

## Supplementary information for:

### **Thienoisindigo-based recyclable conjugated polymers for organic electronics.**

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## General

### **Materials**

All chemicals and solvents were of reagent grade purchased from 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 <sup>1</sup>H-NMR spectra were reported in parts per million and were referenced to residual protonated solvent (CDCl<sub>3</sub>: δ 7.25, DMSO-*d*<sub>6</sub>: δ 3.33, 1,1,2,2-tetrachloroethane-*d*<sub>2</sub>: δ 5.96-5.97), and that for <sup>13</sup>C-NMR spectra were reported in parts per million and were referenced to solvent (CDCl<sub>3</sub>: δ 77.1, DMSO-*d*<sub>6</sub>: δ 40.0).

### **Mass spectrometry**

The mass for H-TII was detected by using a JEOL JMS-Q1050GC with an electron ionization.

### **High resolution mass spectrometry**

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 (M<sub>n</sub>), weight average molecular weight (M<sub>w</sub>), and dispersity (Đ) were characterized by gel permeation chromatography (GPC) on a Tosoh EcoESC instrument (model HLC®-8321GPC/HT) equipped with two Tosoh TSKgel GMH<sub>HR</sub>-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 purchased from Tosoh Bioscience LLC (oligomer kit) using A1000, A-2500, A-5000, F-1, F-2, F-4, F-10, F-20, F-40, F-80, and F-128. The calibration curve was fitted to a cubic function (At<sup>3</sup>+Bt<sup>2</sup>+Ct+D+(E/(L-t)<sup>2</sup>) <hyperbolic>) and data processing was performed using the EcoSEC Data Analysis software (version 1.14).

All GPC samples were prepared with concentrations of ~0.25 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 3 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 them into the GPC vials.

### **Thermogravimetry**

Thermogravimetry analysis (TGA) curves were measured using a Rigaku Thermo plus EVO TG 8120 thermal analyzer under N<sub>2</sub> 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<sub>2</sub> atmosphere. The scanning was conducted at a temperature area from -50°C to 250°C with two scanning cycles for both samples.

### **Ultraviolet-visible-near-infrared 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<sub>3</sub>, the working electrode was glassy carbon with polymer films, and the counter electrode was Pt. 0.1 M tetrabutylammonium hexafluorophosphate (TBA PF<sub>6</sub>) / acetonitrile solution was used as an electrolyte and ferrocene was used as a standard calibration. The scanning rate was 50 mV/sec.

### **Field effect transistors**

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

### **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 (Pilatus3 2M, Dectris, Ltd. for **p(TII-PD)** pattern and Eiger2 S 500K, Dectris, Ltd. for **p(TII-2,6ND)** pattern). The wavelength of the X-ray beam was 0.1 nm (energy of 12.39 KeV) and the camera length was 343.6 mm at **p(TII-PD)** measurement and 112.0 mm at **p(TII-2,6ND)** measurement.

### **AFM**

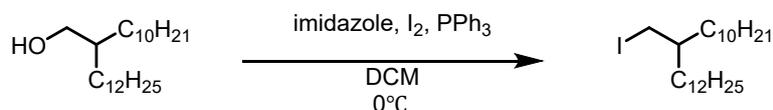
Atomic force microscopy (AFM) images were collected on an SII Nanonavi SPA400 scanning probe microscope with an SII SI-DF20 cantilever in tapping mode at room temperature. The scanning area was 2000 nm × 2000 nm.

**Thin film preparation**

Polymer solutions (2mg/mL in chloroform) were heated for 30min at 70°C before use. Thin films were prepared on 300nm SiO<sub>2</sub> 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 min. For FET measurements, Au electrode was deposited with 1000µm width and 50 µm channel length, and then bottom-gate top-contact thin film transistors were fabricated. To prepare OTMS-treated SiO<sub>2</sub> 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.

## Synthesis

### Preparation of Side chain synthesis: 11-(iodomethyl)tricosane



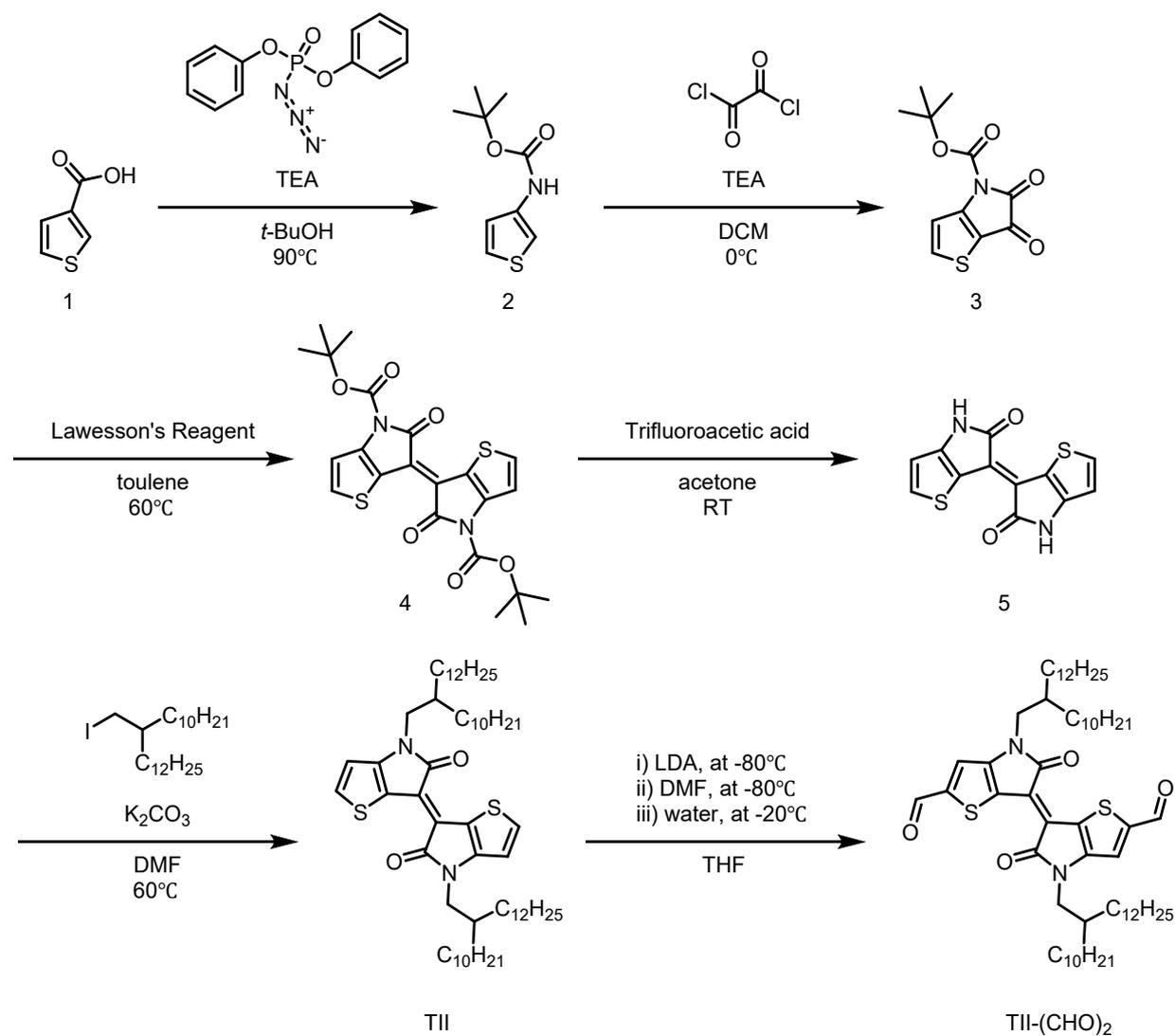
To a 200 ml two-necked round bottom flask, 2-decyltetradecan-1-ol (11.88 g, 33 mmol, 1 equiv.), imidazole (3.42 g, 50 mmol, 1.5 equiv.), and iodine (11.06 g, 44 mmol, 1.3 equiv.) were added. Anhydrous dichloromethane (100 mL) was added, and the reaction was cooled to 0 °C. Then triphenylphosphine (11.42 g, 44 mmol, 1.3 equiv.) was added in small portions. After complete addition, the reaction was stirred for an additional two hours at 0 °C, then allowed to warm up to room temperature. A day later, the solvent was removed via a rotary evaporator. The crude was extracted by hexane and the solution was filtered to remove triphenylphosphine oxide. After that, the crude was purified by silica gel chromatography with hexane, resulting in a colorless oil. Yield: 13.08 g (88%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 3.26 (d, J = 4.6 Hz, 2H), 1.30-1.21 (m, 47H), 0.87 (t, J = 6.9 Hz, 6H)

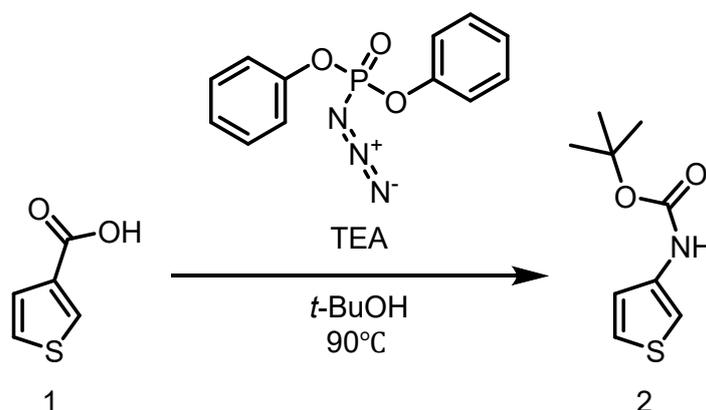
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 38.7, 34.5, 31.9, 29.8-29.5, 26.6, 22.8, 16.9, 14.2

## Overall synthetic scheme for TII-(CHO)<sub>2</sub>

Each step is detailed below. All reactions were performed under inert conditions with anhydrous solvents unless indicated otherwise. To produce product **5**, we followed the method reported in our previous work.<sup>1</sup>



## Preparation of tert-butyl thiophen-3-ylcarbamate

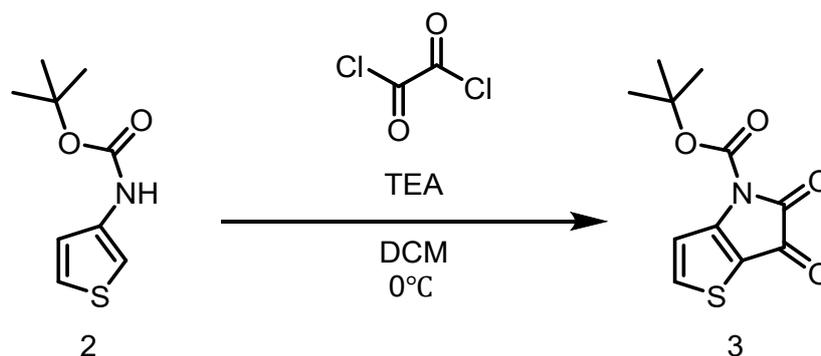


To a 100ml two-necked round bottom flask, thiophene-3-carboxylic acid (2.11 g, 16 mmol, 1 equiv.), *t*-BuOH(40mL), diphenylphosphoryl azide (4.5mL, 21 mmol, 1.3 equiv.), and triethylamine (4.5 mL, 32 mmol, 2 equiv.) were added, and the mixture was heated at 90°C overnight. Then, *t*-BuOH was removed, and the reaction mixture was poured into water (150 mL) and extracted with dichloromethane (150 mL), dried with Na<sub>2</sub>SO<sub>4</sub>, and dried in vacuo. The crude was purified by silica gel chromatography (dichloromethane) to yield a slightly orange-clear solution. After evaporation, the solid was obtained and washed with hexane, eventually yielding white needle-shaped crystals. Yield: 2.41 g (75%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.17 (dq, *J* = 15.0, 2.7 Hz, 2H), 6.89 (d, *J* = 5.9 Hz, 1H), 6.66 (s, 1H), 1.66-1.42 (m, 9H)

