# **Electronic Supplementary Information (ESI)**

# An indacenodithiophene-based semiconducting polymer with high ductility for stretchable organic electronics

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#### Experimental

**Synthesis**. Chemicals used in this study were purchased from Sigma-Aldrich, TCI America, Alfa Aesar and Combi-Blocks and were used as received. All reactions were carried out in air unless specified. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were collected on a 500 MHz Bruker Avance DRX-499 NMR spectrometer. Infrared spectroscopy measurement was conducted with a PerkinElmer Frontier Fourier transform infrared (FTIR) spectroscope using Attenuated Total Reflectance (ATR) techniques. CHN elemental analysis was performed on an Exeter Analytical CE-440 CHN analyzer. The polymer molecular weights were determined using a TDA 305 size exclusion chromatogram (SEC) by Viscotek at 30 °C using THF as the eluent *vs.* narrow dispersity polystyrene standards.

Reaction (i): *diethyl 2,5-dibromoterephthalate* (1). In a round-bottom flask equipped with a condenser, a suspension of 2,5-dibromoterephtalic acid (15.0 g, 46.3 mmol) in ethanol (100 mL) with the addition of concentrated sulfuric acid (5 mL, 98%) was refluxed for 16 h. The reaction mixture was then cooled to room temperature and dichloromethane (100 mL) was added to dissolve the precipitate. The mixture was extracted with dichloromethane and washed with brine. The organic phase was collected and dried over anhydrous magnesium sulfate. The mixture was filtered and the solvent was removed. The residue was purified by column chromatography on silica, eluting with hexanes/dichloromethane (3:2) to afford a white solid in 83% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.03 (s, 2H), 4.42 (q, 4H, J = 7.1 Hz), 1.42 (t, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 164.2, 136.4, 135.7, 120.1, 62.3, 14.2.

Reaction (ii): *diethyl 2,5-di(thiophen-2-yl)terephthalate* (**2**). In a round-bottom flask equipped with a condenser, a mixture of **1** (3.0 g, 7.9 mmol), 2-(tributylstannyl)thiophene (6.5 g, 17.4 mmol) and tetrakis(triphenylphosphine)palladium(0) (228 mg, 2.5 mol%) in anhydrous toluene (40 mL) was degassed and then refluxed in a nitrogen atmosphere for 16 h. The reaction mixture was then cooled to room temperature and the solvent was removed. The residue was purified by column chromatography on silica, eluting with hexanes/dichloromethane (1:1), to afford a pale yellow solid in 95% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.82 (s, 2H), 7.36 (dd, 2H, J = 5.1 Hz), 7.09 (dd, 2H, J = 3.5 Hz), 7.06 (dd, 2H, J = 5.1 Hz), 4.21 (q, 4H), 1.14 (t, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 167.7, 140.5, 134.1, 133.5, 131.9, 127.4, 127.0, 126.5, 61.6, 13.8.

Reaction (iii): 2,5-di(thiophen-2-yl)terephthalic acid (3). In a round-bottom flask equipped with a condenser, a mixture of 2 (4.0 g, 10.4 mmol) and sodium hydroxide (6.0 g, 150.0 mmol) in methanol/water (80 mL, 1:1) was refluxed for 16 h. The reaction mixture was then cooled to room temperature, added to hydrochloric acid (150 mL, 2 M) and stirred for 30 min. The precipitate was extracted with ethyl acetate. The organic phase was collected and dried over anhydrous magnesium sulfate. The mixture was filtered and the solution was concentrated to 40 mL. The precipitate was filtered and washed by ethyl acetate to afford a pale green solid in 83% yield. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 13.41 (s, 2H), 7.73 (s, 2H), 7.66 (dd, 2H, J = 5.1 Hz), 7.23 (dd, 2H, J = 3.5 Hz), 7.16 (dd, 2H, J = 5.0 Hz). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 169.2, 140.2, 135.0, 132.0, 130.7, 128.3, 127.9, 127.6.

