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Supporting information

Rational Molecular Design for Isoindigo-Based Polymer Semiconductors with High Ductility and High Electrical Performance

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Contents

1. Synthetic procedures

All solvents and starting materials for the reactions were purchased from Sinopharm Chemical Reagent Co., Ltd, Sigma-Aldrich Chemical Company, Tokyo Chemical Industry Co., Alfa Aesar Company, and used directly without further purification. The monomers 6,6'-dibromo-bis (2-decanoyl-1-tetradecyl) isoindigo,[1] 5,5'-bis (trimethyltin) -2,2'-bithiophene,[2] 6,6'-dibromo-bis (2-ethyl-1-hexadecyl) isoindigo,[1] 5,5'-bis (trimethyltin) -3,3'-bis (dodecyl) -2,2'-bithiophene,[3] (3E,7E)-3,7-bis(6-bromo-1-(2-decyltetradecyl)-2-oxoindolin-3-ylidene)benzo[1,2-b:4,5-b']difuran-2,6(3H,7H)-dione,[3,4] were synthesized following the method reported by previous literature. Tetrahydrofuran (THF) was freshly distilled over sodium wire under nitrogen prior to use.

Synthesis of PIID-BT：

6,6'-dibromo-bis (2-decanoyl-1-tetradecyl) isoindigo (0.178 g, 0.163 mmol) and 5,5'-bis (trimethyltin) -2,2'-bithiophene (0.08g, 0.163 mmol) were added, and anhydrous chlorobenzene (12 mL) were added to a 100 mL Schlenck tube. After the tube was charged with nitrogen through a freeze-pump-thaw cycle for three times, $Pd_2(dba)_3$ (0.0059 g, 0.0065 mmol) and $P(o\text{-tol})_3$ (0.0079 g, 0.026 mmol) were added quickly in one portion. The mixture was stirred at 130 ^{o}C for 48 h. After being cool to room temperature, the reaction mixture was poured into 80 mL methanol and was stirred for another 2h. The precipitation was collected by filtration and purified by Soxhlet extraction using methanol and dichloromethane for the removal of low-molecular-weight. Finally, the remaining solid was extracted with hot chloroform. After removal of the solvent under reduced pressure, a black-blue solid was collected (0.142 g, 79%). Elemental analysis: $(C_{72}H_{108}N_2O_2S_2)_n$ theoretical value (%): C, 78.83, H, 9.85, N, 2.56, S 5.84, measured value (%): C, 78.71, H, 9.61, N, 2.67, S, 5.26.

Synthesis of PIID-BTC12:

6,6'-dibromo-bis (2-ethyl-1-hexadecyl) isoindigo blue (0.123 g, 0.191 mmol) and 5,5'-bis (trimethyltin) -3, 3'-bis (dodecyl) -2, 2'-bithiophene (0.158 g, 0.191 mmol) were added, and anhydrous chlorobenzene (10 mL) were added to a 100 mL Schlenck tube.

After the tube was charged with nitrogen through a freeze-pump-thaw cycle for three times, $Pd_2(dba)_3$ (0.007 g, 0.0076 mmol) and P(*o*-tol)$_3$ (0.0093 g, 0.031 mmol) were added quickly in one portion. The mixture was stirred at 130 ^oC for 48 h. After being cool to room temperature, the reaction mixture was poured into 80 mL methanol and was stirred for another 2h. The precipitation was collected by filtration and purified by Soxhlet extraction using methanol and dichloromethane for the removal of low-molecular-weight. Finally, the remaining solid was extracted with hot chloroform. After removal of the solvent under reduced pressure, a black-blue solid was collected (0.115 g, 69.3%). Elemental analysis: $(C_{64}H_{92}N_2O_2S_2)_n$ theoretical value (%): C, 78.05, H, 9.35, N, 2.84, S 6.50, measured value (%): C, 77.78, H, 9.29, N, 2.91, S, 6.65.

Synthesis of PBIBDF-BT:

Tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$, 0.0059 g, 0.0065 mmol), tri(o-tolyl)phosphine (P(o-tol)$_3$, 0.0079 g, 0.026 mmol) were added to a solution of 5,5′-bis(tributylstannyl)-3,3′-bis(dodecyl)-2,2′-bithiophene (0.13 g, 0.156 mmol) and (3E,7E)-3,7-bis(6-bromo-1-(2-decyltetradecyl)-2-oxoindolin-3-ylidene)benzo[1,2-b:4,5-b’]difuran-2,6(3H,7H)-dione (0.201 g, 0.156 mmol) in toluene (12 mL) under nitrogen. The solution was subjected to three cycles of evacuation and admission of nitrogen. The mixture was then heated to 110 ^oC for 48 h. After cooled to room temperature, the mixture was poured into methanol and stirred for 2 h. A black precipitate was collected by filtration. The product was purified by washing with methanol and petroleum ether in a Soxhlet extractor for 24 each. It was extracted with hot chloroform in an extractor for 24 h. After removing solvent, a black solid was collected (0.187g, 79.2%). Elemental analysis: $(C_{106}H_{158}N_2O_6S_2)_n$ theoretical value (%): C, 78.61, H, 9.77, N, 1.73, S 3.96, measured value (%): C, 77.95, H, 9.19, N, 1.85, S, 3.95.