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 152.9, 136.2, 124.7, 120.7, 107.4, 80.6, 28.4

## Preparation of tert-butyl 5,6-dioxo-5,6-dihydro-4H-thieno[3,2-b]pyrrole-4-carboxylate

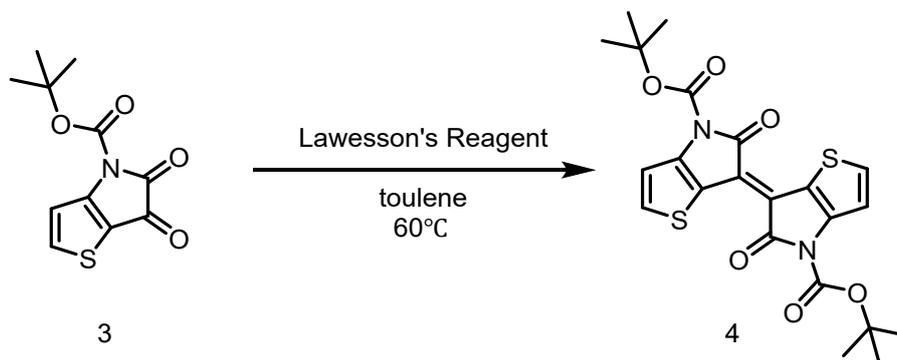


To a 100 mL three-necked round bottom flask with a dropping funnel, oxalyl dichloride (1.4 mL, 16 mmol, 1.3 equiv.) and dichloromethane (10 mL) were added and cooled at 0 °C. tert-butyl thiophen-3-ylcarbamate (2.39 g, 12 mmol, 1 equiv.) dissolved in dichloromethane (40 mL) was added dropwise via the dropping funnel for 30 minutes and the color changed from colorless to clear-yellow. Then, triethylamine (3.4 mL, 24 mmol, 2 equiv.) dissolved in dichloromethane (26.6 mL) was added via syringe for 3 hours and the color changed to yellow-green. After stirring overnight, the reaction was washed with water (150 mL), dried with Na<sub>2</sub>SO<sub>4</sub>, and dried in vacuo. The crude was washed with hexanes, and we obtained a yellow-green powder. Yield: 1.70 g (56%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (dd, J = 20.4, 5.7 Hz, 1H), 7.54-7.49 (m, 1H), 1.69-1.58 (m, 9H)

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 170.0, 160.4, 158.2, 146.8, 143.8, 118.7, 116.2, 85.8, 28.1

**Preparation of di-tert-butyl (E)-5,5'-dioxo-[6,6'-bithieno[3,2-b]pyrrolylidene]-4,4'(5H,5'H)-dicarboxylate**

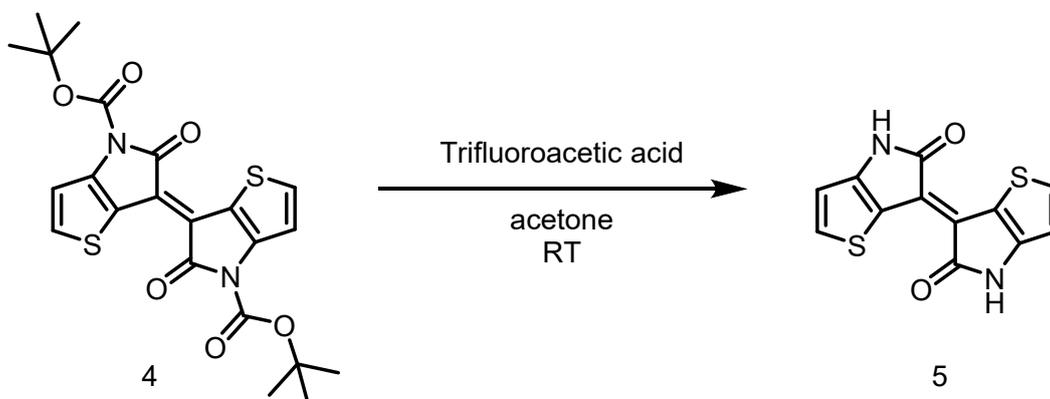


To a 100 mL two-necked flask, tert-butyl 5,6-dioxo-5,6-dihydro-4-thieno[3,2-b]pyrrole-4-carboxylate (1.70 g, 6.71 mmol, 1 equiv.), Lawesson's Reagent (1.36 g, 3.36 mmol, 0.5 equiv.), and anhydrous toluene (20 mL) were added. The reaction was heated at 60 °C for 3 hours and the color changed from yellow-green to wine-red. After evaporation, the crude was purified by silica gel chromatography using dichloromethane to yield a bloody-red solution. The solution was evaporated and washed with methanol to obtain a brown powder. Yield: 0.61 g (38%).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J = 5.0$  Hz, 2H), 7.33 (d,  $J = 5.5$  Hz, 2H), 1.66 (s, 18H)

$^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  168.4, 147.1, 136.7, 132.9, 120.0, 117.6, 117.3, 84.6, 28.2

**Preparation of (E)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'(4H,4'H)-dione (thienoisindigo, H-TII)**



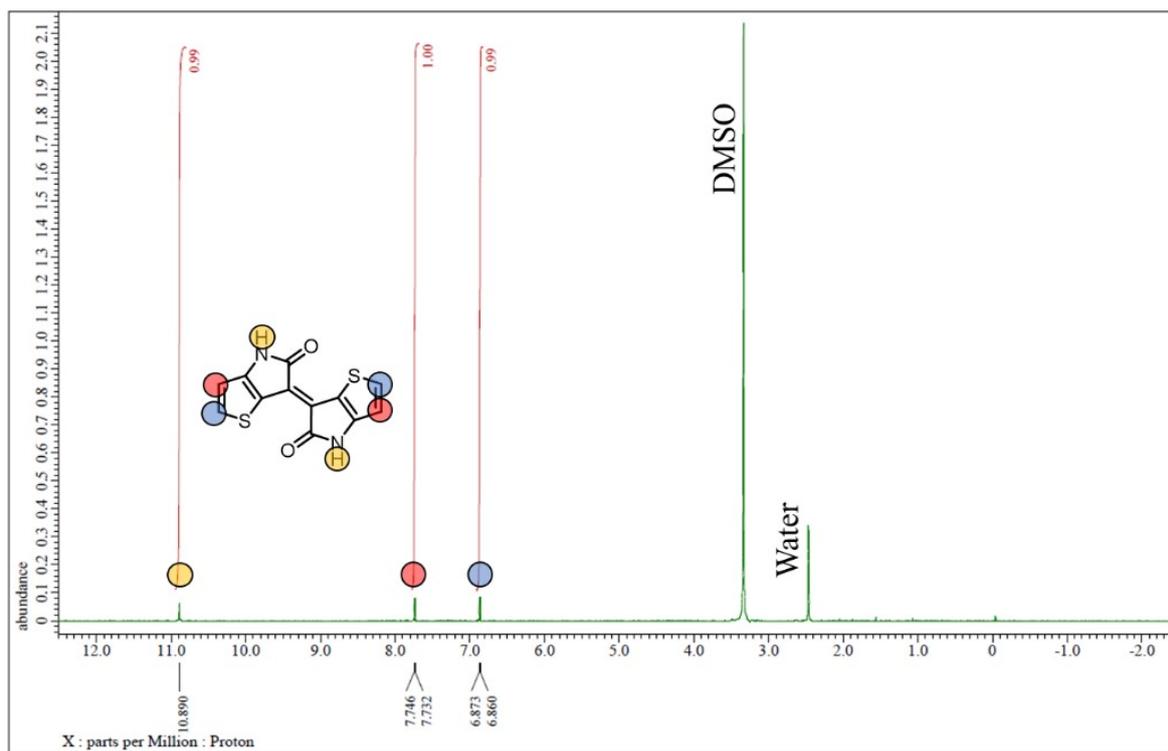
To a 200 mL conical flask, di-tert-butyl (E)-5,5'-dioxo-[6,6'-bithieno[3,2-b]pyrrolylidene]-4,4'(5H,5'H)-dicarboxylate (0.61 g, 1.29 mmol, 1 equiv.), acetone (50 mL), and trifluoroacetic acid (10 mL) were added. After stirring for 3 hours, the reaction was filtered and washed with water, acetone, hexane, and chloroform. After drying in vacuo, a dark purple solid was obtained. Yield: 0.34 g (96%).

$^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.89 (s, 2H), 7.74 (d,  $J = 5.5$  Hz, 2H), 6.87 (d,  $J = 5.0$  Hz, 2H)

$^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  172.99, 150.47, 135.96, 120.65, 114.43, 113.22.

EI-MS  $m/z$ : observed 274  $[\text{M}]^+$  (expected: 274  $[\text{M}]^+$ )

(a)



(b)

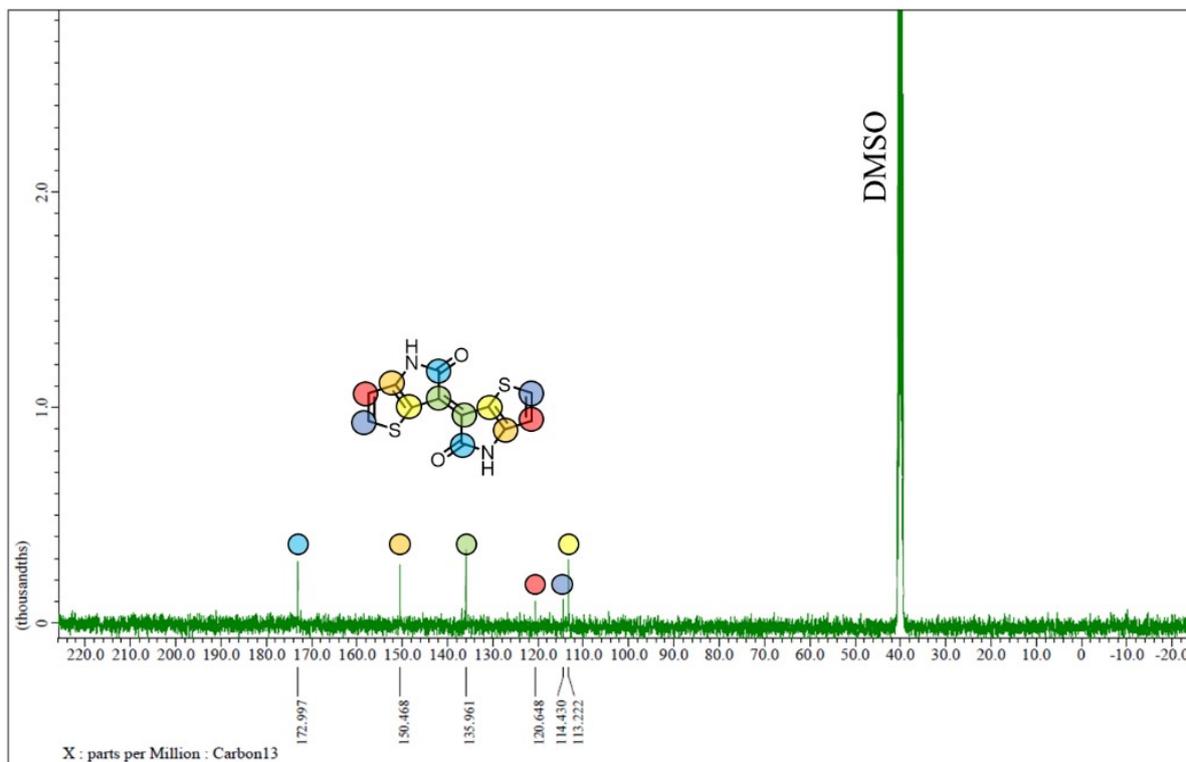
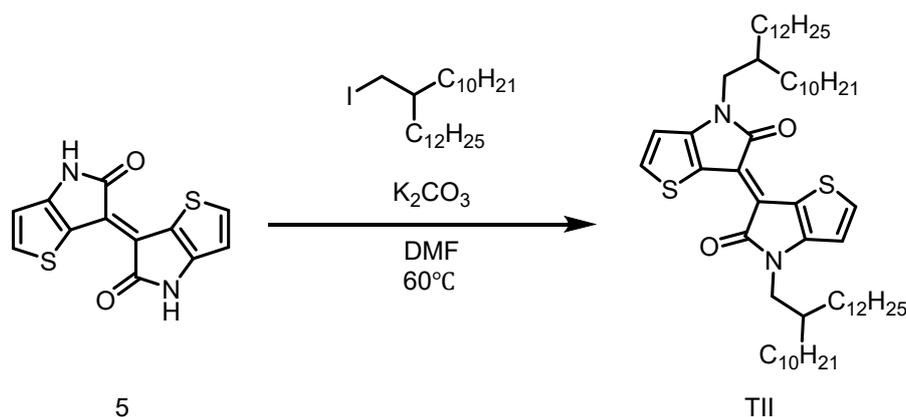


Figure S1. (a) <sup>1</sup>H-NMR and (b) <sup>13</sup>C-NMR spectra of H-TII.

