAXS)

Two-dimensional grazing incidence wide-angle X-ray scattering (GIWAXS) patterns were measured at SPring-8 on beamline BL40B2. The samples were irradiated at a fixed incident angle on the order of 0.10 ° and the GIWAXS patterns were recorded with a photon-counting detector (Eiger2 S 500K, Dectris, Ltd.). The wavelength of the X-ray beam was 0.1 nm (energy of 12.39 KeV) and the camera length was 111.0240 mm for pristine polymer thin films and 107.9015 mm for protonated ones. In this study, Scherrer's equation was used for the CCL determination as shown below,

$$CCL = \frac{2\pi K}{FWHM} = \frac{2K\sqrt{ln2/\pi}\lambda}{\Delta(s)_{hkl}}$$

, where K=1 and $\lambda = 0.1$nm. $\Delta(s)_{hkl}$ was extracted from Gaussian fitting.

Thin film preparation & Field-effect transistors (FET)

Polymer solutions (2mg/mL in chloroform) were heated for 30 minutes at 70°C before use. Thin films were prepared on 300 nm SiO_2 treated with octadecyltrimethoxysilane (OTMS). The spin-coating conditions were 0 rpm for 30 seconds, then 1000 rpm for 60 seconds. The as-spun substrates were heat-annealed at 250°C for 15 minutes. To prepare the protonated samples, a saturated PTSA/chloroform solution (14.7 mmol/L, *ca.* 15 equiv. to the repeating unit of polymers) was made at room temperature. Protonated polymer thin films were prepared following the same method as the pristine polymers.

For FET measurements, Au electrode was deposited with 1000 μm width and 50 μm channel length, and then bottom-gate top-contact thin film transistors were fabricated. To prepare OTMS-treated SiO_2 a solution of OTMS (20μL OTMS in 20 mL trichloroethylene) was spin-coated on silicon wafers at 3000 rpm for 30 sec. Subsequently, the wafers were exposed to saturated ammonium hydroxide vapor and then washed with toluene and water.

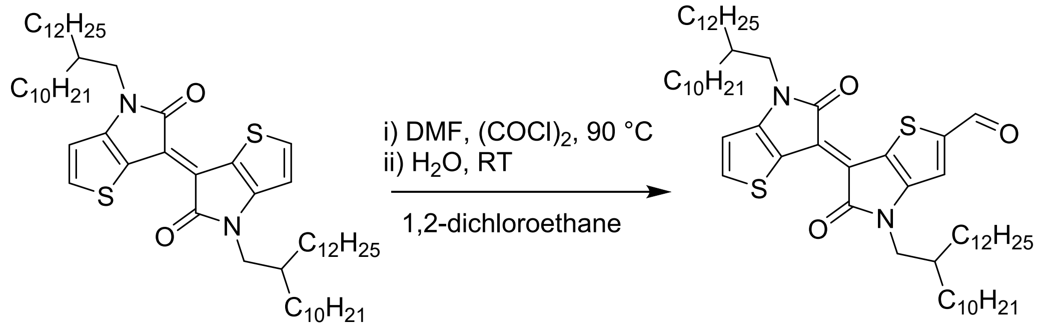
All field effect transistors (FET) were electrically characterized using a Keithley4200 semiconductor parameter analyzer under vacuum at room temperature.

Infrared Spectroscopy (IR)

JASCO FT/IR-6300 was used to collect IR spectra. The samples and KBr were grinded and mixed using a mortar, and pellets were made using a mold with a diameter of 3 mm. The measurements were conducted by integrating over 256 scans.

Synthesis

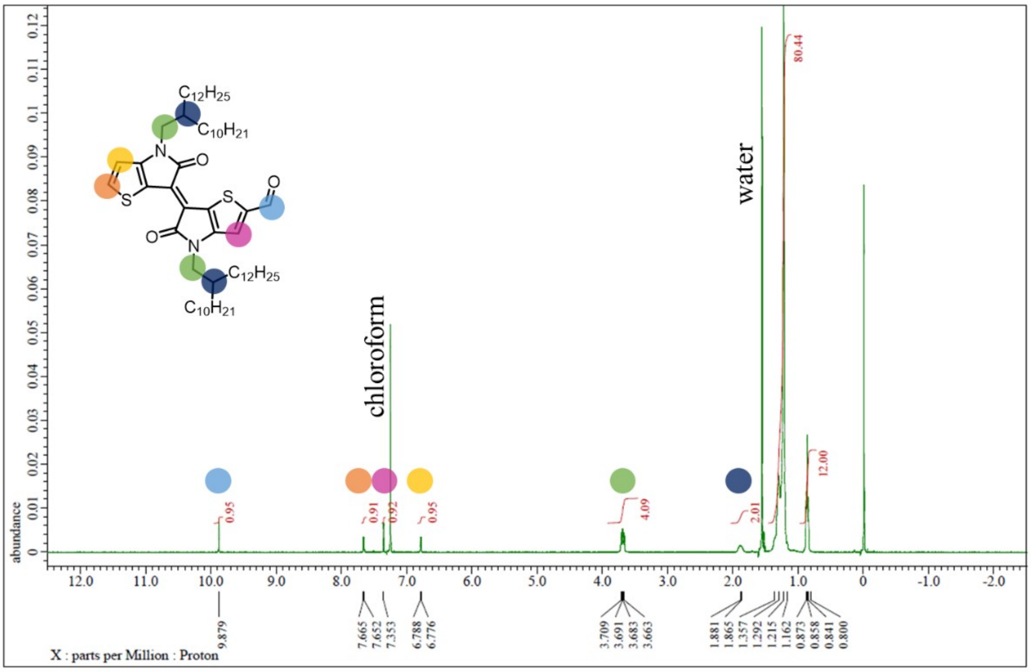
Preparation of thienoisoindigo monoaldehyde (TII-CHO)



To a flame dried 100 mL two-necked round flask, TII (0.38 g, 0.40 mmol, 1 equiv.),[2] 1,2-dichloroethane (40 mL) were added. Then, DMF (0.31 mL, 4.01 mmol, 10 equiv.) and oxalyl chloride (0.34 mL, 4.01 mmol, 10 equiv.) to synthesize Vilsmeier reagent *in situ* and heated to 90°C overnight. After, water (10mL) was poured into the reaction mixture with color changing from green to indigo blue. The reaction mixture was washed with water (150 mL), dried with Na_2SO_4, and the solvent removed in vacuo. The crude was purified *via* silica chromatography (9:1 to 0:1 of hexane: dichloromethane) to yield a dark blue oil after evaporation. Yield: 0.38 g (97.1%)

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.66 (d, J = 5.0 Hz, 1H), 7.35 (s, 1H), 6.78 (d, J = 5.0 Hz, 1H), 3.69 (dd, J = 10.7, 7.5 Hz, 4H), 1.87 (d, J = 6.4 Hz, 2H), 1.36-1.16 (m, 80H), 0.87-0.80 (m, 12H)
^{13}C-NMR (100 MHz, $CDCl_3$) δ 182.9, 171.2, 170.3, 154.3, 150.3, 146.9, 138.0, 125.0, 123.2, 119.4, 115.1, 114.6, 111.7, 110.8, 46.3, 37.2, 37.1, 32.0, 31.5, 30.1, 30.0, 29.8, 29.7, 29.7, 29.5, 29.4, 26.5, 22.8, 14.3
ESI-HRMS m/z observed: 997.7224 [M + Na^+] (expected: 997.7332 [M + Na^+])

(a)



(b)