Reaction (iv): 2,5-di(thiophen-2-yl)terephthaloyl dichloride (4). In a round-bottom flask equipped with a septum, oxalyl chloride (12.1 mL, 2.0 M in dichloromethane) was added to a suspension of **3** (2.0 g, 6.1 mmol) in anhydrous dichloromethane (30 mL) in a nitrogen atmosphere at room temperature. Anhydrous dimethylformamide (1 mL) was added dropwise to the mixture. During the addition, a large amount of gas was released and the suspension was dissolved. The reaction mixture was then stirred for 2 h and the solvent was removed to afford the crude product as a yellow solid, which was used immediately in next step. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.90 (s, 2H), 7.50 (d, 2H, J = 5.0 Hz), 7.18 (d, 2H, J = 3.4 Hz), 7.14 (t, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 167.7, 138.4, 137.7, 132.8, 131.8, 128.8, 128.3, 128.2.

Reaction (v): *s-indaceno[1,2-b:5,6-b']dithiophene-4,9-dione* (5). In a round-bottom flask equipped with a septum, a solution of 4 (2.2 g, 6.0 mmol) in anhydrous dichloromethane (50 mL) was added to a suspension of anhydrous aluminum chloride (4 g, 30 mmol) in anhydrous dichloromethane (30 mL) in a nitrogen atmosphere at room temperature. After the reaction mixture was stirred for 16 h, the solvent was removed to afford a black solid. After water (80 mL) was added into the flask and the suspension was stirred, the suspension was filtered and washed by water and acetone to afford a deep blue solid in 93%

yield. NMR spectra could not be taken for the compound because of its poor solubility in common deuterated solvents. IR (v, cm<sup>-1</sup>): 3110, 3075, 1702.

Reaction (vi): 4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (6). In a round-bottom flask equipped with a condenser, a mixture of 5 (500 mg, 1.7 mmol), hydrazine monohydrate (1.7 g, 34.0 mmol) and potassium hydroxide (1.9 g, 34.0 mmol) in diethylene glycol (50 mL) was heated at 110 °C for 1 h. The condenser was then removed and the reaction mixture was heated at 180 °C for 4 h. After being cooled to room temperature, the reaction mixture was poured into hydrochloric acid (150 mL, 2.0 M) and stirred overnight under room temperature. The mixture was filtered and the filter cake was suspended in acetone. The suspension was sonicated for 30 min and anhydrous magnesium sulfate was added. The mixture was filtered and the solvent was removed. The residue was roughly purified by column chromatograph on silica, eluting with hexanes/dichloromethane (1:1), to afford the crude product. The crude product was recrystallized in acetone in a freezer and then purified by column chromatography on silica, eluting with hexanes/dichloromethane (10:1), to afford a nearly white solid in 50% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.58 (s, 2H), 7.26 (d, 2H, J = 4.7 Hz), 7.09 (d, 2H, J = 4.6 Hz), 3.70 (s, 4H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 147.0, 145.4, 143.5, 136.1, 126.3, 122.8, 115.8, 33.9. Anal. (%): calcd (found) for C<sub>16</sub>H<sub>10</sub>S<sub>2</sub>: C: 72.14 (71.96), H: 3.78 (3.74).

Reaction (vii): 4,4,9,9-tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (**IDT**). In a round-bottom flask with a septum, a suspension of **6** (100 mg, 0.38 mmol) in anhydrous toluene/dimethyl sulfoxide (1:1, 10 mL) was slightly heated until the dissolution of the solid, followed by the addition of sodium *tert*-butoxide (216 mg, 2.3 mmol) in one portion. The reaction mixture was heat at 80 °C for 1 h. After the addition of 1-bromohexadecane (687 mg, 2.3 mmol) dropwise, the reaction mixture was heat to 85 °C for 16 h. After being cooled to room temperature, the reaction mixture was poured into brine and extracted with hexanes. The organic phase was collected and dried over anhydrous magnesium sulfate. The mixture was filtered and the solvent was removed. The liquid residue was placed overnight at room temperature and filtered. The obtained solid residue was recrystallized in petroleum ether. Further recrystallization of the solid in petroleum ether twice at room temperature afforded a nearly white solid in 40% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.31 (s, 2H), 7.28 (d, 2H, J = 4.8 Hz), 6.99 (d, 2H, J = 4.8 Hz), 2.04-1.98 (m, 4H), 1.91-1.85 (m, 4H), 1.28-1.13 (m, 112H), 0.91 (t, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 155.1, 153.3, 141.7, 135.6, 126.1, 121.7, 113.1, 53.7, 39.2, 32.0, 30.1, 29.7, 29.6, 29.4, 24.2, 22.7, 14.1. Anal. (%): calcd (found) for C<sub>80</sub>H<sub>138</sub>S<sub>2</sub>: C: 82.54 (82.81), H: 11.95 (11.62).