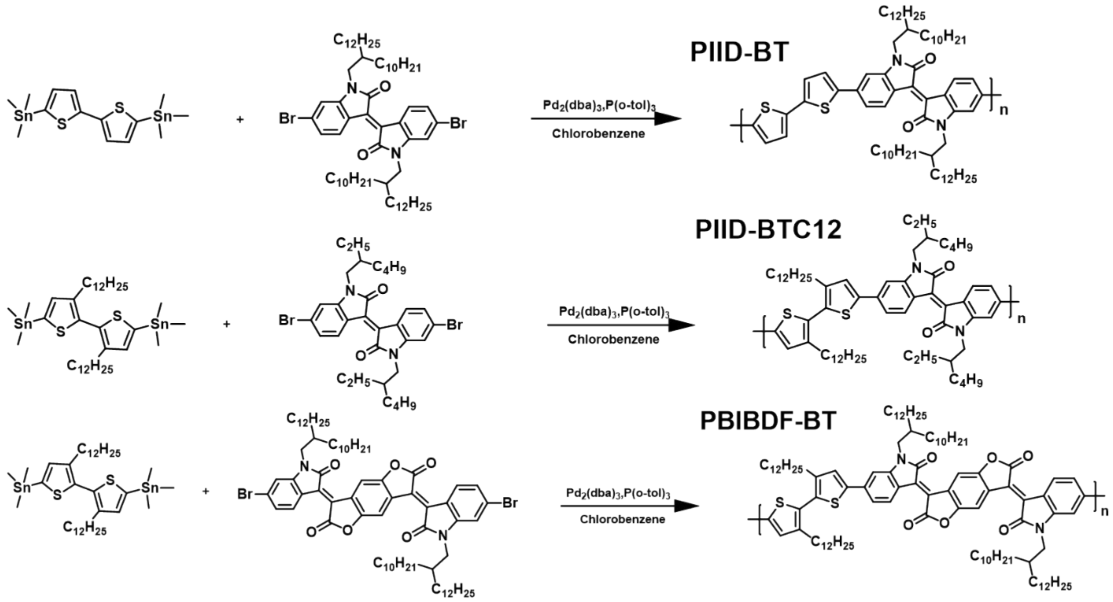

Figure S1. Polymers PIID-BT, PIID-BTC12 and PBIBDF-BT synthesis route

2.General procedures and Experimental details

Nuclear magnetic resonance (NMR) spectra were record on an Agilent VNMRS600 (600 MHz) spectrometer. the number-average molecular weight (Mn) of the polymers was characterized on Waters Series 1525 gel permeation chromatography (GPC) analysis at 100 °C with 1,2,4-trichlorobenzene as eluent and polystyrene as the standard. Elemental analysis was performed on a Vario EL instrument. Thermo-gravimetric analyses (TGA) were performed on a TA Instruments QS000IR under a nitrogen atmosphere and a heating rate of 10 °C/min. Ultraviolet-Visible (UV-Vis) spectra were carried out on an Agilent Cary 5000 UV-vis-NIR spectrophotometer with samples in both solution and thin film. Cyclic voltammetry (CV) measurements were conducted on a CHI 660 D electrochemical workstation under nitrogen equipped with a three-electrode system containing Bu_4NPF_6 (0.1 M) in deoxygenated anhydrous acetonitrile and at a scan rate of 100 mV/s, polymer thin film was coated on surface of Pt disc that acted as the working electrode, another platinum wire was ultilized as the auxiliary electrode, meanwhile an Ag/Ag^+ electrode acted as the reference electrode. and ferrocene was selected as the standard. Grazing-incidence-X-ray diffraction (GIXD) measurements were performed using 9A and 3C beamlines at the Pohang Accelerator Laboratory (PAL) in Korea. The atomic force microscopy (AFM) images of the polymer films was investigated using a SPA300HV instrument.