### Preparation of thienoisindigo-alkyl (TII)



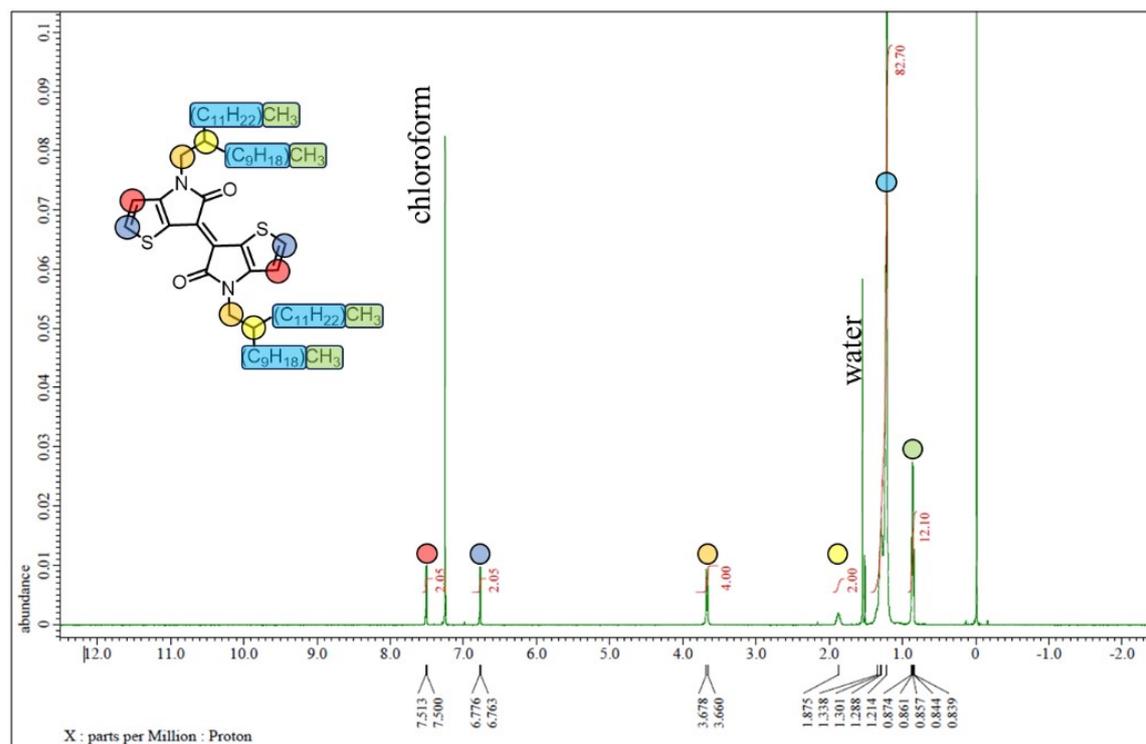
To a 100 mL two-necked round-bottom flask, H-TII (0.35 g, 1.30 mmol, 1 equiv.), 11-(iodomethyl)tricosane (1.30 g, 2.81 mmol, 2.2 equiv.), and DMF (20 mL) were added. Then,  $K_2CO_3$  was added, and the reaction mixture was heated to 60 °C overnight. Then, DMF was removed via evaporation, and dichloromethane (50 mL) was added. The solution was washed with water (200 mL) and dried with  $Na_2SO_4$ . The crude was purified by silica gel chromatography (9:1 to 0:1 of hexane: dichloromethane) to yield a dark purple solid after precipitation in cold methanol. Yield: 0.99 g (77%).

$^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.51 (d,  $J = 5.0$  Hz, 2H), 6.77 (d,  $J = 5.5$  Hz, 2H), 3.67 (d,  $J = 7.3$  Hz, 4H), 1.87 (s, 2H), 1.30-1.21 (m, 86H), 0.87-0.84 (m, 12H)

$^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  171.39, 151.61, 134.31, 121.15, 114.29, 111.46, 46.21, 37.21, 32.03, 31.51, 30.05, 29.76, 29.67, 29.47, 29.44, 26.49, 22.08, 14.24.

ESI-HRMS  $m/z$ : observed 969.7262 [ $M + Na^+$ ] (expected: 969.74 [ $M + Na^+$ ])

(a)



(b)

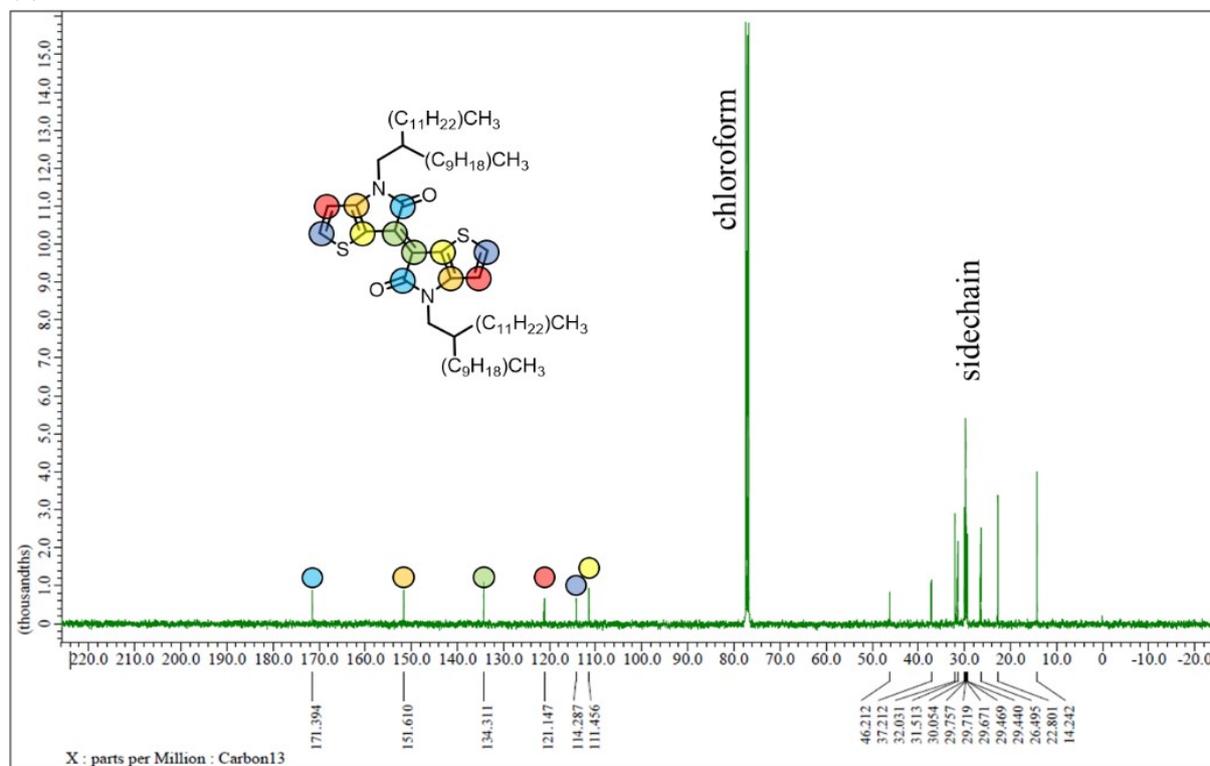
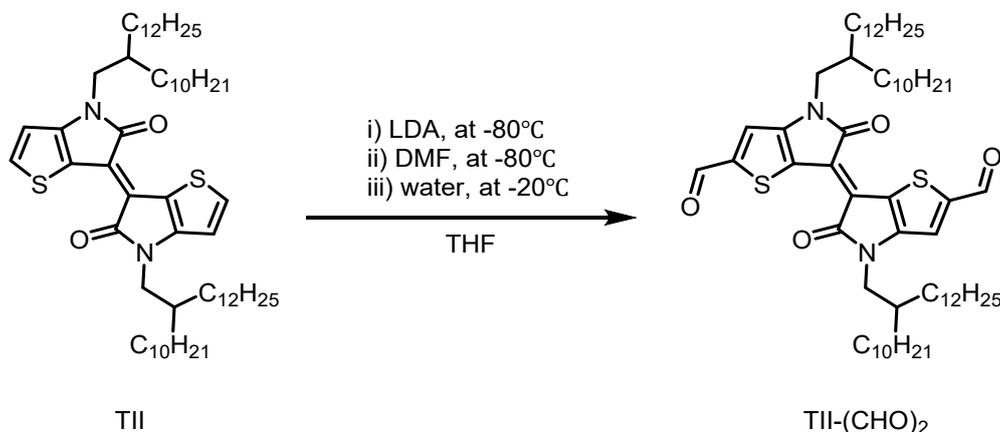


Figure S2. (a)  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$ -NMR spectra of TII.