Reaction (viii): 4,7-dibromo-2-methylisoindoline-1,3-dione (**BPD**). In a round-bottom flask with a septum, 3,6-dibromophthalic anhydride (1.0 g, 3.3 mmol) was dissolved in anhydrous tetrahydrofuran (10 mL) and the solution was degassed with nitrogen at 0 °C. Methylamine (2.0 mL, 33 wt% in ethanol) was slowly injected into the solution. Precipitate was formed during the addition and dissolved after methanol (10 mL) was added. The reaction mixture was stirred for 16 h at room temperature, poured into hydrochloric acid (50 mL, 2 M) and extracted with dichloromethane twice. The organic phase was collected and dried over anhydrous magnesium sulfate. The mixture was filtered and solvent was removed. The residue was mixed with sodium acetate (27 mg, 10 mol%) in acetic anhydride (10 mL) and the mixture was heated at 90 °C for 16 h. After being cooled to room temperature, the reaction mixture was added into water (50 mL) and stirred for 1 h. The mixture was extracted with dichloromethane twice. The organic phase was collected and dried over anhydrous magnesium sulfate. The mixture was filtered and solvent was removed. The residue was filtered for 1 h. The mixture was extracted with dichloromethane twice. The organic phase was collected and dried over anhydrous magnesium sulfate. The mixture was filtered and solvent was removed. The residue was purified by column chromatography on silica, eluting with hexanes/dichloromethane (1:1) to afford an off-white solid in 55% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.65 (s, 2H), 3.20 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 164.9, 139.5, 131.4, 117.5, 24.5.

Reaction (ix): *poly(2-methyl-4-(4,4,9,9-tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophen-2-yl)isoindoline-1,3-dione)* (**PIDTBPD**). A mixture of **IDT** (58.2 mg, 0.05 mmol), **BPD** (15.9 mg, 0.05 mmol), tris(dibenzylideneacetone)dipalladium(0) (2.3 mg, 5 mol%), tris(*o*-anisyl)phosphine (1.8 mg, 10 mol%), cesium carbonate (81 mg, 0.25 mmol) and pivalic acid (2.6 mg, 0.025 mmol) in *o*-xylene (1 mL) was degassed and filled with nitrogen in a sealed pressure tube. After being heated at 100 °C for 16 h, the reaction mixture was cooled to room temperature and added to methanol (100 mL). The precipitation was

filtered through a Soxhlet thimble and then purified by Soxhlet extraction with methanol, acetone and hexanes to remove catalytic and low molecular weight residues. The hexanes extraction was collected and the solvent was removed. The residue was dissolved in chloroform and precipitated by methanol. The precipitation was collected by filtration and dried in vacuum to afford a deep orange solid in 87% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.91 (s, 4H), 7.39 (s, 2H), 3.25 (s, 3H), 2.10 (s, 4H), 1.93 (s, 4H), 1.23-1.21 (m, 112H), 0.87 (t, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 167.6, 156.0, 153.8, 144.3, 139.0, 136.0, 135.0, 132.6, 127.3, 125.4, 113.7, 54.4, 39.1, 32.0, 30.1, 29.8, 29.4, 24.4, 22.7, 14.1. GPC:  $M_n = 18,000 \text{ g} \cdot \text{mol}^{-1}$ .

Reaction (x): poly(4-(4,4,9,9-tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophen-2-yl)benzo[c][1,2,5]thiadiazole) (IDTBT). A mixture of **IDT** (58.2 mg, 0.05 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (14.7 mg, 0.05 mmol), tris(dibenzylideneacetone)dipalladium(0) (2.3 mg, 5 mol%), tris(*o*-anisyl)phosphine (1.8 mg, 10 mol%), cesium carbonate (81 mg, 0.25 mmol) and pivalic acid (2.6 mg, 0.025 mmol) in *o*-xylene (1 mL) was degassed and filled with nitrogen in a sealed pressure tube. After being heated at 100 °C for 16 h, the reaction mixture was cooled to room temperature and added to methanol (100 mL). The precipitation was filtered through a Soxhlet thimble and then purified by Soxhlet extraction with methanol, acetone and hexanes to remove catalytic and low molecular weight residues. The hexanes extraction was collected and the solvent was removed. The residue was dissolved in chloroform and precipitated by methanol. The precipitation was collected by filtration and dried in vacuum to afford a deep blue solid in 83% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.11 (s, 2H), 7.95 (s, 2H), 7.41 (s, 2H), 2.11 (s, 4H), 1.97 (s, 4H), 1.21-1.17 (m, 112H), 0.86 (t, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 156.4, 153.7, 152.7, 143.7, 141.5, 136.2, 126.3, 124.7, 122.1, 113.5, 54.3, 39.2, 32.0, 30.1, 29.7, 29.4, 24.3, 22.7, 14.1. GPC:  $M_n = 15,000$  g·mol<sup>-1</sup>.