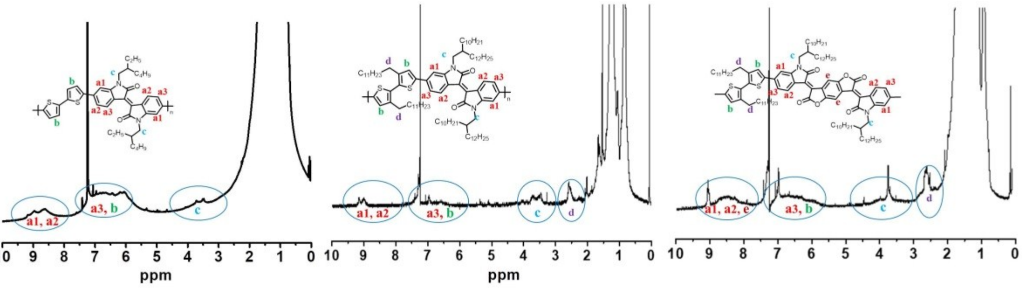

Figure S2. Nuclear magnetic resonance (NMR) of polymers PIID-BT,PIID-BTC12, and PBIBDF-BT.

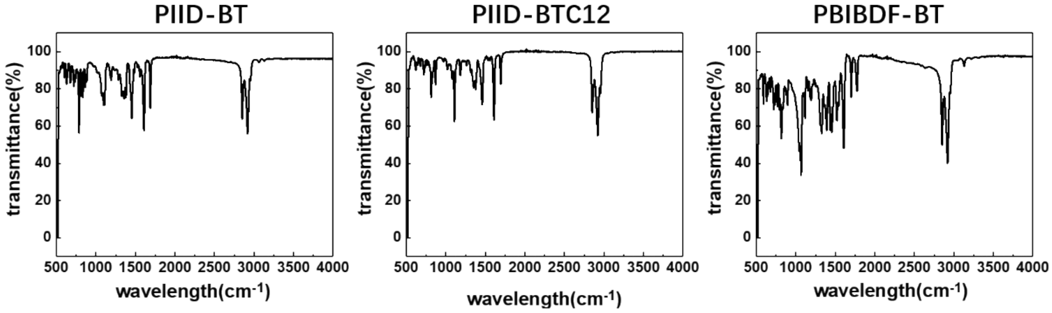

Figure S3. Fourier transform infrared spectroscopy (FTIR) of polymers PIID-BT,PIID-BTC12, and PBIBDF-BT.

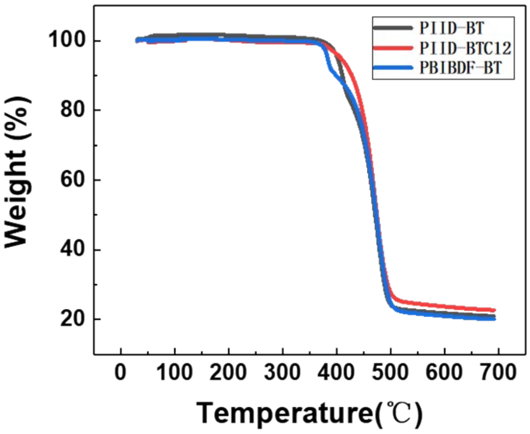

Figure S4. Thermogravimetric curves of polymers PIID-BT, PIID-BTC12, and PBIBDF-BT in nitrogen.

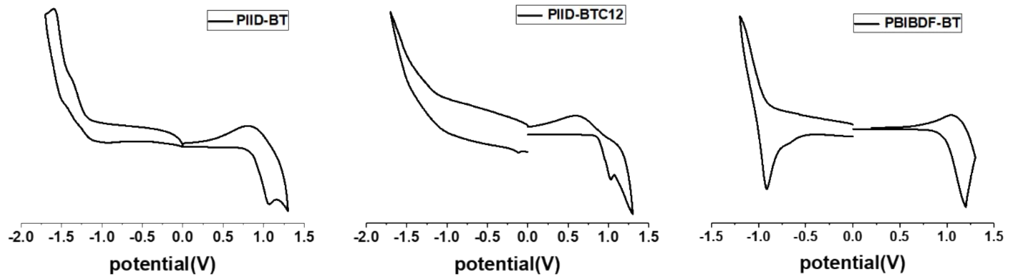

Figure S5. Cyclic voltammograms (CV) of polymers PIID-BT, PIID-BTC12 and PBIBDF-BT.

polymer	temp	$\mu_h^{average}$	V_{th}	I_{on}/I_{off}	$\mu_e^{average}$	V_{th}	I_{on}/I_{off}
	℃	$cm^{-2}V^{-1}s^{-1}$	V		$cm^{-2}V^{-1}s^{-1}$	V	
PIID-BT	RT	0.07	-21	10^4	N/A	N/A	N/A
	260 °C	0.79	-14	10^5	N/A	N/A	N/A
PIID-BTC12	RT	N/A	N/A	N/A	N/A	N/A	N/A
	260 °C	4.61×10^{-3}	-29	10^4	N/A	N/A	N/A
PBIBDF-BT	RT	0.21	-27	10^4	0.42	23	10^5
	260 °C	0.65	-26	10^4	0.73	21	10^5

Table S1. OFETs performances of polymers without and with annealing at 260 °C.