## Preparation of thienoisindigo dialdehyde (TII-(CHO)<sub>2</sub>)



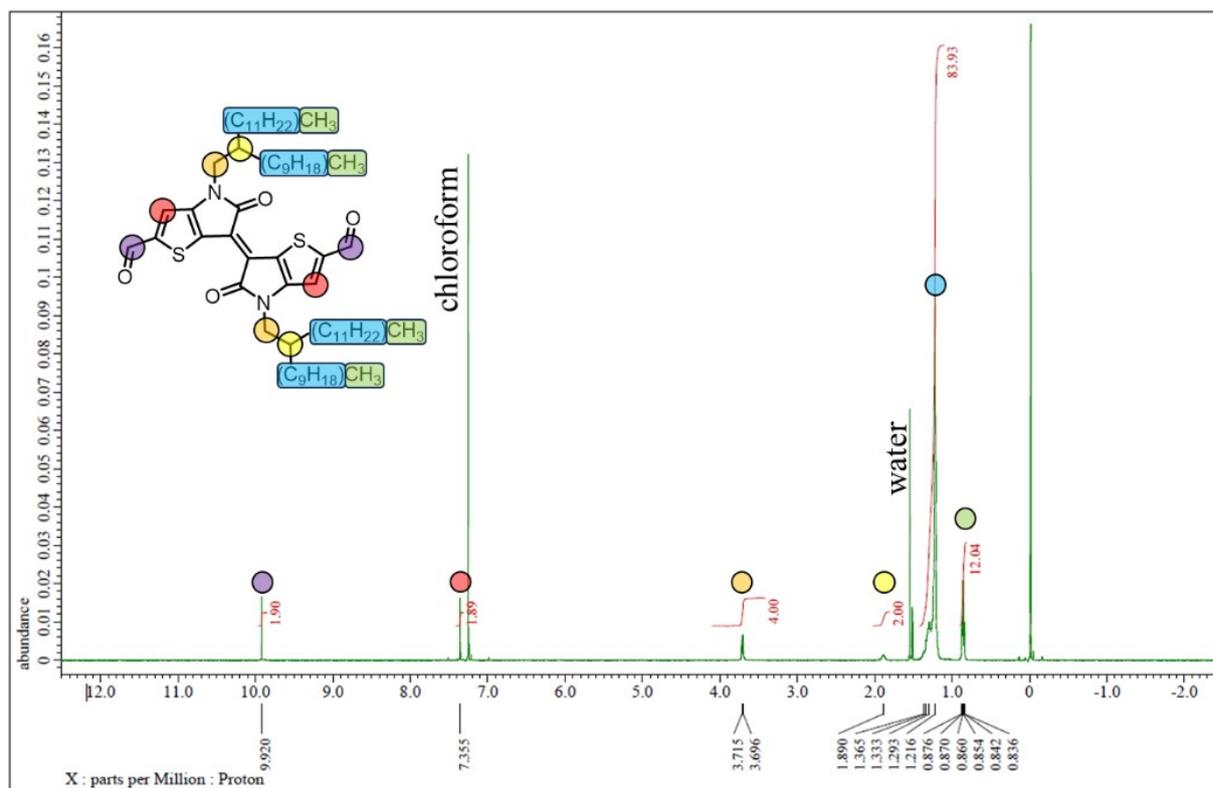
To a flame dried 100 mL two-necked round flask, anhydrous tetrahydrofuran (7 mL) was added. Then, the flask was cooled at 0 °C and diisopropylamine (0.25 mL, 1.8 mmol, 9 equiv.) and 1.6 M n-BuLi in hexanes (1mL, 1.6 mmol, 8 equiv.) were added. The reaction mixture was cooled from 0 °C to -80 °C, and then TII (0.18 g, 0.19 mmol, 1 equiv.) dissolved in anhydrous THF (20 mL) was added dropwise via a syringe. After complete addition, the reaction mixture was stirred for 1 hour, and DMF (0.15 mL, 1.9 mmol, 10 equiv.) was added. After stirring for 1 hour at -80°C, the reaction mixture was warmed up to -20 °C. When the reaction temperature reached -20 °C, the reaction was quenched with water (10 mL) and warmed up to room temperature. Dichloromethane (50 mL) was added and washed with water, dried with Na<sub>2</sub>SO<sub>4</sub>, and dried in vacuo. The crude was purified twice with silica chromatography (9:1 to 0:1 of hexane: dichloromethane) to yield a bluish-purple solid after precipitation in cold methanol. Yield: 0.14 g (74%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 9.92 (s, 2H), 7.36 (s, 2H), 3.71 (d, J = 7.3 Hz, 4H), 1.89 (s, 2H), 1.37-1.22 (m, 86H), 0.86 (td, J = 6.9, 2.3 Hz, 12H)

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 182.9, 170.0, 152.6, 149.3, 123.6, 122.3, 115.2, 46.4, 37.1, 32.0, 31.5, 30.1, 29.8, 29.7, 29.7, 29.5, 29.4, 26.4, 22.8, 14.2

ESI-HRMS m/z observed: 1025.7154 [M + Na<sup>+</sup>] (expected: 1025.74 [M + Na<sup>+</sup>])

(a)



(b)

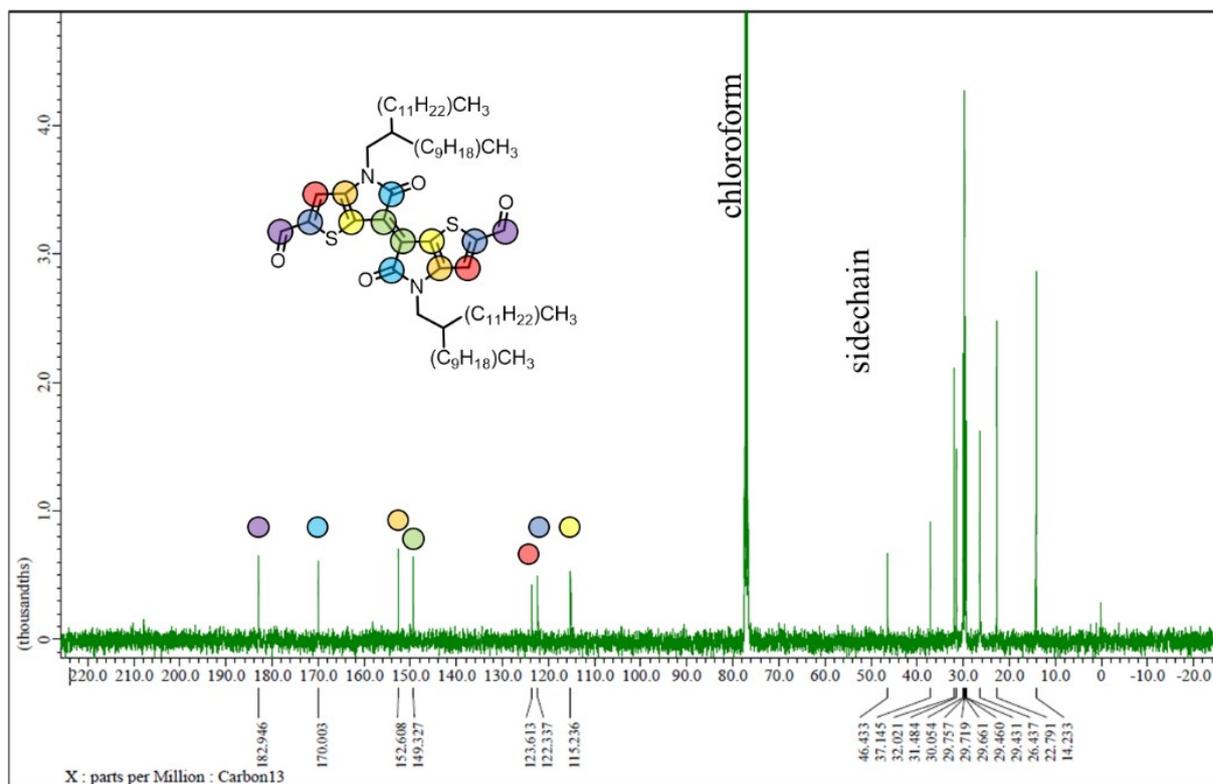
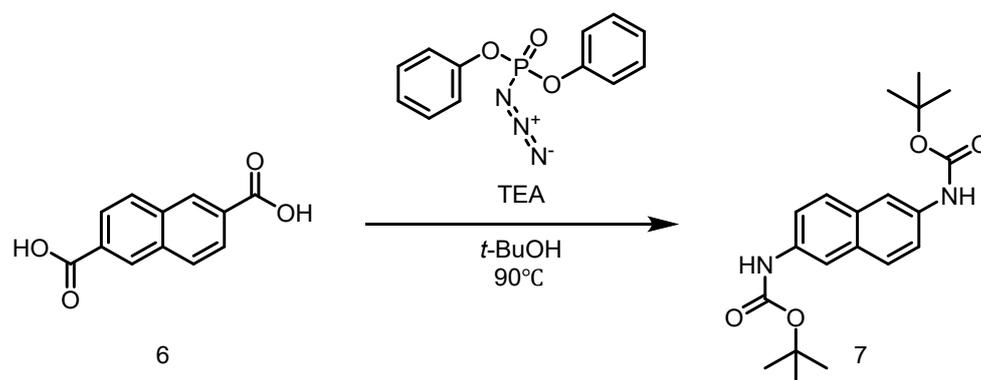


Figure S3. (a)  $^1H$  and (b)  $^{13}C$  NMR spectra of TII-(CHO) $_2$

## Preparation of di-tert-butyl naphthalene-2,6-diylldicarbamate

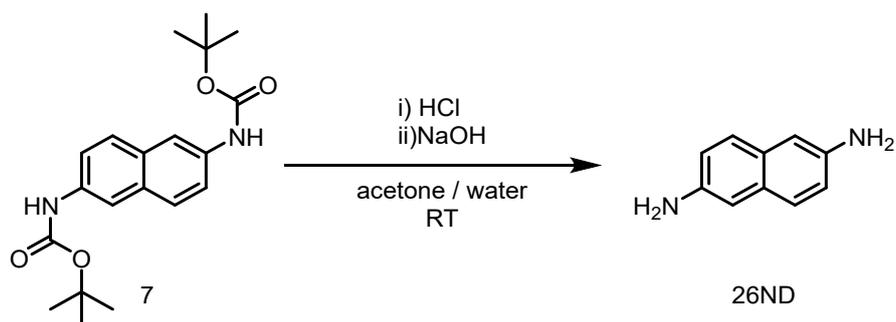


To a 100 ml two-necked round flask, naphthalene-2,6-dicarboxylic acid (2.00 g, 9.25 mmol, 1 equiv.), *t*-BuOH (40 mL), diphenylphosphoryl azide (4.4 mL, 20.4 mmol, 2.2 equiv.), and triethylamine (5.2 mL, 37.0 mmol, 4.0 equiv.) were added and heated to 90°C overnight. Next, *t*-BuOH was removed via a rotary evaporator, and dichloromethane (150 mL) was added. The reaction mixture was washed with water (150 mL), dried with Na<sub>2</sub>SO<sub>4</sub>, and the solvent removed in vacuo. The crude was purified via silica chromatography (dichloromethane) to yield a colorless solution. After evaporation, a solid was obtained, and subsequently washed with hexanes, resulting in a white powder. Yield: 1.76 g (53.1%)

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (s, 2H), 7.66 (d, J = 8.7 Hz, 2H), 7.25 (dd, J = 8.7, 2.3 Hz, 2H were overlapped with chloroform), 6.56 (s, 2H), 1.53 (s, 18H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 153.0, 134.7, 130.6, 128.3, 119.9, 114.6, 80.7, 28.5

## Preparation of 2,6-naphthyl diamine (2,6ND)

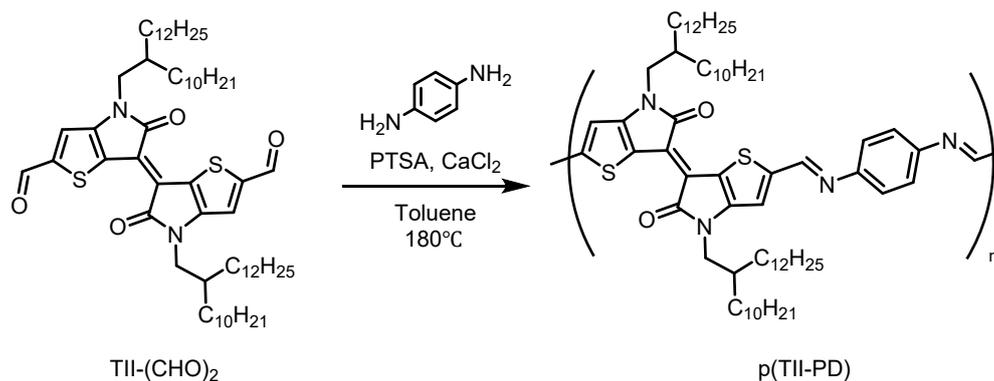


To a 200 mL conical flask, di-tert-butyl naphthalene-2,6-diyl dicarbamate (320 mg, 0.89 mmol, 1 equiv.), acetone (20 mL), and 36 wt% hydrochloric acid (5 mL, 59 mmol, 66 equiv.). After stirring for 3 hours, water (100 mL) and NaOH (5.00 g, 125 mmol, 140 equiv.) were added into the reaction. Then, the reaction mixture was filtered and washed with water and hexanes. After drying in vacuo, a pale-yellow powder was obtained. Yield: 122 mg (86.3%).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 8.7$  Hz, 2H), 6.89 (td,  $J = 8.2, 2.3$  Hz, 4H), 3.66 (s, 4H)

$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.5, 129.3, 127.2, 119.0, 109.5

## Preparation of p(TII-PD)



To a 5 mL microwave tube, **TII-(CHO)<sub>2</sub>** (48.4 mg, 48.2 mmol, 1.0 equiv.), *p*-phenylenediamine (5.2089 mg, 48.2 mmol, 1.0 equiv.), PTSA (0.5 mg, 2.62 mmol, 0.05 equiv.), and CaCl<sub>2</sub> (21.2 mg, 191 mmol, 4.0 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 5.5 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<sub>2</sub>SO<sub>4</sub> 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: 41.4 mg (78%).