**DFT calculations**. Theoretical calculations using B3LYP as functional and 6-31G(d) as basis set in Gaussian 09 were used to optimized the ground state geometries of the structures with different number of repeating unit. The charge distribution on HOMO and LUMO was analyzed by Chemissian from the output of single point calculation on the optimal ground state geometry using the same functional and basis set.

**Mechanical property measurements.** Glass substrates were prepared by sonicating for 15 min each in Micro 90 soap solution, DI water, acetone, and isopropyl alcohol (IPA). Following sonication, substrates were dried under a dry airflow, then plasma cleaned in a plasma cleaner for 10 min. 120 uL of PEDOT:PSS solution (Clevios P VP AI 4083, Heraeus) was spin-coated at 2500 rpm for 60 s on the plasma cleaned glass and then annealed at 140 °C for 15 min in air. 100 µL of the PIDTBPD solution in chloroform at concentration of 30 mg/mL was spin-coated on the dried substrates at 2,000 rpm for 60 s. The film thickness was measured using a Bruker OM-DektakXT profilometer. The thickness of the polymer film ( $d_f = 0.22$ µm) was calculated by subtracting the thickness of PEDOT:PSS film from the total film thickness. PDMS substrates were produced from DOW Corning's Sylgard 184. The components (silicone elastomer and curing agent) were mixed at a 10:1 ratio according to the accompanying product information, then degassed under vacuum for 1-2 h. Samples were then cured at 60 °C for 4 h in air. The side exposed to air during curing was used for all buckling and crack-onset strain measurements. To introduce a buckling instability, PDMS substrates were extended under tension using a homemade strain stage to an elongation of 15%. The polymer film was transferred onto the PDMS substrate by adhering the previously produced film on glass face-down to the pre-strained PDMS substrate. The substrates were soaked at room temperature in DI water for 30 min to dissolve the PEDOT:PSS laver remove the glass substrate, resulting in the semiconducting polymer film on the pre-strained PDMS. The pre-strain was then slowly relaxed to compress the film, typically to 5% compression. Due to the instability of the buckles, the samples were immediately analyzed using a Bruker Icon AFM in quantitative nanomechanical mapping mode to determine the buckling wavelength ( $\lambda_b = 4.56 \,\mu\text{m}$ ). The elastic modulus of the polymer film ( $E_f$ ) is obtained by the following equation:

$$E_f = 3E_s \left(\frac{1-\nu_f^2}{1-\nu_s^2}\right) \left(\frac{\lambda_b}{2\pi d_f}\right)^3$$
 Eq. S1

where  $E_s$  is the elastic modulus of PDMS substrate ( $E_s = 1.6$  MPa, measured from stress-strain experiment);  $v_f$  and  $v_s$  are Poisson's ratios for the polymer film ( $v_f = 0.35$ ) and PDMS substrate ( $v_s = 0.50$ ), respectively.<sup>8</sup> In order to measure the crack-onset strain, the polymer film deposited on a PDMS substrate was placed onto our homemade strain stage and slowly extended until cracks were observed under an optical microscope. In the case of IDTBT, the measured  $d_f$  and  $\lambda_b$  are 0.21 µm and 5.22 µm, respectively.