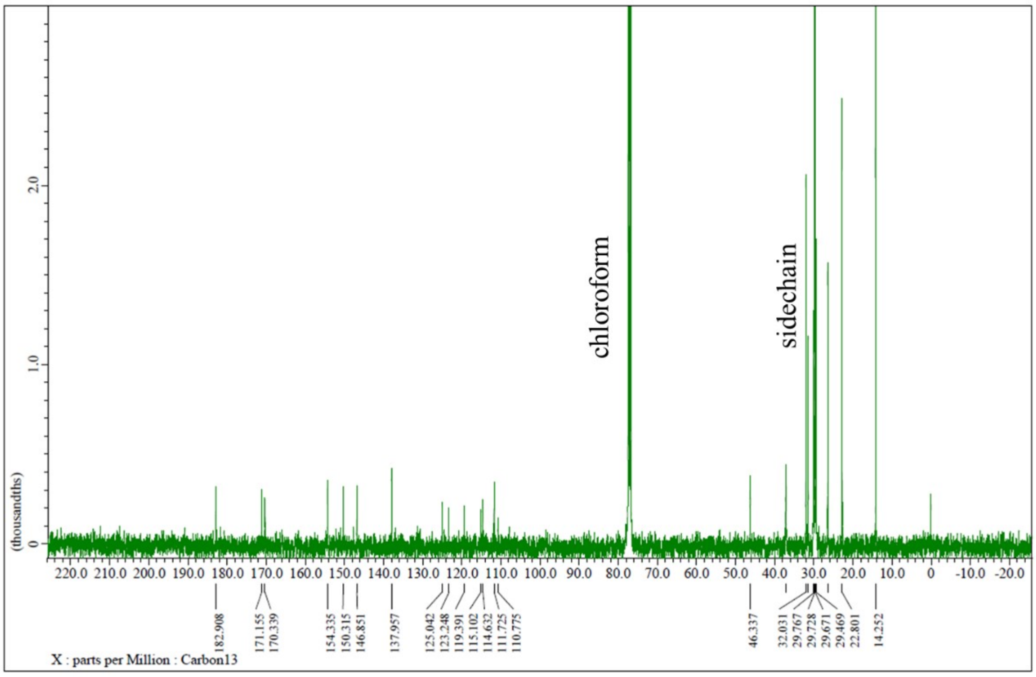


Figure S1. (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of TII-CHO.

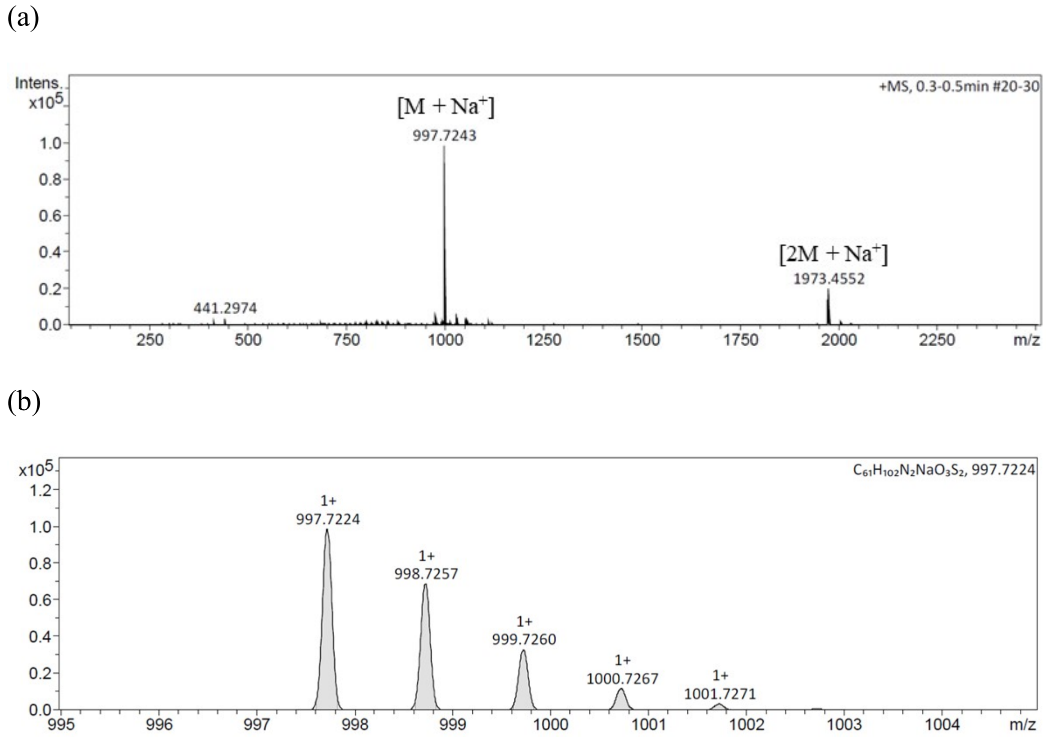
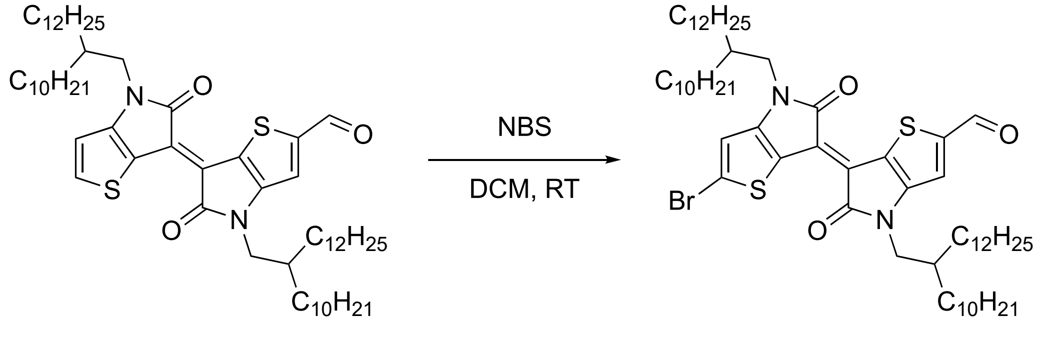


Figure S2. High-resolution ESI-MS results of TII-CHO. (a) Overall and (b) zoomed spectra.

Preparation of thienoisoindigo monoaldehyde bromide (Br-TII-CHO)



TII-CHO Br-TII-CHO

To a flame dried 100 mL two-necked round flask, TII-CHO (0.38 g, 0.29 mmol, 1 equiv.), dichloromethane (40 mL) and NBS (0.076 g, 0.43 mmol, 1.1 equiv.) were added, and the reaction mixture was stirred at room temperature overnight. Then, the reaction mixture was washed with water (150 mL), dried with Na_2SO_4, and the solvent removed in vacuo. The crude was purified *via* silica chromatography (9:1 to 0:1 of hexane: dichloromethane) to yield a dark bluish purple solid precipitation in cold methanol. Yield: 0.36 g (87.6%)

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.34 (s, 1H), 6.83 (s, 1H), 3.66 (dd, J = 23.1, 7.5 Hz, 4H), 1.86 (d, J = 28.8 Hz, 2H), 1.28-1.18 (m, 80H), 0.87-0.82 (m, 12H)
^{13}C-NMR (100 MHz, $CDCl_3$) δ 182.9, 170.4, 170.2, 152.8, 150.4, 147.1, 127.0, 123.9, 123.1, 118.9, 115.3, 115.2, 115.0, 46.3, 37.3, 37.1, 32.0, 31.5, 31.4, 30.1, 29.8, 29.7, 29.7, 29.5, 26.4, 22.8, 14.3
ESI-HRMS m/z observed: 1075.6312 [M + Na$^+$] (expected: 1075.6437 [M + Na$^+$])