<sup>1</sup>H NMR: (400 MHz, 1,1,2,2-tetrachloroethane-*d*<sub>2</sub>) δ 8.67, 7.40-7.22, 7.40-7.15, 6.71, 3.80, 2.02, 1.37, 1.12

GPC: *M<sub>n</sub>* (kDa): 22.3; *M<sub>w</sub>* (kDa): 154; Đ: 6.91

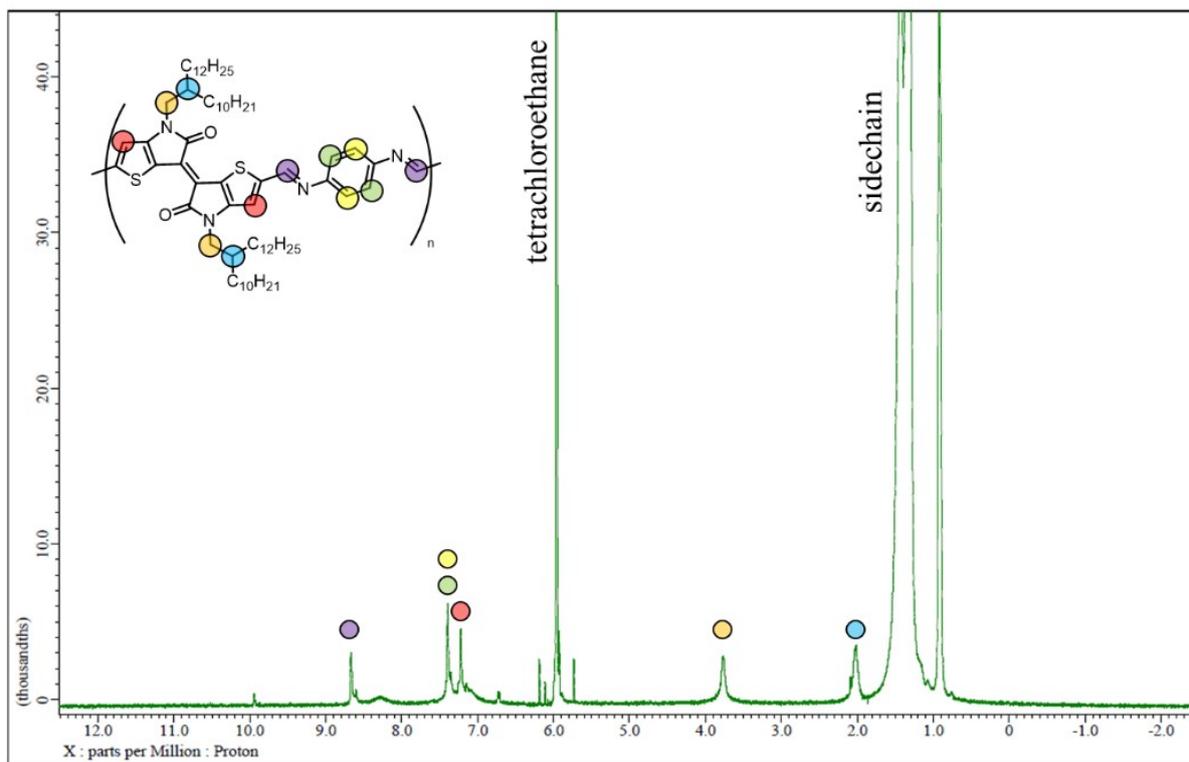
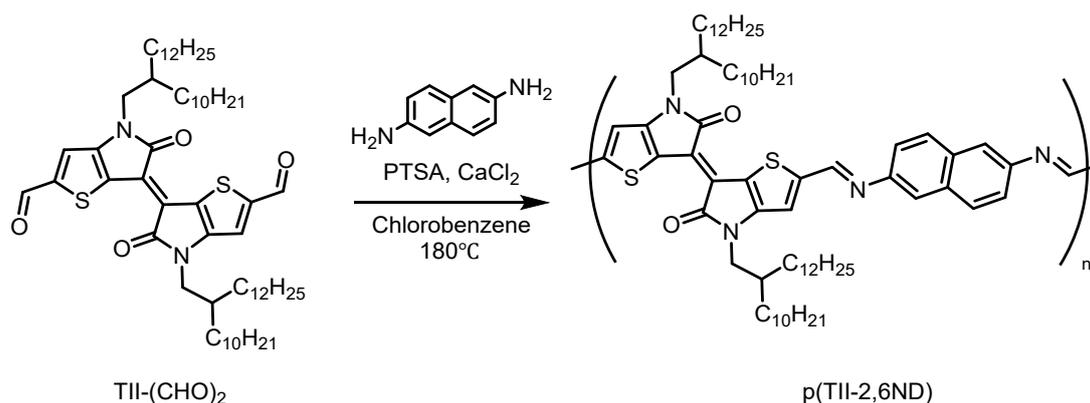


Figure S4.  $^1\text{H-NMR}$  spectra of p(TII-PD).

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



To a 5 mL microwave tube, **TII-(CHO)<sub>2</sub>** (45.8 mg, 45.63 mmol, 1.0 equiv.), 2,6-naphthalenediamine (7.25 mg, 45.8 mmol, 1.0 equiv.), PTSA (2.5 mg, 13.1 mmol, 0.29 equiv.), and CaCl<sub>2</sub> (24 mg, 216 mmol, 4.7 equiv.) were added. After adding 4 mL of 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 5.5 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<sub>2</sub>SO<sub>4</sub> 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: 36.0 mg (72%).

<sup>1</sup>H NMR: (400 MHz, 1,1,2,2-tetrachloroethane-*d*<sub>2</sub>) δ 8.78, 7.93, 7.75, 7.55, 7.32, 7.00, 3.80, 2.05, 1.37, 1.11

GPC: *M*<sub>n</sub> (kDa): 19.2; *M*<sub>w</sub> (kDa): 85.8; Đ: 4.48

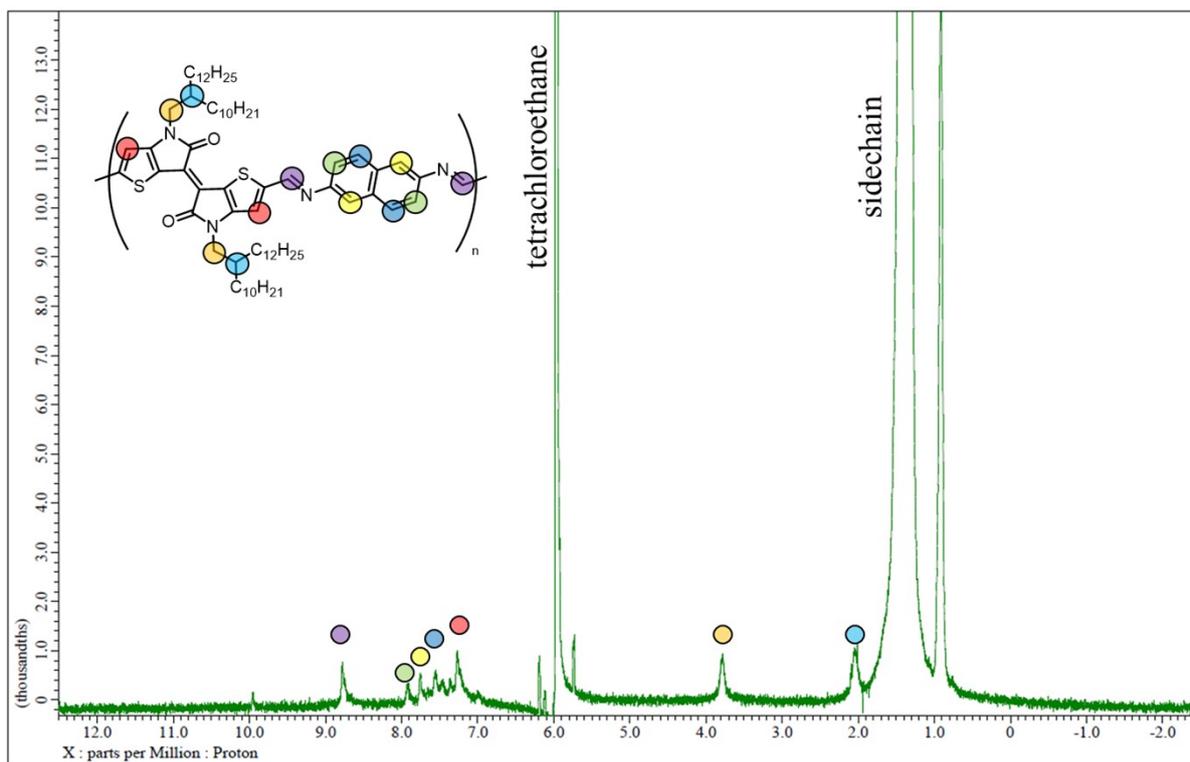
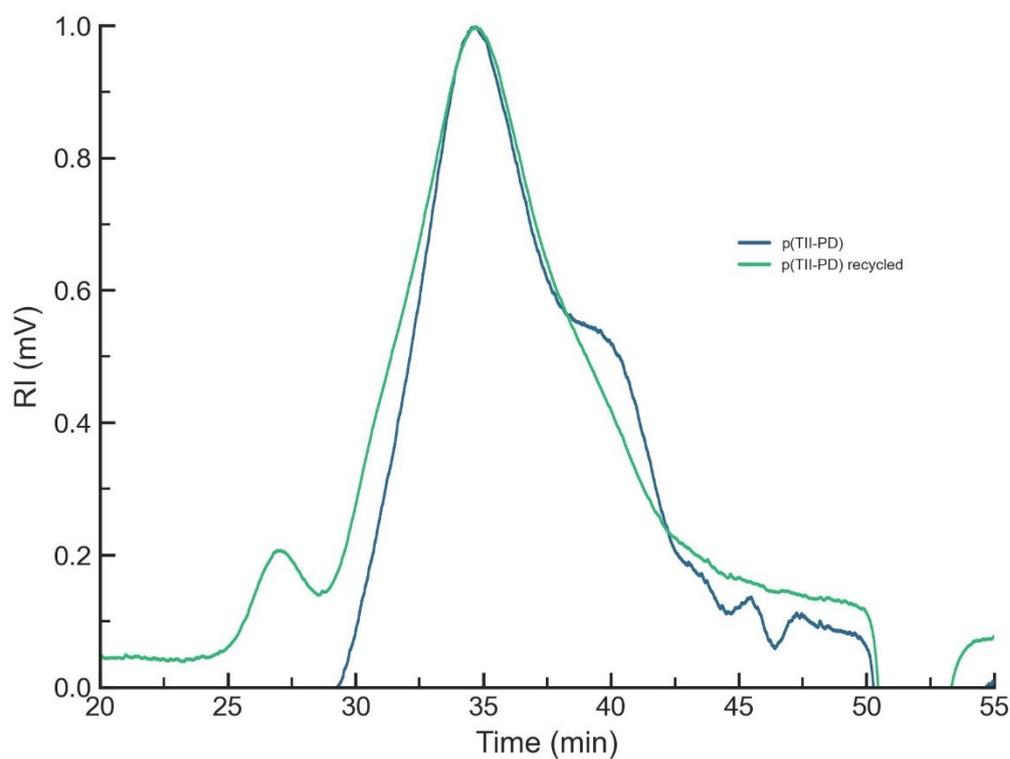