**OFET fabrication and charge carrier mobility measurements**. Heavily boron-doped silicon substrates with a 300 nm ( $\pm$  5 nm) thick thermal oxide layer (WRS Materials) were used as substrates for the organic field-effect transistors (OFETs). The substrates were first scrubbed with detergent and water and then sonicated in DI water, acetone, and IPA for 15 min per solvent. Next, the substrates were dried under air and immediately cleaned in a plasma cleaner for 15 min. In order to passivate the thermal oxide, a vacuum vapor deposition of octadecyltrichlorosilane (OTS) on the cleaned substrates was used. After the OTS deposition, the substrates were rinsed with chloroform and IPA to remove any physically absorbed OTS from the surface. The semiconducting polymer layer was then spin-coated at 1500 rpm for 60 s onto the OTS passivated substrates. Gold electrodes were thermally evaporated onto the active layer to a thickness of 60 nm at a rate of 1 Å·s<sup>-1</sup>. The gold was evaporated from a Mo boat and the electrodes were deposited through a shadow mask. After electrode deposition, the devices were annealed as described below and tested for charge mobility and on/off ratio. The devices that were tested were top-contact bottom-gate architecture and had a channel width of 1000 µm and a channel length of 50 µm. The saturation regime of the *Ips-V<sub>G</sub>* curve was fitted to estimate the charge carrier mobility using the following equation:

$$I_{DS} = \frac{\mu \cdot W \cdot C}{2L} \cdot (V_G - V_t)^2$$
 Eq. S2

where  $I_{DS}$  is the drain-source current;  $\mu$  is the charge carrier mobility; W is the channel width; L is the channel length; C is the capacitance per unit area of the insulator (SiO<sub>2</sub>, 300 nm, 10 nF·cm<sup>-2</sup>);  $V_G$  is the gate voltage; and  $V_t$  is the threshold voltage. Using the passivated substrates, optimization experiments were run to determine the best conditions for processing the polymer into OFETs. The conditions that were optimized include casting solvent and spin speed. A final batch of devices was made using the optimized conditions. At least 8 devices across 4 substrates were tested to obtain an average value for the charge carrier mobility.

**Spectroscopic measurements**. Ultraviolet-visible (UV-Vis) spectra were measured on a Varian Cary 5000 UV-Vis-NIR spectrometer. The measuring range was from 200 nm to 800 nm. The absorption below 400 nm were not shown because there were no characteristic peaks in this spectral range except instrumental artifacts. Photoluminescence (PL) spectra were measured on a Horiba Fluorolog FL-3 spectrometer. The excitation wavelength was 470 nm and the measuring range was from 500 nm to 800 nm. Note that the absorption (or emission) spectra were averaged spectra from different conditions because the measured absorption (or emission) spectra in solution (solvent: chloroform or chlorobenzene) were identical and so were the spectra in film (spin-coated on a glass substrate from the solution of chloroform or chlorobenzene, annealed or not annealed).

**Cyclic voltammetry** (CV). Cyclic voltammograms were obtained against  $Ag/Ag^+$  as the reference electrode, indium-tin-oxide (ITO) as the working electrode, and Pt wire electrode in an 0.1 M electrolyte containing tetra-*n*-butylammonium fluoride (TBAF) in acetonitrile (bubbled with nitrogen before measurement) with a scan rate of 1 mV·s<sup>-1</sup>. The polymer sample was prepared by drop-casting the polymer solution in chloroform on the ITO slide and dried in air. The ferrocene sample was prepared by directly dissolving the ferrocene into the electrolyte.

**Thermal measurements**. Thermal gravimetric analysis (TGA) curve was obtained on TA Instruments TGA Q50 V20.13 Build 39. The sample weight was 3.099 mg. The measurement was taken from room

temperature to 480 °C at the rate of 10 °C·min<sup>-1</sup> under nitrogen atmosphere. Differential scanning calorimetry (DSC) curve was obtained on TA Instruments DSC Q200 V24.11 Build 124. The heat-cool-heat-cool-heat-cool measurement was taken under nitrogen atmosphere, starting and ending at room temperature. The maximum heating temperature was 300 °C and the minimum cooling temperature was - 80 °C. The rate for ascending and descending temperature is 10 °C·min<sup>-1</sup>.

**XRD measurements**. X-ray diffraction (XRD) measurements were performed using a Bruker D8 DISCOVER instrument. The polymer thin films were prepared by drop-casting the polymer solution in chloroform (5 mg/mL) on glass substrates.

# Supplementary figures and tables

**Table S1** Percentage of the charge distribution on the **IDT** and **BPD** units of the structures with different repeating units (n = 1-7) in the HOMO and LUMO.