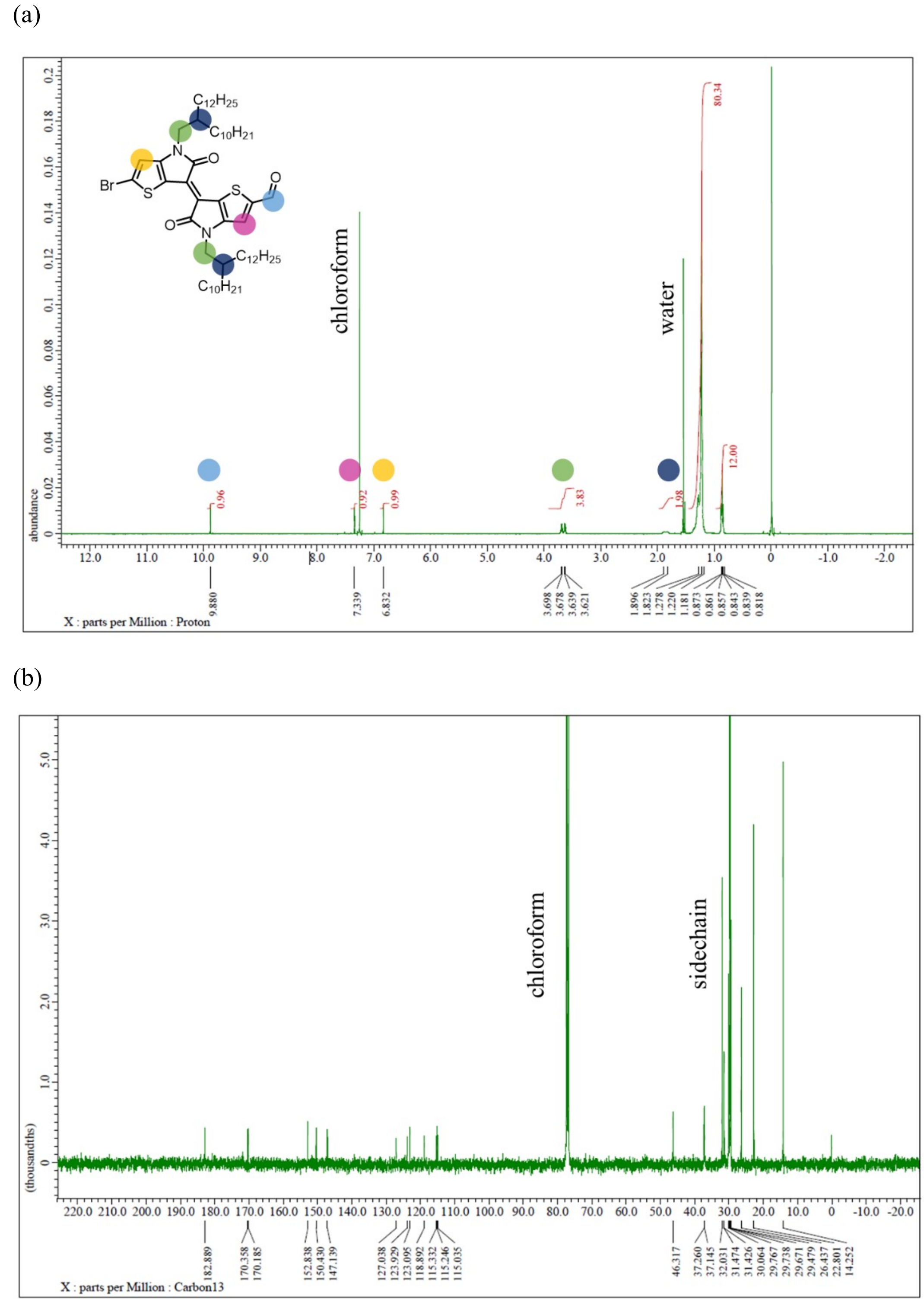


Figure S3. (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of Br-TII-CHO.

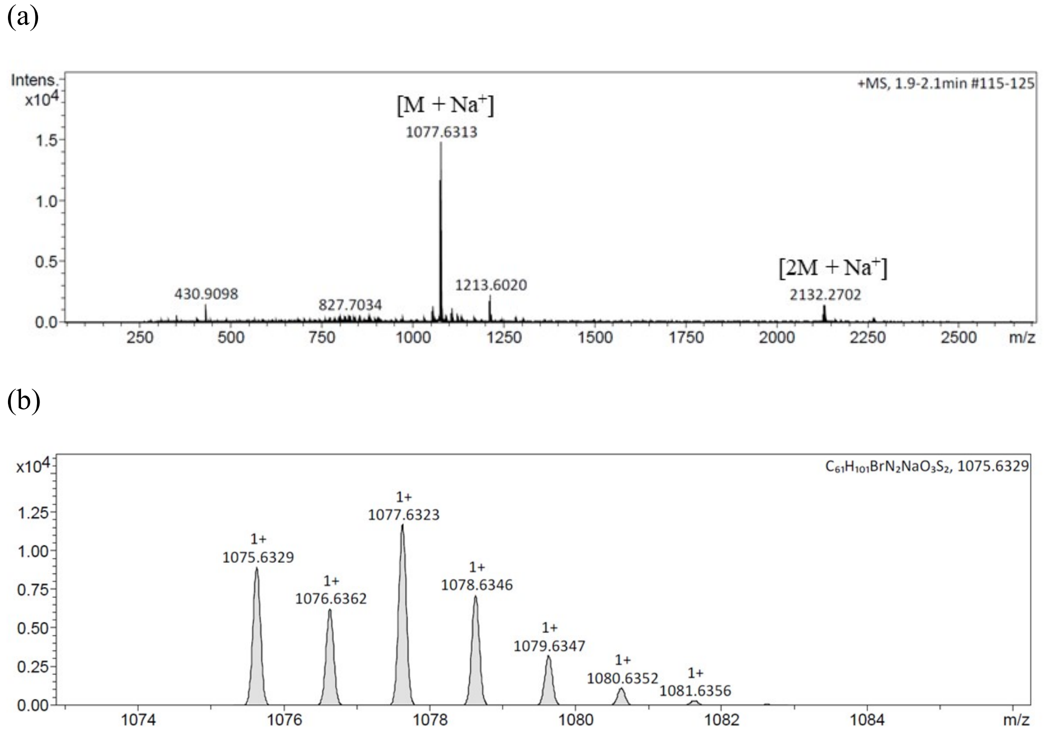
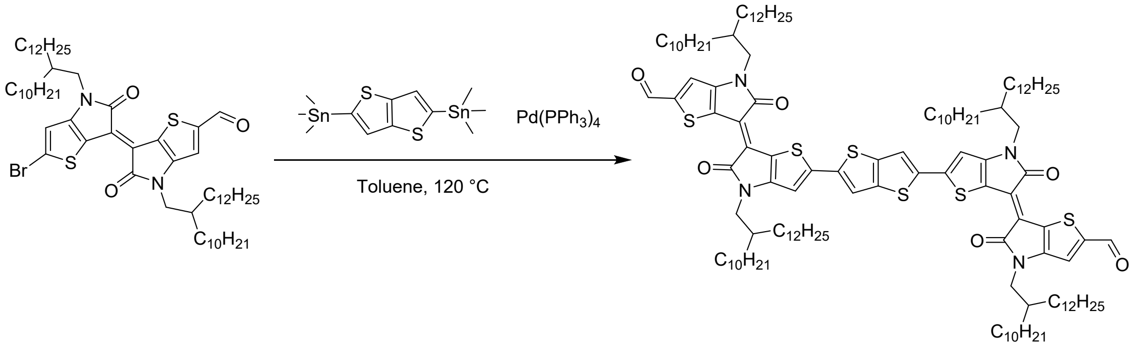


Figure S4. High-resolution ESI-MS results of Br-TII-CHO. (a) Overall and (b) zoomed spectra.