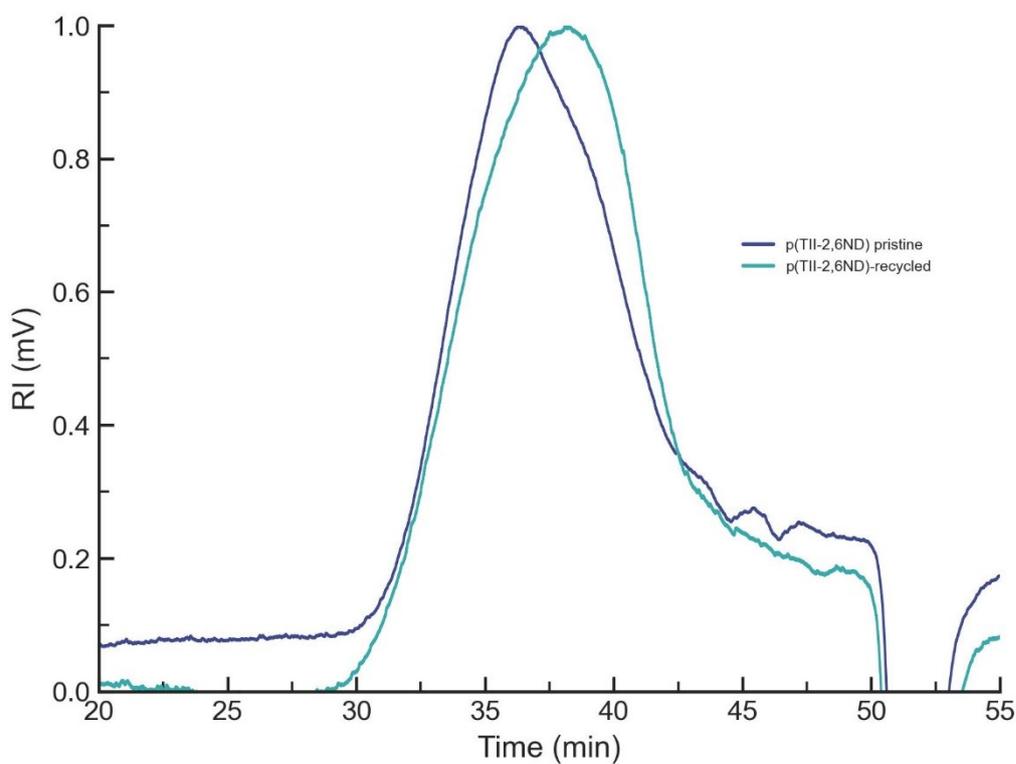
Figure S5.  $^1\text{H-NMR}$  spectra of p(TII-2,6ND).

## HT-GPC data

pristine **p(TII-PD)** and recycled **p(TII-PD)**



pristine **p(TII-2,6ND)** and recycled **p(TII-2,6ND)**



**Figure S6.** HT-GPC traces pristine and recycled polymers (normalized RI signal).

**Table S1. Summary of GPC characterizations**

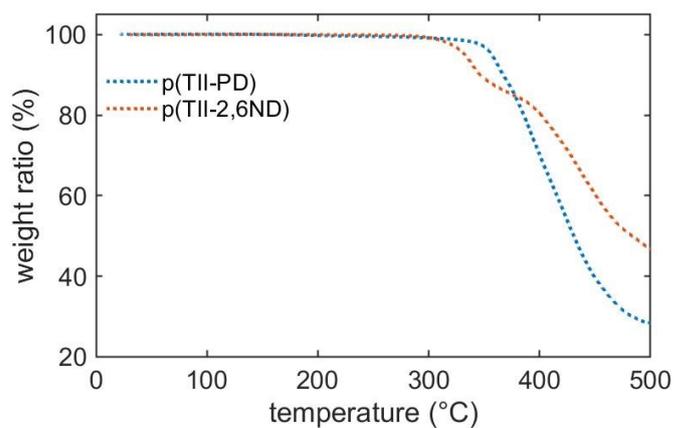
	$M_n$ (kDa)	$M_w$ (kDa)	$\bar{D}$	DP <sup>a</sup>
<b>p(TII-PD)</b>	22.3	154	6.91	20
<b>p(TII-2,6ND)</b>	19.2	85.8	4.48	17
<b>Recycled p(TII-PD)</b>	28.8	200	6.94	26
<b>Recycled p(TII-2,6ND)</b>	21.6	86.5	4.00	19

<sup>a</sup> The degree of polymerization (DP) was calculated from  $M_n$  results from high-temperature gel permeation chromatography (HT-GPC) using polystyrene standards.

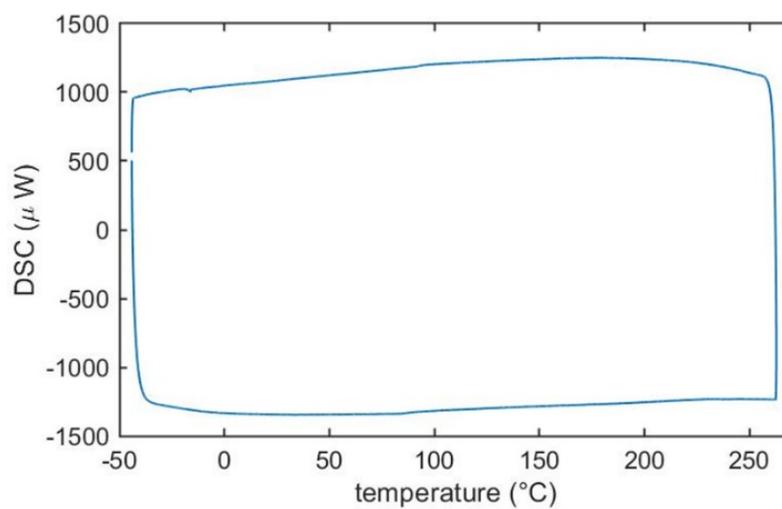
Note: We acknowledge that these HT-GPC values are likely an overestimation because of the structural differences between polystyrene and our polymeric system.

## Thermal properties

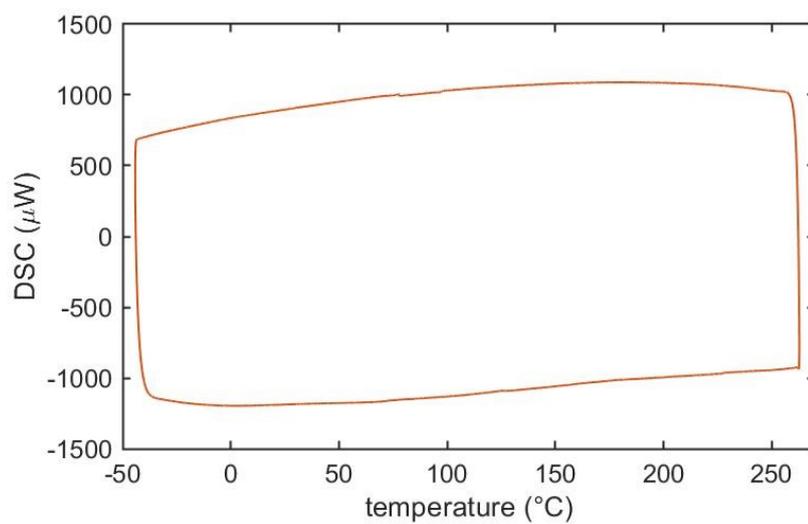
(a)



(b)



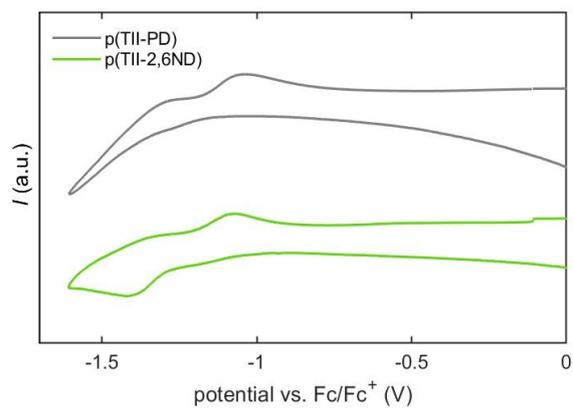
(c)



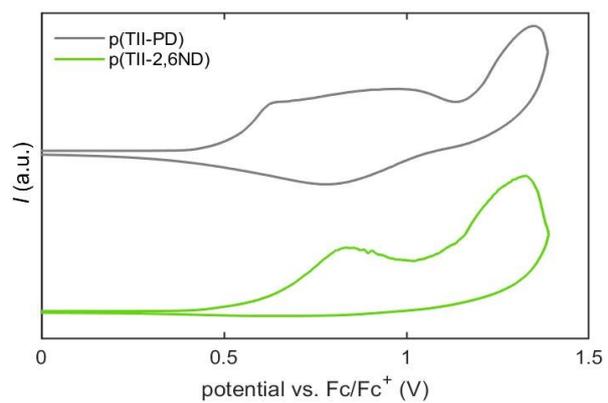
**Figure S7.** Thermal properties, (a) TGA profiles of both polymers, and DSC curves (the 1st cooling and the 2nd heating) of (b) p(TII-PD) and (c) p(TII-2,6ND).

## Cyclic voltammetry

(a)



(b)



**Figure S8.** Normalized CV plots for (a) negative voltage sweeping, and (b) positive voltage sweeping.

## Degradation and Recycling studies

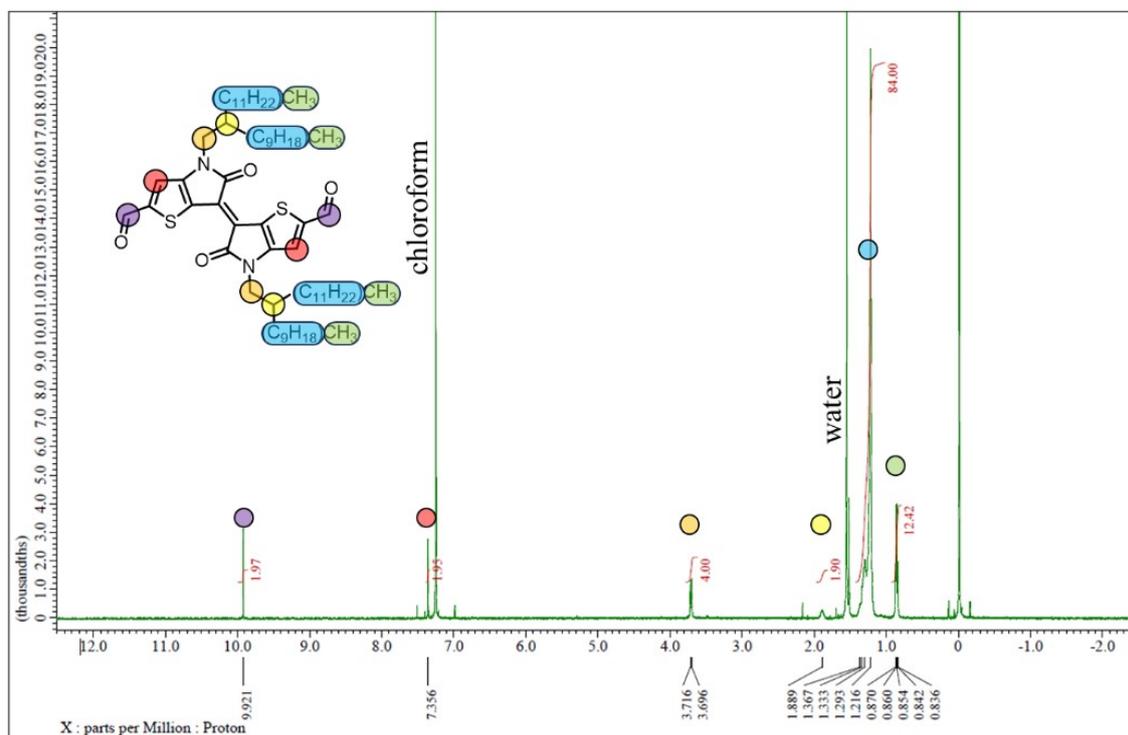
To evaluate the UV-vis-NIR spectra during polymer degradation, a solution of polymers (0.5 mg polymers in 50 mL) was prepared. After collecting spectra of each polymer solution, 250  $\mu\text{L}$  of 1.0 M trifluoroacetic acid aqueous ( $\text{TFA}_{\text{aq}}$ ) was added and stirred at room temperature. Subsequently, 3 mL of each solution was used for the UV-vis-NIR absorption measurements at each time point.