НОМО														
n	IDT1	BPD1	IDT2	BPD2	IDT3	BPD3	IDT4	BPD4	IDT5	BPD5	IDT6	BPD6	IDT7	BPD7
1	89%	11%												
2	46%	13%	39%	3%										
3	25%	9%	43%	7%	15%	1%								
4	16%	6%	35%	7%	25%	4%	7%	0%						
5	11%	5%	27%	7%	26%	5%	14%	2%	3%	0%				
6	8%	3%	21%	5%	24%	5%	18%	3%	9%	1%	2%	0%		
7	6%	3%	17%	5%	21%	5%	19%	4%	12%	2%	6%	1%	1%	0%
	LUMO													
n	IDT1	BPD1	IDT2	BPD2	IDT3	BPD3	IDT4	BPD4	IDT5	BPD5	IDT6	BPD6	IDT7	BPD7
1	16%	84%												
2	1%	24%	23%	52%										
3	0%	0%	1%	26%	24%	48%								
4	0%	0%	0%	1%	2%	25%	25%	47%						
5	0%	0%	0%	0%	0%	1%	2%	24%	25%	47%				
6	0%	0%	0%	0%	0%	0%	0%	1%	2%	24%	25%	47%		
7	0%	0%	0%	0%	0%	0%	0%	0%	0%	1%	2%	24%	25%	47%

Table S2 Assessing the purities of 6 and IDT by CHN elemental analysis.

Compound	$C\%^{calcd}$ ( $C\%^{found}$ )	H% <sup>calcd</sup> (H% <sup>found</sup> )	Purity (%)
6	72.14 (71.96)	3.78 (3.74)	(71.96/72.14+3.74/3.78)/2 = 99.28%
IDT	82.54 (82.81)	11.95 (11.62)	(82.54/82.81+11.62/11.95)/2 = 98.46%



**Scheme S1** Synthetic route of IDTBT. Reagents and conditions: (x) **IDT**, Pd<sub>2</sub>(dba)<sub>3</sub>, P(*o*-anisyl)<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, PivOH, *o*-xylene, 100 °C, 16 h.



Fig. S1 GPC spectrum of PIDTBPD.



**Fig. S2** Photograph of the homemade strain stage. A screw (1) is used to adjust the distance between two clamps (2) which holds the PDMS substrate. The displacement is indicated on the meter (3).



Fig. S3 Images from the optical microscope showing polymer films a) without and b) with cracks during the measurement of crack-onset strain at the maximum extension (ca. 41%) of the homemade strain stage.



Fig. S4 Image from the optical microscope showing the buckling pattern of IDTBT.



Fig. S5 CV of the oxidative process of **PIDTBPD** with respect to ferrocene. Its  $E_{HOMO}$  with respect to ferrocene ( $E_{HOMO} = -4.8 \text{ eV}$ ) is -5.58 eV.



Fig. S6 Finding the direct allowed band gap of the polymer by Tauc plot:  $\varepsilon hv = C(hv - E_g)^{1/2}$ . Plot  $E_g$  vs.  $(\varepsilon hv)^2$  and fit the linear part of the data. The intercept on x-axis is the direct allowed band gap.



**Fig. S7** Result of IDTBT from DSC measurement. Note that peaks 1 and 3 are ascribed to the polymer's  $T_m$  and  $T_c$ , respectively, which are below room temperature but over 0 °C. The reason for peak 2 is unknown.



**Fig. S8** Result of **PIDTBPD** from TGA. Note that the polymer kept 100% of its weight before 250 °C, which ruled out moisture absorption or residual solvent-based plasticization. Its decomposition temperature ( $T_d$ , defined as temperature at 5% weight loss) is 403 °C.

# Compound characterization data













![](_page_13_Figure_1.jpeg)

![](_page_13_Figure_2.jpeg)

![](_page_14_Figure_0.jpeg)

![](_page_14_Figure_2.jpeg)

![](_page_15_Figure_0.jpeg)

![](_page_16_Figure_0.jpeg)

![](_page_16_Figure_1.jpeg)

![](_page_17_Figure_0.jpeg)

![](_page_17_Figure_1.jpeg)

0

![](_page_17_Figure_2.jpeg)

![](_page_18_Figure_0.jpeg)

![](_page_18_Figure_1.jpeg)

![](_page_18_Figure_2.jpeg)

![](_page_19_Figure_0.jpeg)

![](_page_19_Figure_1.jpeg)

![](_page_19_Figure_2.jpeg)

![](_page_20_Figure_0.jpeg)

![](_page_20_Figure_1.jpeg)

![](_page_20_Figure_2.jpeg)