Preparation of (6*E*,6''*E*)-2',2'''-(thieno[3,2-*b*]thiophene-2,5-diyl)bis(4,4'-bis(2-decyltetradecyl)-5,5'-dioxo-4,4',5,5'-tetrahydro-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-2-carbaldehyde) (TT-(TII-CHO)$_2$)



To a flame dried 100 mL two-necked round flask, Br-TII-CHO (796.7 mg, 0.76 mmol, 2.2 equiv.), 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (160.2 mg, 0.34 mmol, 1 equiv.), toluene (40 mL), and tetrakis(triphenylphosphine)palladium(0) (43.7 mg, 0.038 mmol, 0.05 equiv.) were added and the reaction mixture was stirred at 120°C for 2 days. After cross coupling, the reaction mixture was washed with water (150 mL) and dried with Na_2SO_4. The crude was purified by silica gel chromatography (9:1 to 0:1 of hexane: ethyl acetate) to yield a dark green solid after precipitation in cold acetone. Yield: 627.9 mg (87.5%)

^{1}H-NMR (400 MHz, dichloromethane-*d*$_2$) δ 9.70 (s, 2H), 7.24 (s, 2H), 7.15 (s, 2H), 6.85 (s, 2H), 3.68 (dd, J = 20.1, 6.9 Hz, 8H), 1.90 (d, J = 43.9 Hz, 4H), 1.39-1.20 (m, 160H), 0.84-0.81 (m, 24H)

^{13}C-NMR (100 MHz, dichloromethane-*d*$_2$) δ 182.6, 170.3, 169.6, 154.8, 149.9, 148.3, 146.4, 140.7, 140.4, 122.8, 122.6, 117.0, 116.3, 115.0, 107.1, 46.4, 46.3, 37.5, 37.1, 32.0, 31.5, 30.3, 30.2, 29.8, 29.8, 29.5, 26.5, 26.4, 22.8, 14.0

ESI-HRMS m/z observed: 2085.4100 $[M]^+$ (expected: 2085.4105 $[M]^+$)

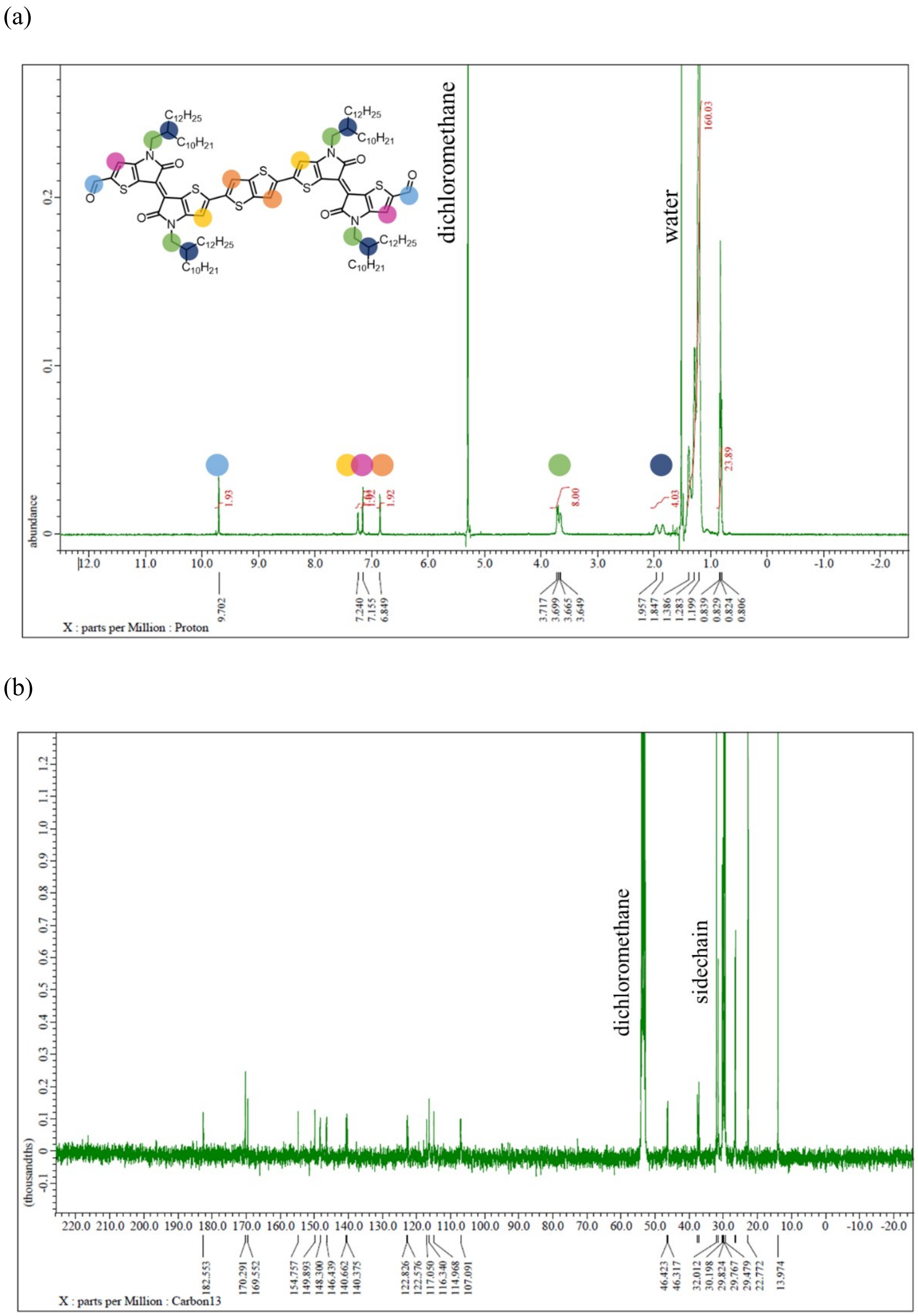


Figure S5. (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of TT-(TII-CHO)$_2$.

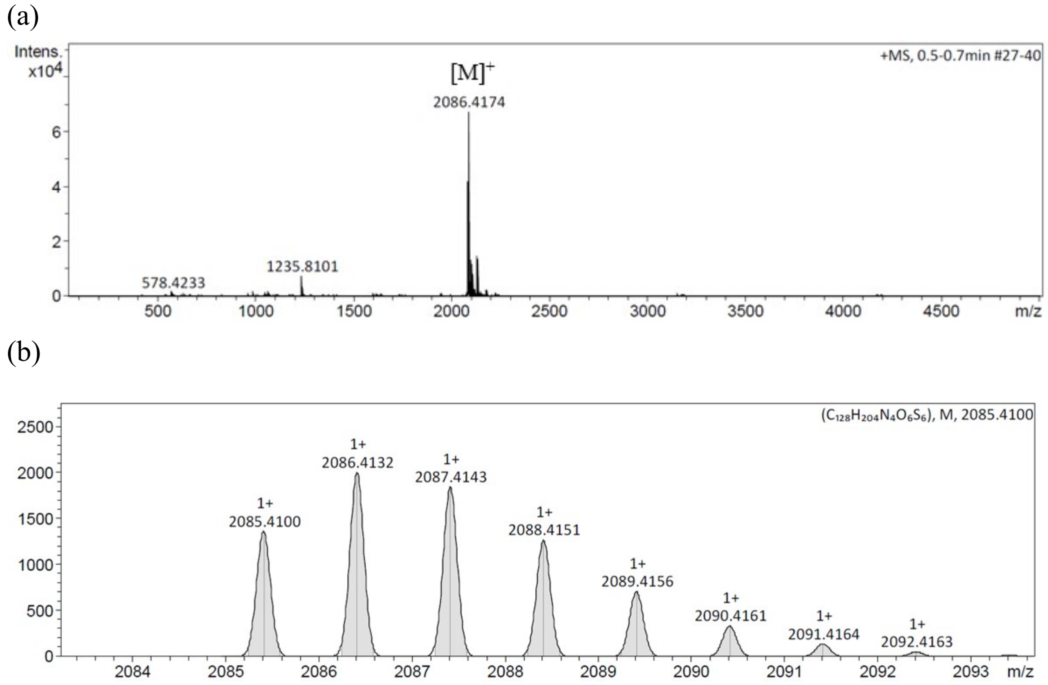
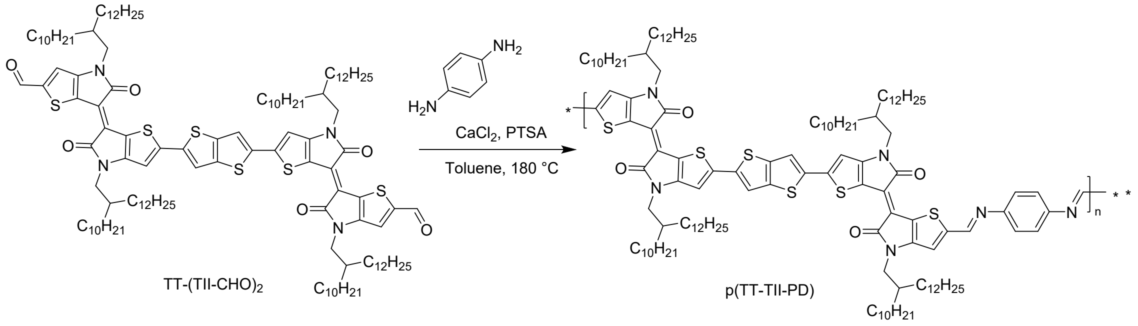