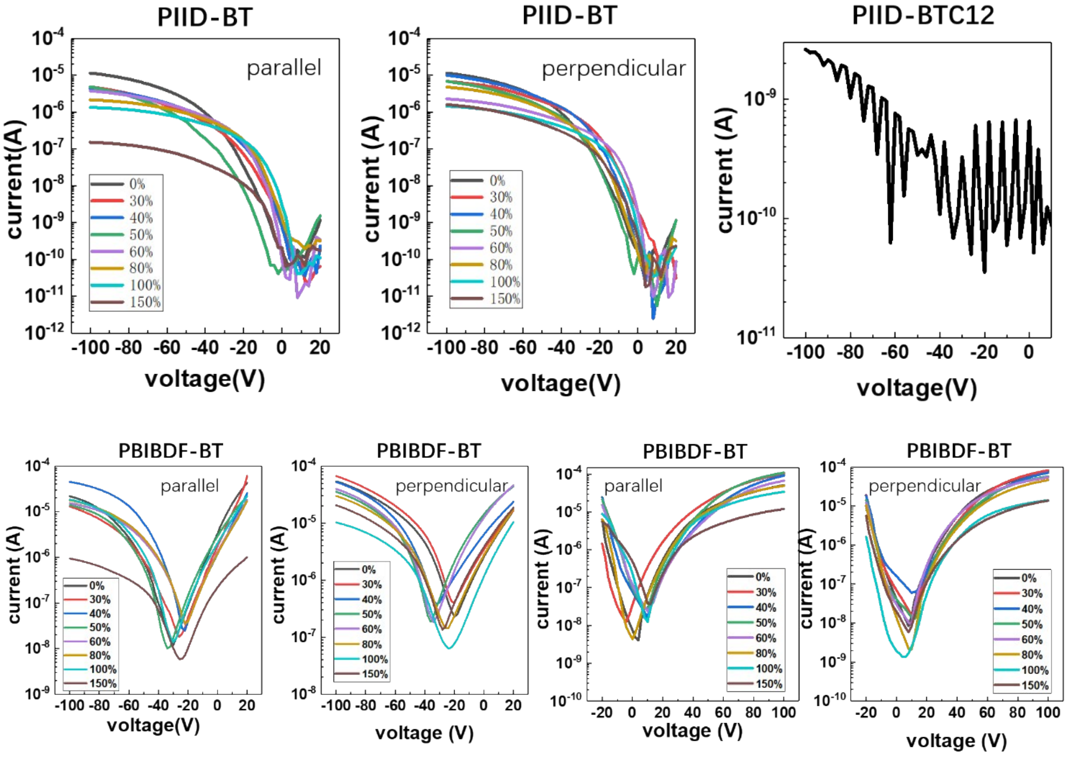

Figure S6. Transfer curves of polymers PIID-BT, PIID-BTC12 and PBIBDF-BT thin films with different strain.