For the characterization of the degradation products, 31.2 mg of **p(TII-PD)** and 63.7 mg of **p(TII-2,6ND)** were each dissolved in 10 mL of chloroform. Then 5 mL of 1.0 M  $\text{TFA}_{\text{aq}}$  was added to each solution and stirred at 45°C for 2 days to accelerate and ensure the polymer degradation. After that, the solution was poured into 50 mL of water. The organic layer containing **TII-(CHO)<sub>2</sub>** was extracted with 150 mL of dichloromethane and washed with 100 mL of water and dried with  $\text{Na}_2\text{SO}_4$ . **TII-(CHO)<sub>2</sub>** was purified using silica gel chromatography with dichloromethane/hexane = 1/1 to 9/1 and obtained 27.1 mg (95%) and 50.9 mg (91%) of the products, respectively. These products were identified using  $^1\text{H-NMR}$  and ESI-HRMS to compare with the pure **TII-(CHO)<sub>2</sub>**.

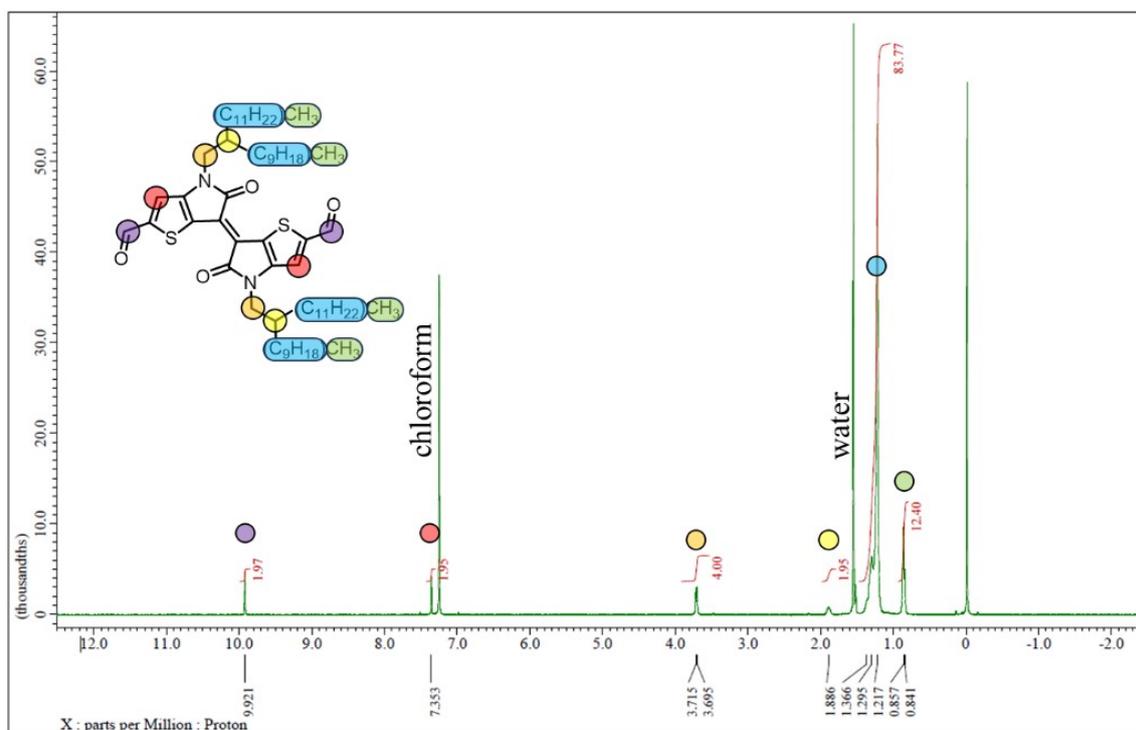
Additionally, the water layer containing diamine salts of **PD** and **2,6ND** was treated with an aqueous saturated solution of  $\text{NaOH}$ . Then, the aqueous mixture was poured into 50 mL of dichloromethane, and the organic layer extracted to obtain the diamines. After evaporation and drying, **PD** and **2,6ND** were obtained and identified by  $^1\text{H-NMR}$  spectra (Figure S10).

# <sup>1</sup>H-NMR spectra

(a)

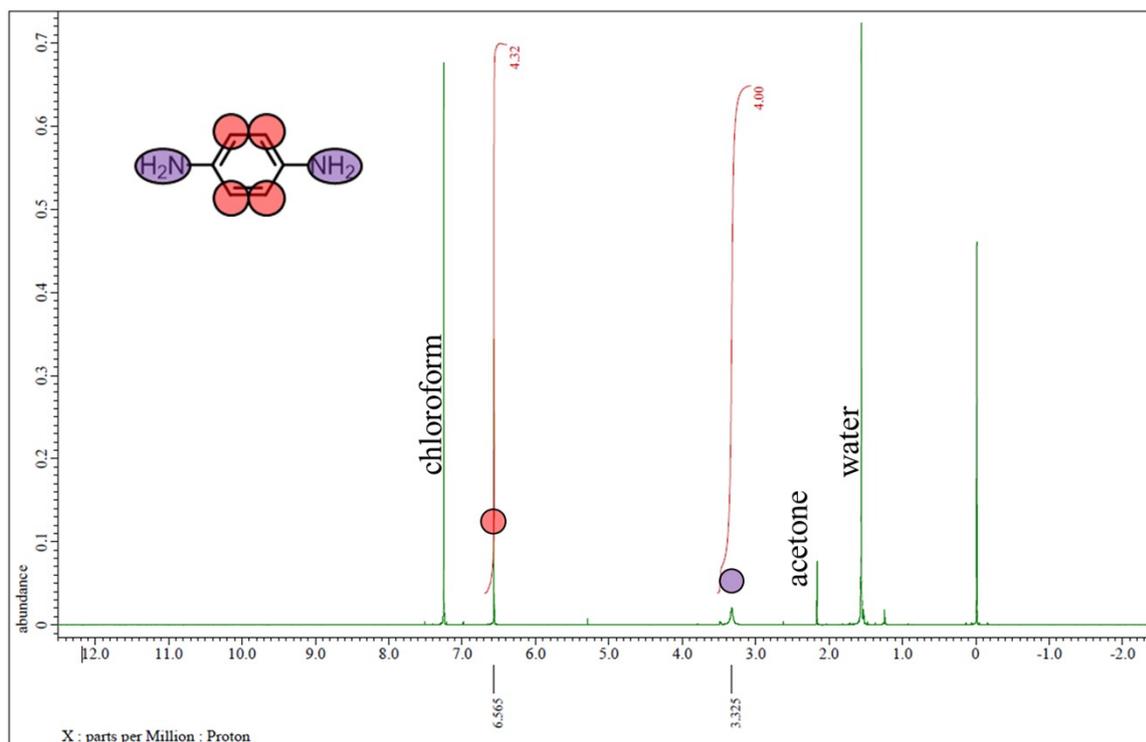


(b)

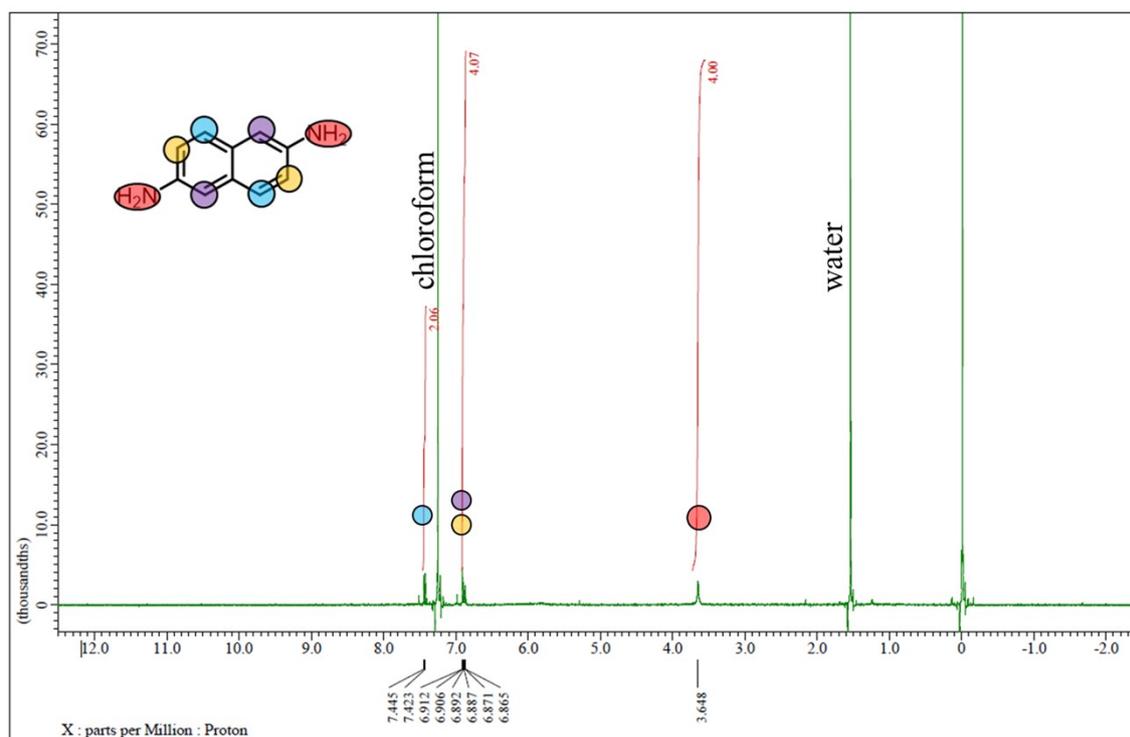


**Figure S9.** Characterization of <sup>1</sup>H-NMR spectra for recycled TII-(CHO)<sub>2</sub> from (a) p(TII-PD) and (b) p(TII-2,6ND).

(a)

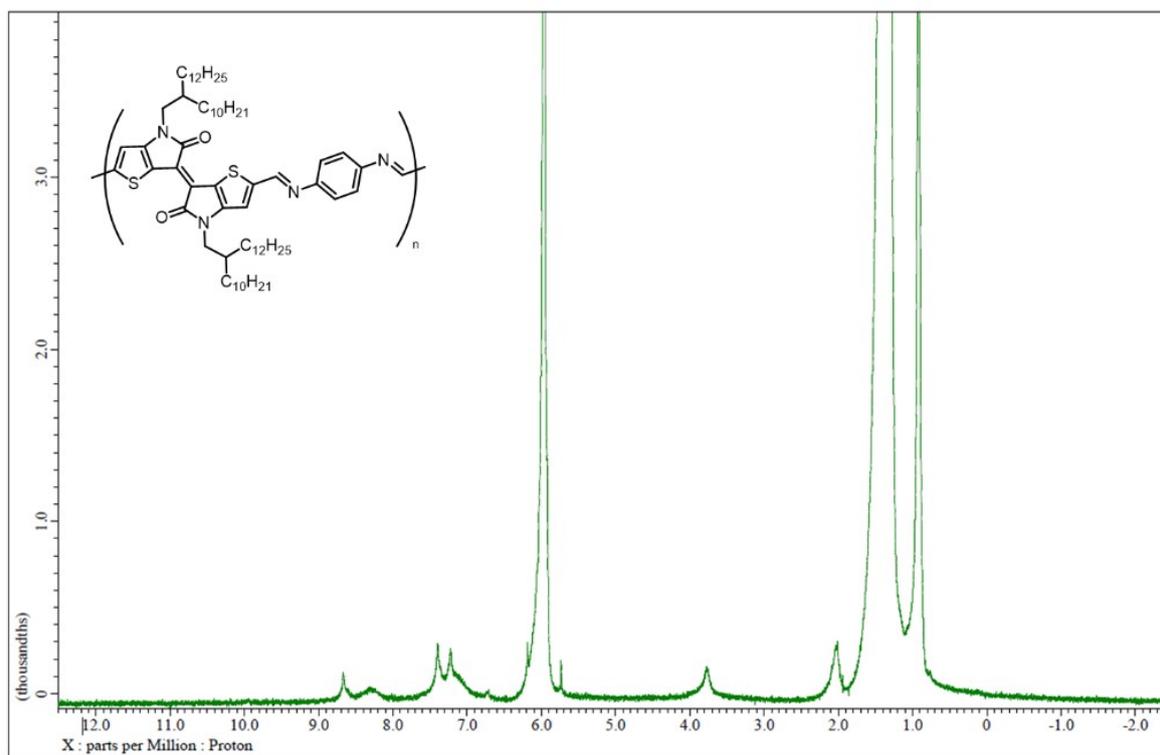


(b)



**Figure S10.** Characterization of <sup>1</sup>H-NMR spectra for (a) recycled PD recovered from p(TII-PD) and (b) recycled 2,6ND recovered from p(TII-2,6ND).