Figure S6. High-resolution ESI-MS results of TT-(TII-CHO)$_2$. (a) Overall and (b) zoomed spectra.

Preparation of p(TT-TII-PD)



To a 5 mL microwave tube, TT-(TII-CHO)$_2$ (104.3 mg, 49.9 µmol, 1.0 equiv.), *p*-phenylenediamine (5.41 mg, 50.0 µmol, 1.0 equiv.), PTSA (0.5 mg, 2.62 µmol, 0.05 equiv.), and CaCl$_2$ (30.0 mg, 270 µmol, 5.4 equiv.) were added. After adding 4 mL of anhydrous toluene as the solvent, the tube was sealed under Ar atmosphere in a glovebox. Then, the reaction tube was set in a microwave reactor and heated for 6 hours at 180°C. Then, the reaction mixture was washed with 150 mL of water and extracted using 100 mL of chloroform. After drying with Na$_2$SO$_4$ and evaporation, 5 mL of chloroform was added to the crude, and it was precipitated in cold methanol. After the Soxhlet purification *via* methanol, acetone, and hexanes (overnight at each time), the polymer was extracted using chloroform. After removing chloroform, the residual solution was precipitated in cold methanol and filtered over a PTFE membrane (0.45 µm pore size). After drying in vacuo, a dark green solid was obtained. Yield: 62.5 mg (58%).

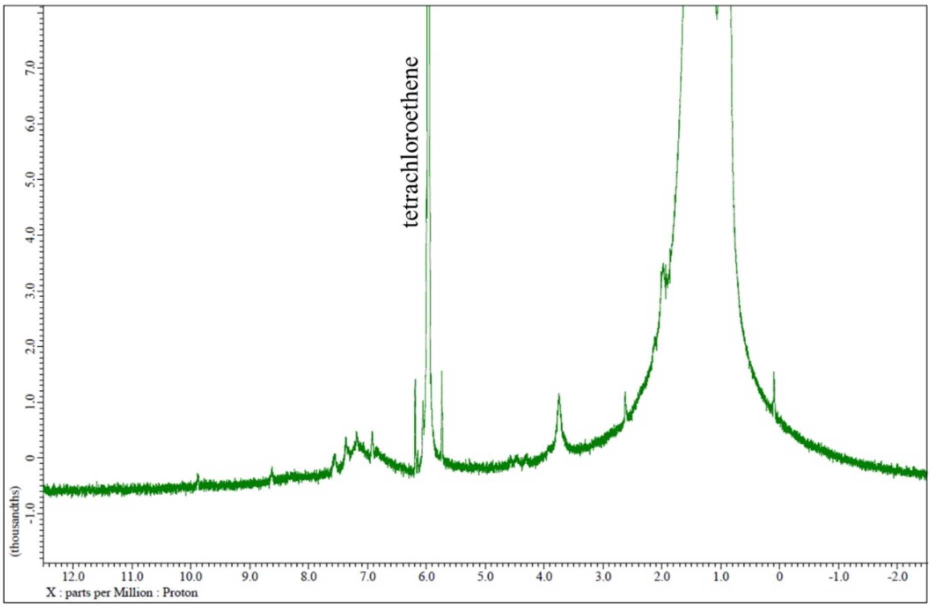
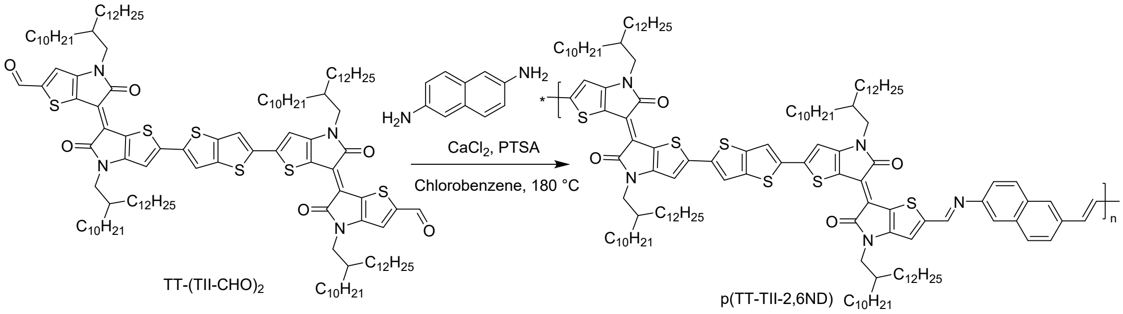


Figure S7. ^{1}H-NMR of p(TT-TII-PD)

Preparation of p(TT-TII-2,6ND)



To a 5 mL microwave tube, TT-(TII-CHO)$_2$ (48.0 mg, 23.0 µmol, 1.0 equiv.), 2,6-naphthalene diamine (3.64 mg, 23.0 µmol, 1.0 equiv.), PTSA (4.0 mg, 21.0 µmol, 0.9 equiv.), and CaCl$_2$ (20.0 mg, 180 µmol, 7.8 equiv.) were added. After adding 4 mL of anhydrous chlorobenzene as the solvent, the tube was sealed under Ar atmosphere in a glovebox. Then, the reaction tube was set in a microwave reactor and heated for 2 hours at 180°C. Then, the reaction mixture was washed with 150 mL of water and extracted using 100 mL of chloroform. After drying with Na$_2$SO$_4$ and evaporation, 5 mL of chloroform was added to the crude, and it was precipitated in cold methanol. After the Soxhlet purification *via* methanol, acetone, and hexanes (overnight at each time), the polymer was extracted using chloroform. After removing chloroform, the residual solution was precipitated in cold methanol and filtered over a PTFE membrane (0.45 µm pore size). After drying in vacuo, a dark green solid was obtained. Yield: 40.3 mg (79%).