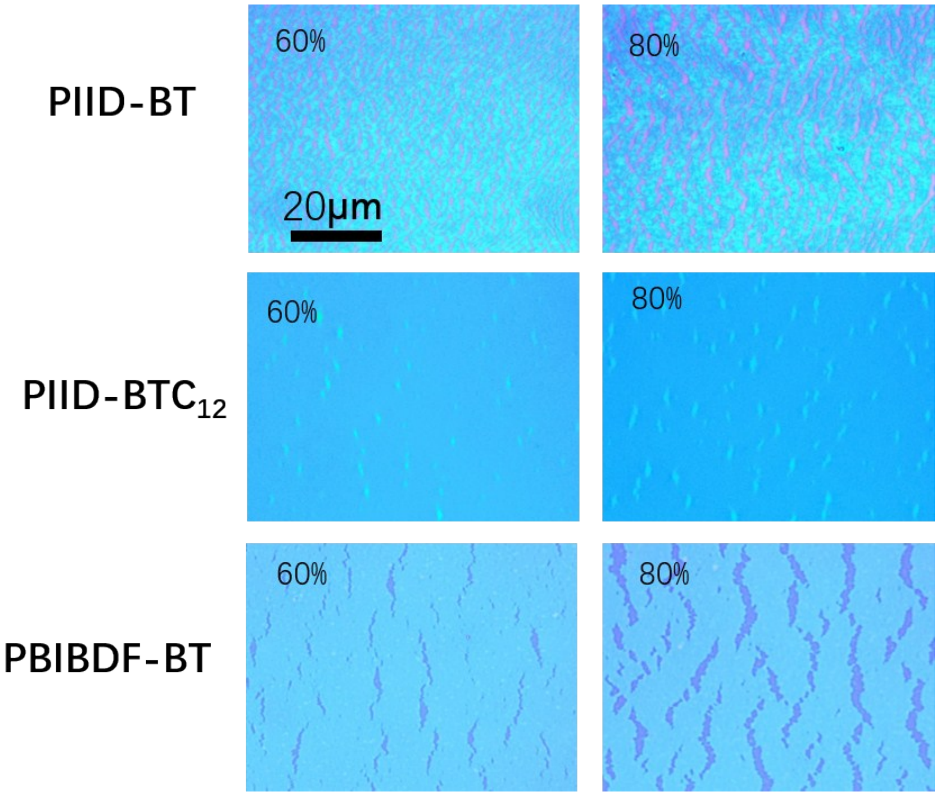

Figure S7. Optical images of thin films under 60%, 80% and 100% strain.

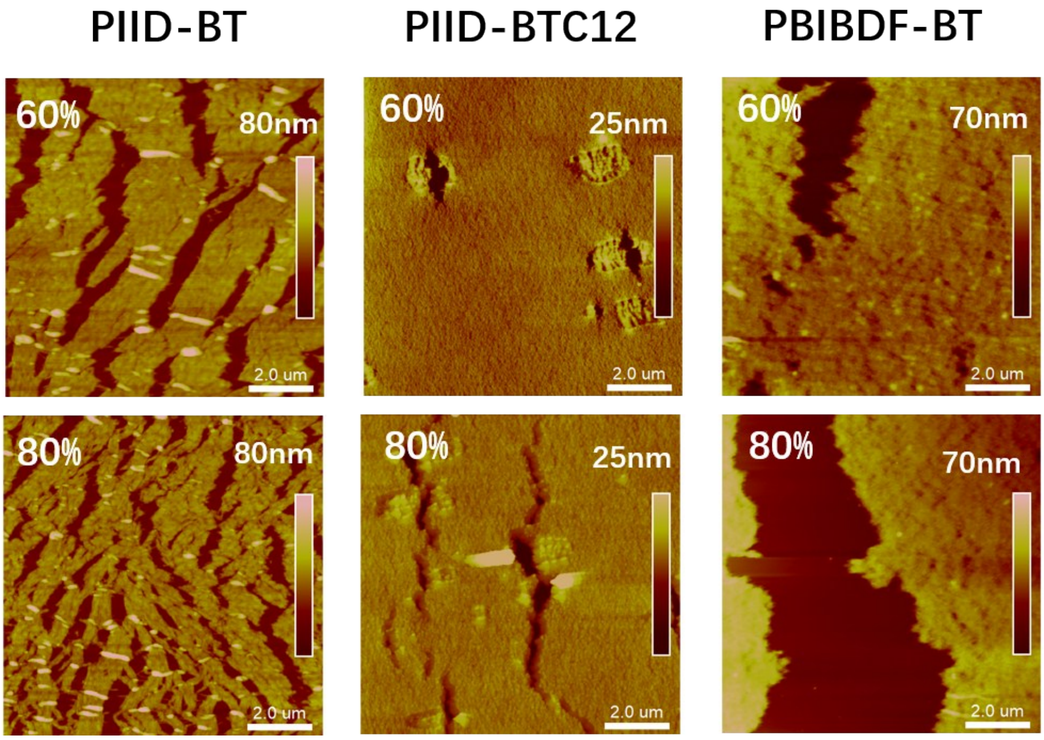

Figure S8. AFM topographies of stretched thin films under 80% and 100% strain.

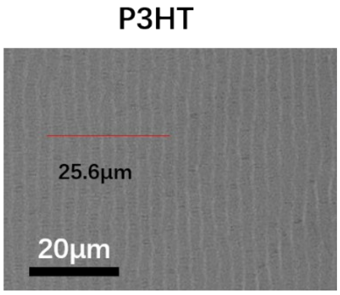

Figure S9. The optical images of buckled P3HT films.

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