(a)



(b)

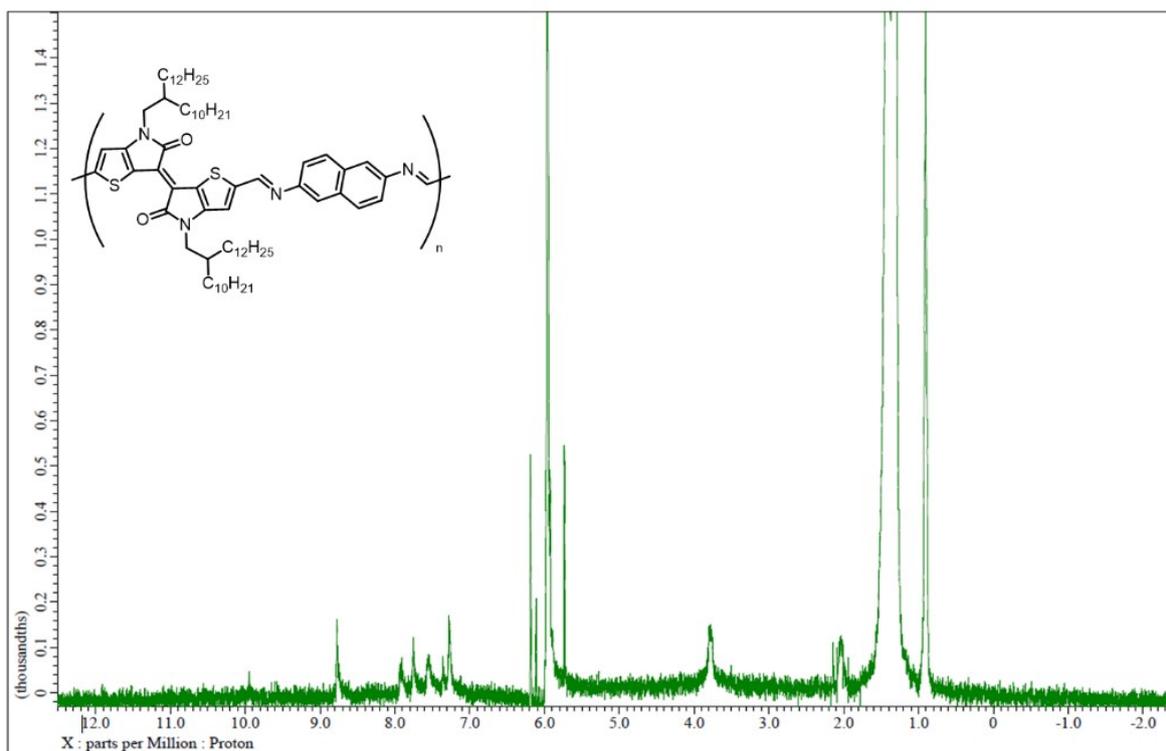
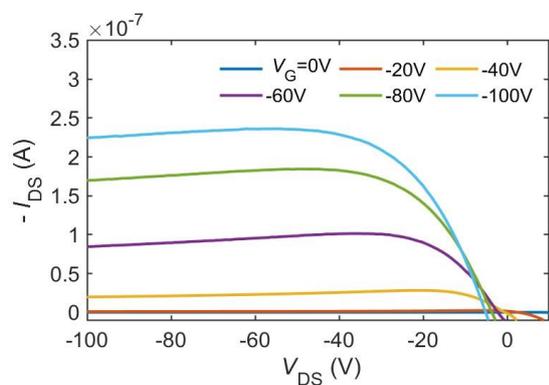


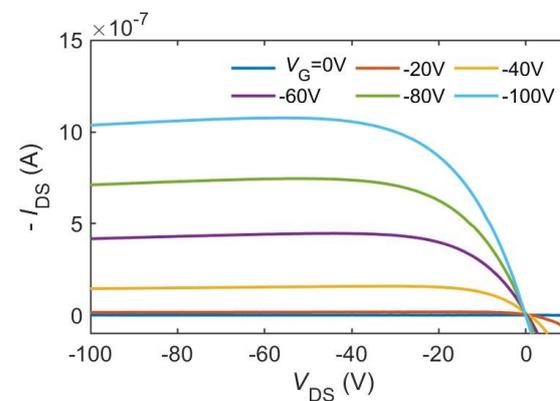
Figure S11. <sup>1</sup>H-NMR spectra of recycled (a) re-p(TH-PD) and (b) re-p(TH-2,6ND).

## FET profiles

(a)

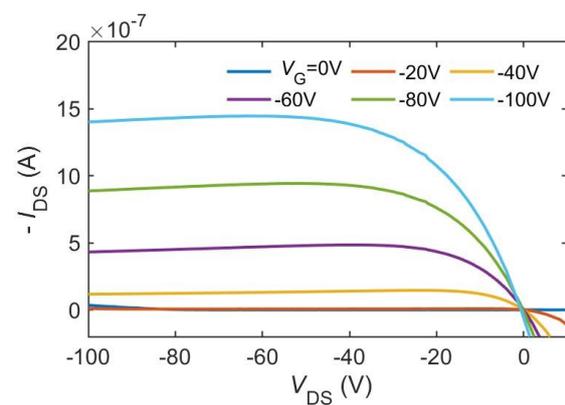


(b)

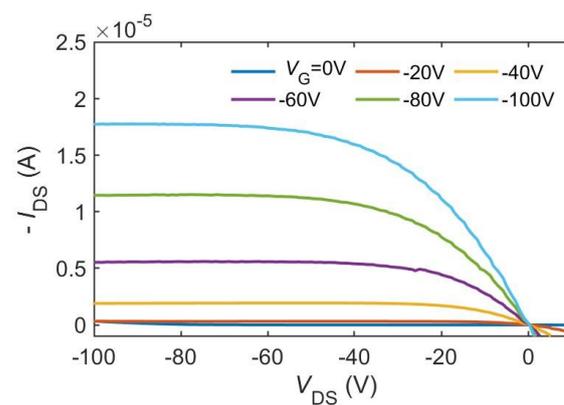


**Figure S12.** Typical output curves of (a) pristine **p(TII-PD)** and (b) pristine **p(TII-2,6ND)**.

(a)

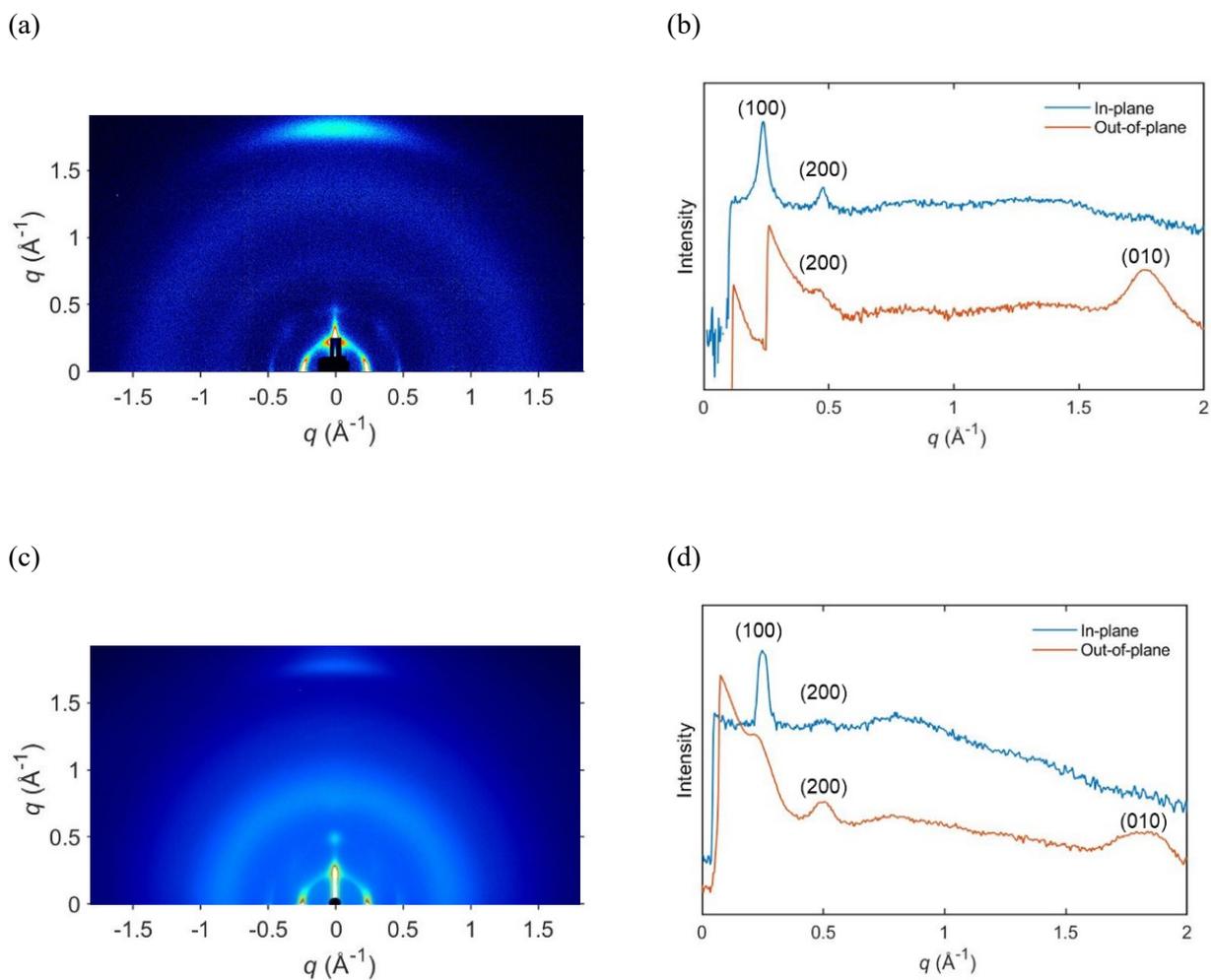


(b)



**Figure S13.** Typical output curves of recycled (a) **re-p(TII-PD)** and (b) **re-p(TII-2,6ND)**.

GIWAXS results of polymer thin films



**Figure S14.** GIWAXS patterns and their 1-D profiles of (a) and (b) for **p(TII-PD)** and (c) and (d) for **p(TII-2,6ND)**.

## References

- (1) D. Yoo, T. Hasegawa, M. Ashizawa, T. Kawamoto, H. Masunaga, T. Hikima, H. Matsumoto and T. Mori, *J. Mater. Chem. C*, 2017, **5**, 2509–2512.
- (2) X. Ji, H. Xie, C. Zhu, Y. Zou, A. U. Mu, M. Al-Hashimi, K. R. Dunbar and L. Fang, *J. Am. Chem. Soc.*, 2020, **142**, 641–648.
- (3) A. Velusamy, C. H. Yu, S. N. Afraj, C. C. Lin, W. Y. Lo, C. J. Yeh, Y. W. Wu, H. C. Hsieh, J. Chen, G. H. Lee, S. H. Tung, C. L. Liu, M. C. Chen and A. Facchetti, *Adv. Sci.*, 2021, **8**, 2002930