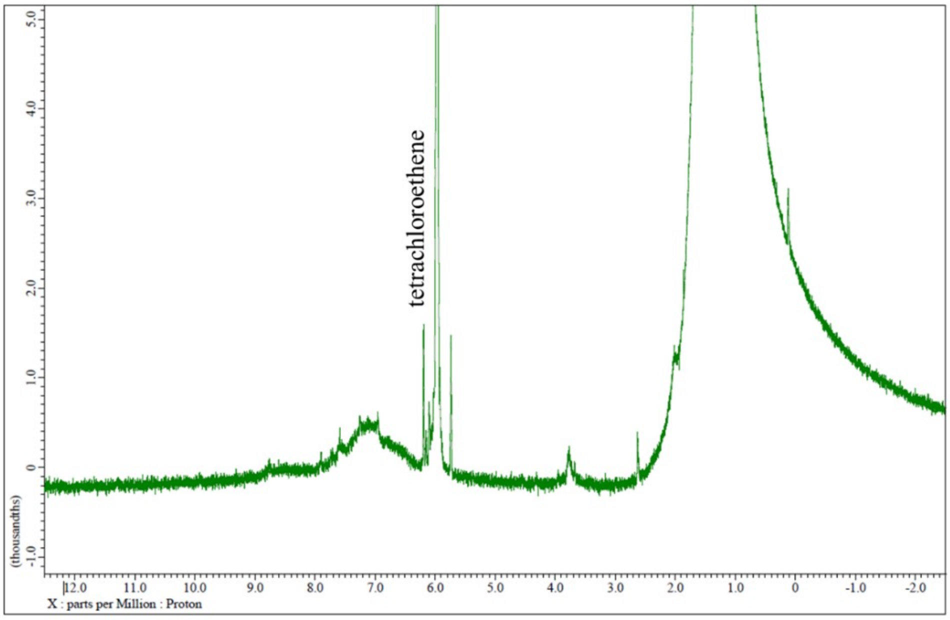


Figure S8. ^{1}H-NMR of p(TT-TII-2,6ND).

Thermal properties

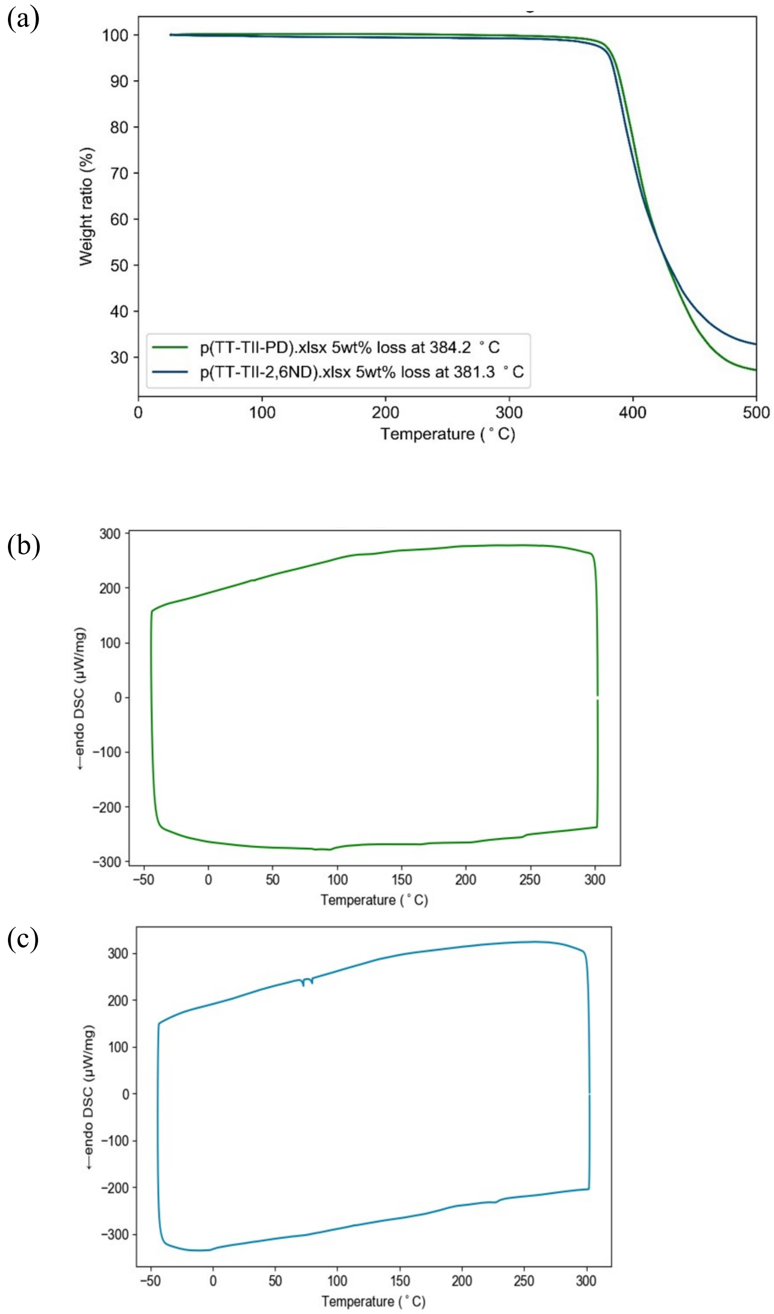


Figure S9. Thermal properties, (a) TGA profiles of both polymers, and DSC curves (the 1st cooling and the 2nd heating) of (b) p(TT-TII-PD) and (c) p(TT-TII-2,6ND).

UV-vis-NIR absorption properties and cyclic voltammetry

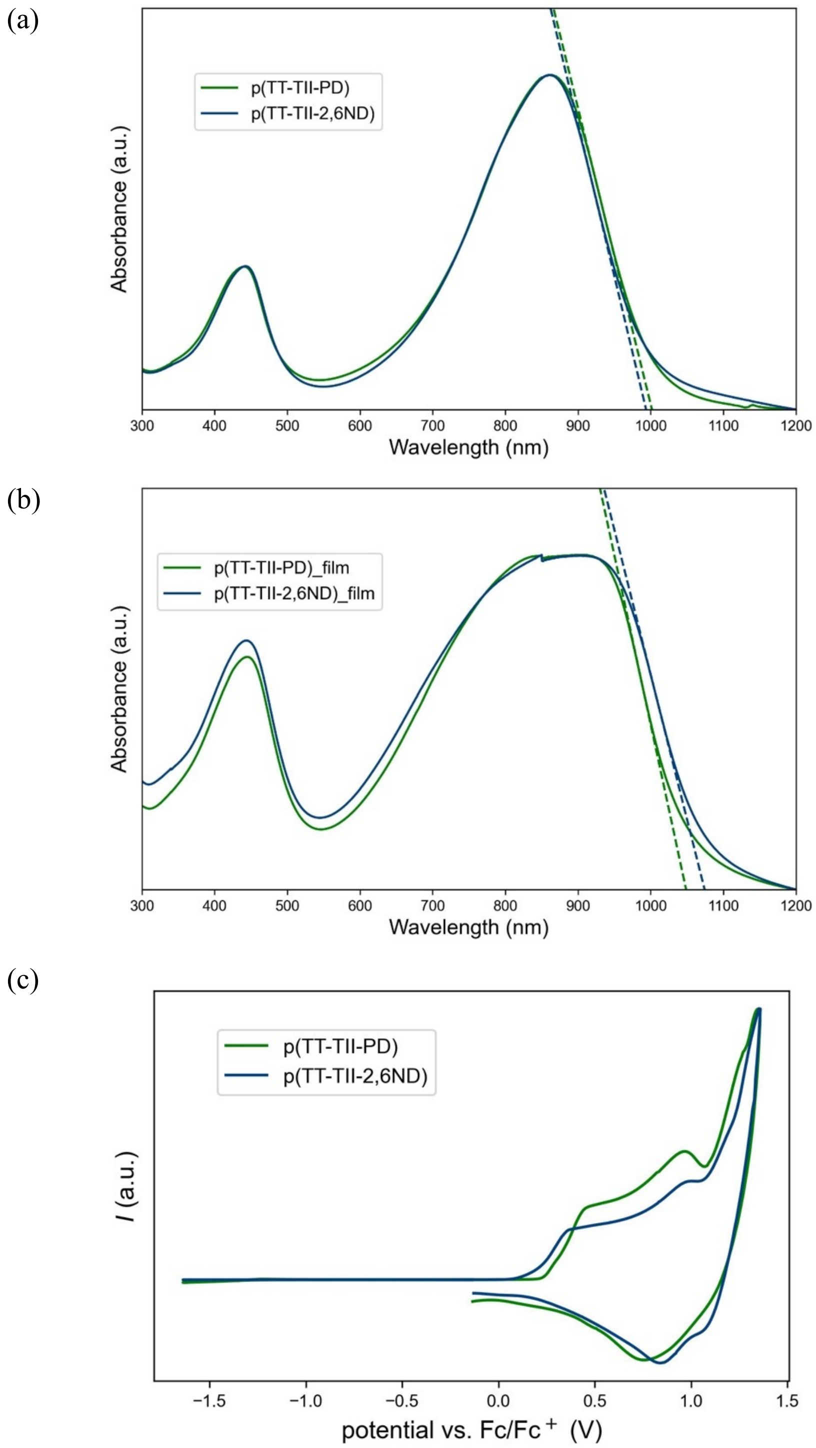


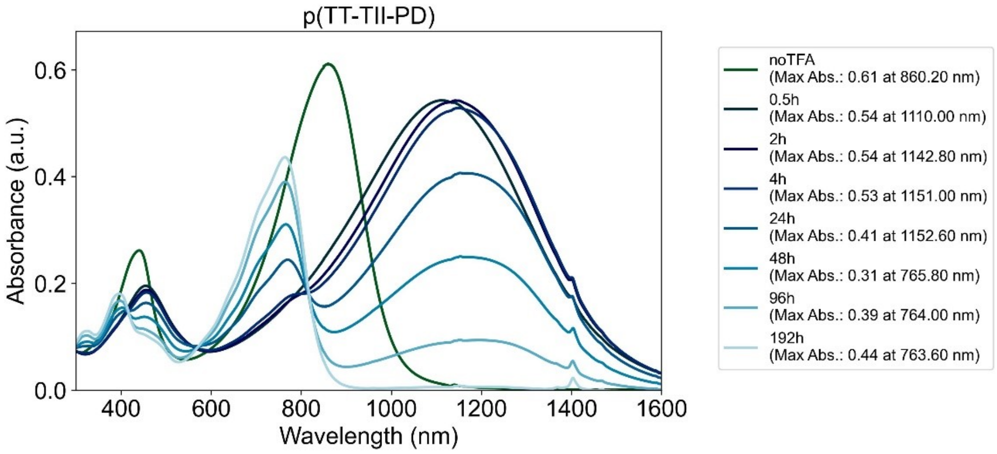
Figure S10. UV-Vis-NIR absorption spectra of p(TT-TII-PD) and p(TT-TII-2,6ND) (a) in chlorobenzene solution and (b) for thin films and (c) CV profiles of p(TT-TII-PD) and p(TT-TII-

2,6ND).

Details for degradation studies

To evaluate the UV-vis-NIR spectra during polymer degradation, a solution of polymers (0.5 mg polymers in 50 mL) was prepared. After collecting spectra of each polymer solution, 250 µL of 1.0 M trifluoroacetic acid aqueous (TFA_{aq}) was added and stirred at room temperature. Subsequently, 3 mL of each solution was used for the UV-vis-NIR absorption measurements at each time point. For p(TT-TII-2,6ND), heating of the reaction mixture at 45°C was started to accelerate hydrolysis, 16 days after adding TFA.

(a)



(b)

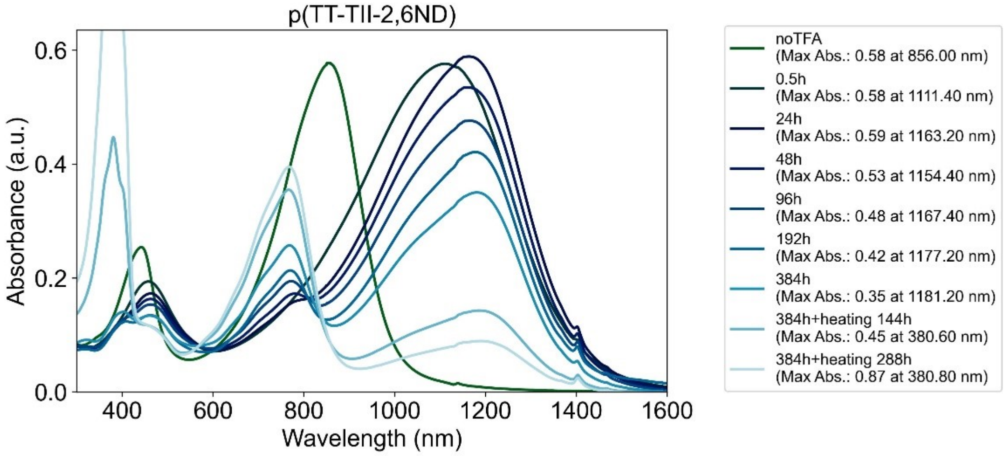


Figure S11. UV-vis-NIR spectra during polymer degradations of (a) p(TT-TII-PD) and (b) p(TT-TII-2,6ND).

Density functional theory (DFT) calculation results

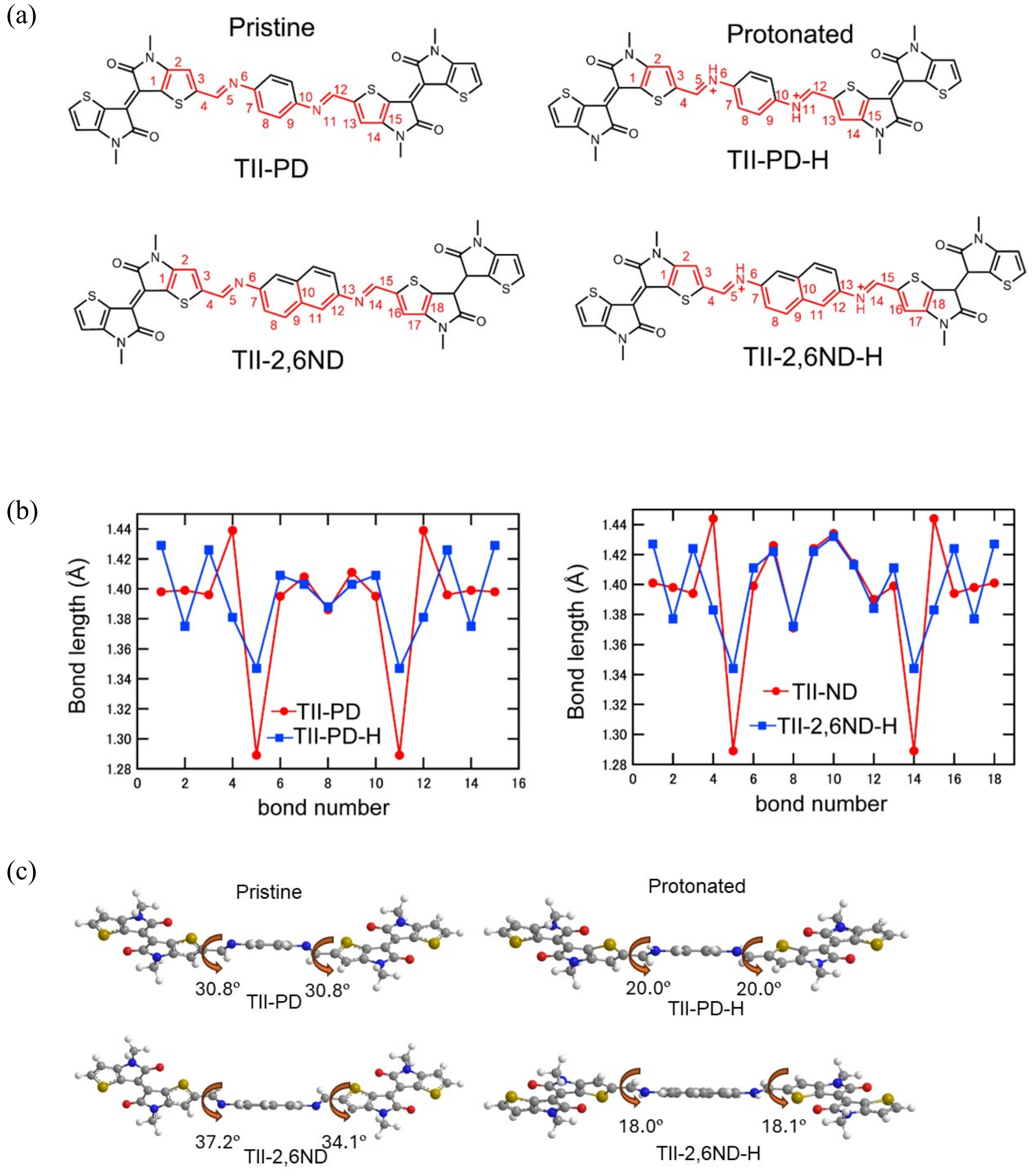


Figure S12. The results of density functional theory (DFT) calculations. (a) Chemical structures and bond numbers of pristine and protonated model molecules, (b) bond length of pristine and protonated model molecules, and (c) coplanarity of pristine and protonated model molecules.

Output Profiles of FETs

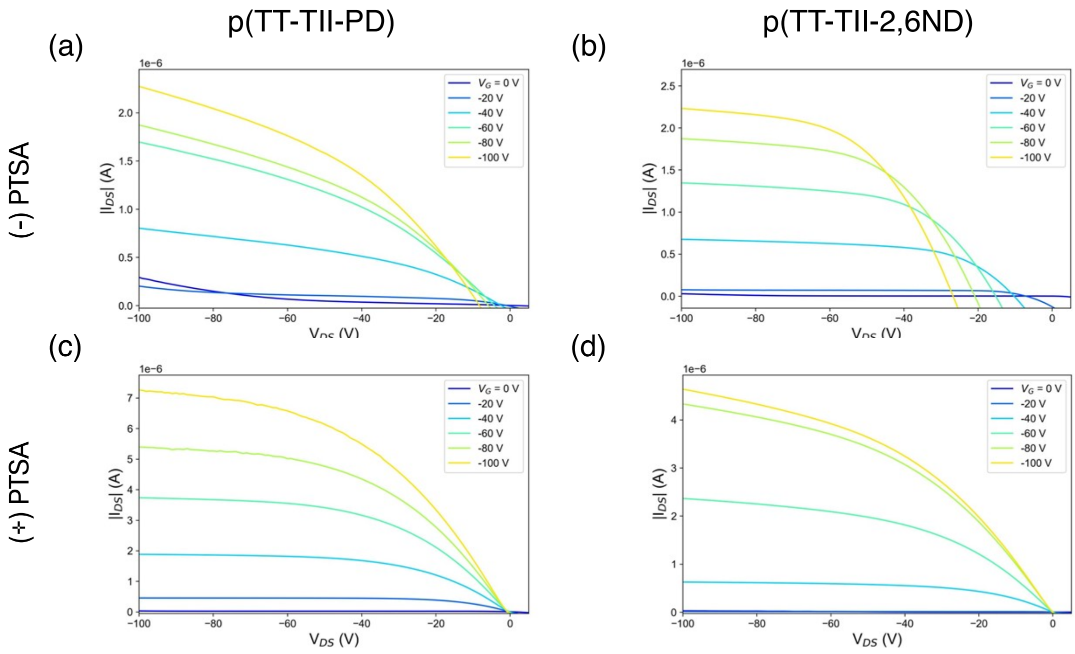


Figure S13. Typical output profiles of pristine ((-)PTSA) and protonated ((+)PTSA) thin films: (a) pristine p(TT-TII-PD), (b) pristine p(TT-TII-2,6ND), (c) protonated p(TT-TII-PD), and (d) protonated p(TT-TII-2,6ND).

Table S1. Morphological properties of pristine polymer thin films.

	Out of plane			
	Lamellar Spacing [a] (Å)	CCL[b] (Å)	π-stacking [c] (Å)	CCL [d] (Å)
p(TT-TII-PD)	26.2	N/A	3.58	44.0
p(TT-TII-2,6ND)	28.2	N/A	3.63	97.5
	In plane			
	Lamellar Spacing [e] (Å)	CCL [d] (Å)		
p(TT-TII-PD)	26.4	204.1		
p(TT-TII-2,6ND)	27.2	164.1		

[a]Estimated from the primal (200) peak. [b] It was impossible to calculate due to the X-ray leakage. [c] π-stacking was estimated from the (010) peak. [d] The CCL was calculated using the Scherrer equation. [e] Estimated from the primal (100) peak.

Table S2. Morphological properties of protonated polymer thin films.

	Out of plane			
	Lamellar Spacing [a] (Å)	CCL [b] (Å)	π-stacking [c] (Å)	CCL[b] (Å)
p(TT-TII-PD)	25.4	57.2	3.52	17.1
p(TT-TII-2,6ND)	23.7	83.7	3.48	23.1

	In plane			
	Lamellar Spacing [d] (Å)	CCL [b] (Å)	π-stacking [c] (Å)	CCL[b] (Å)
p(TT-TII-PD)	26.7	112.1	3.49	28.4
p(TT-TII-2,6ND)	26.2	88.7	3.46	24.8

[a] Estimated from the primal (200) peak. [b] The CCL was calculated using the Scherrer equation. [c] π-stacking was estimated from the (010) peak. [d] Estimated from the primal (100) peak.

GIWAXS results (one-dimensional linecut profiles)

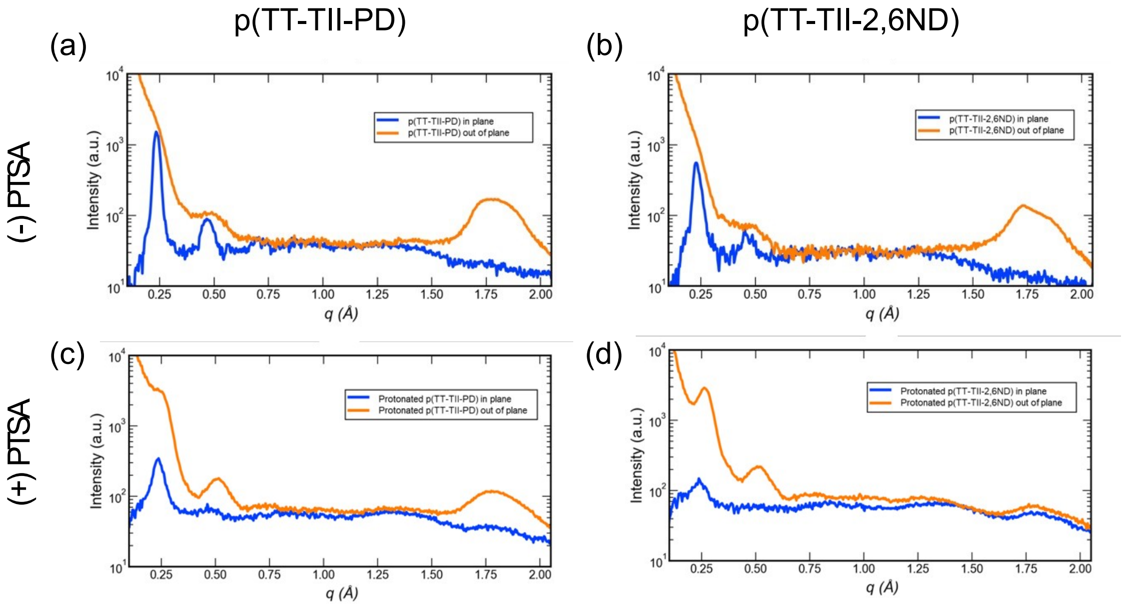


Figure S14. one-dimensional (1-D) profiles of pristine ((-)PTSA) and protonated ((+)PTSA) thin films: (a) pristine p(TT-TII-PD), (b) pristine p(TT-TII-2,6ND), (c) protonated p(TT-TII-PD), and (d) protonated p(TT-TII-2,6ND).

References

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