Electronic Supplementary Information

Isoindigo-based polymer field-effect transistors: effects of selenophene-substitution toward high charge carrier mobility

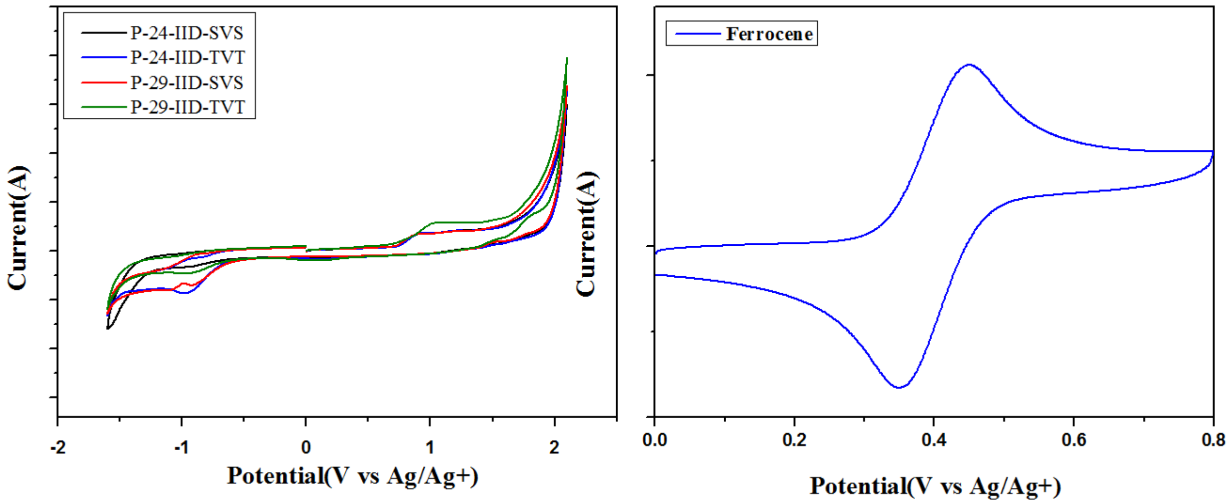


Figure S1. Cyclic voltammetry curves of (left) polymeric semiconductors used in this study and (right) ferrocene reference.

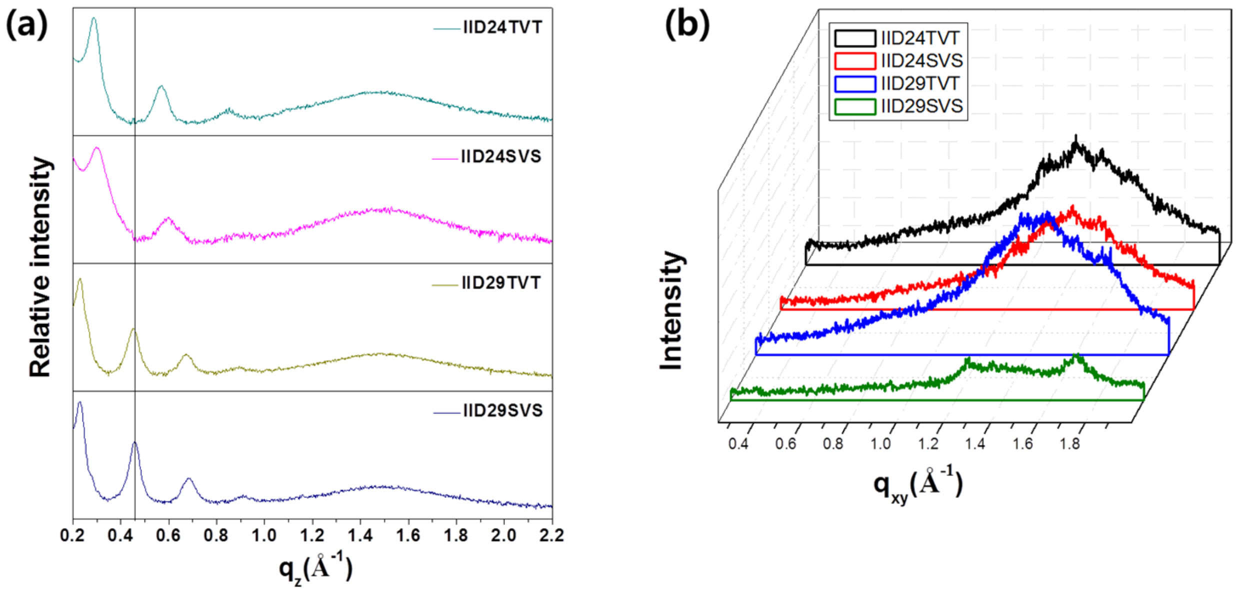


Figure S2. Extracted (a) out-of-plane and (b) in-plane diffraction profiles of polymers

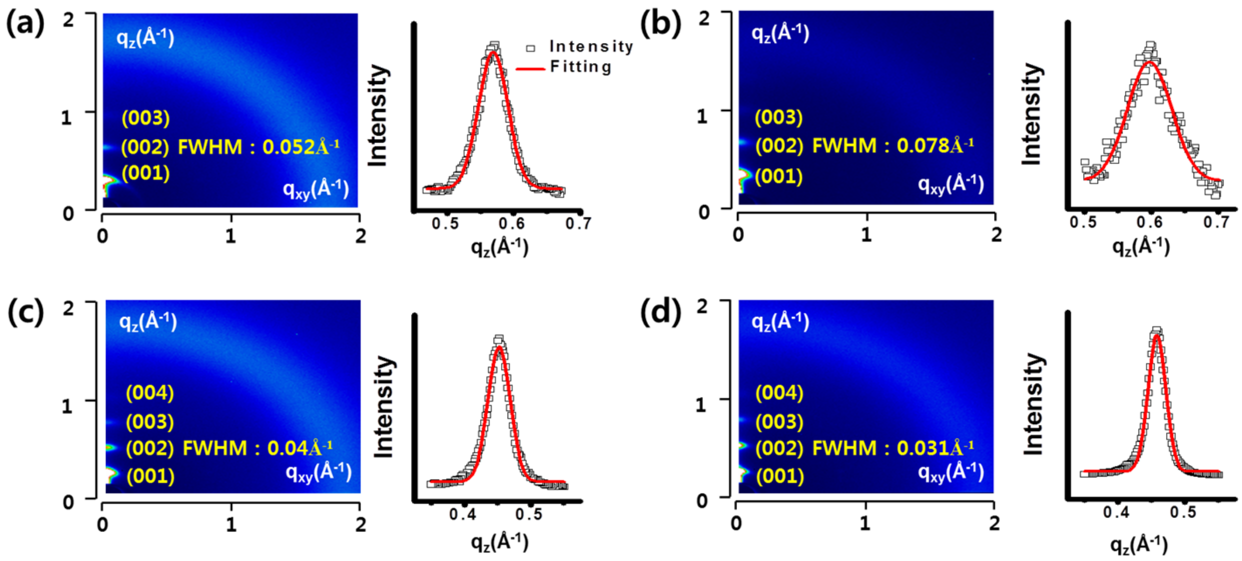


Figure S3. The comparison of FWHM between all polymers

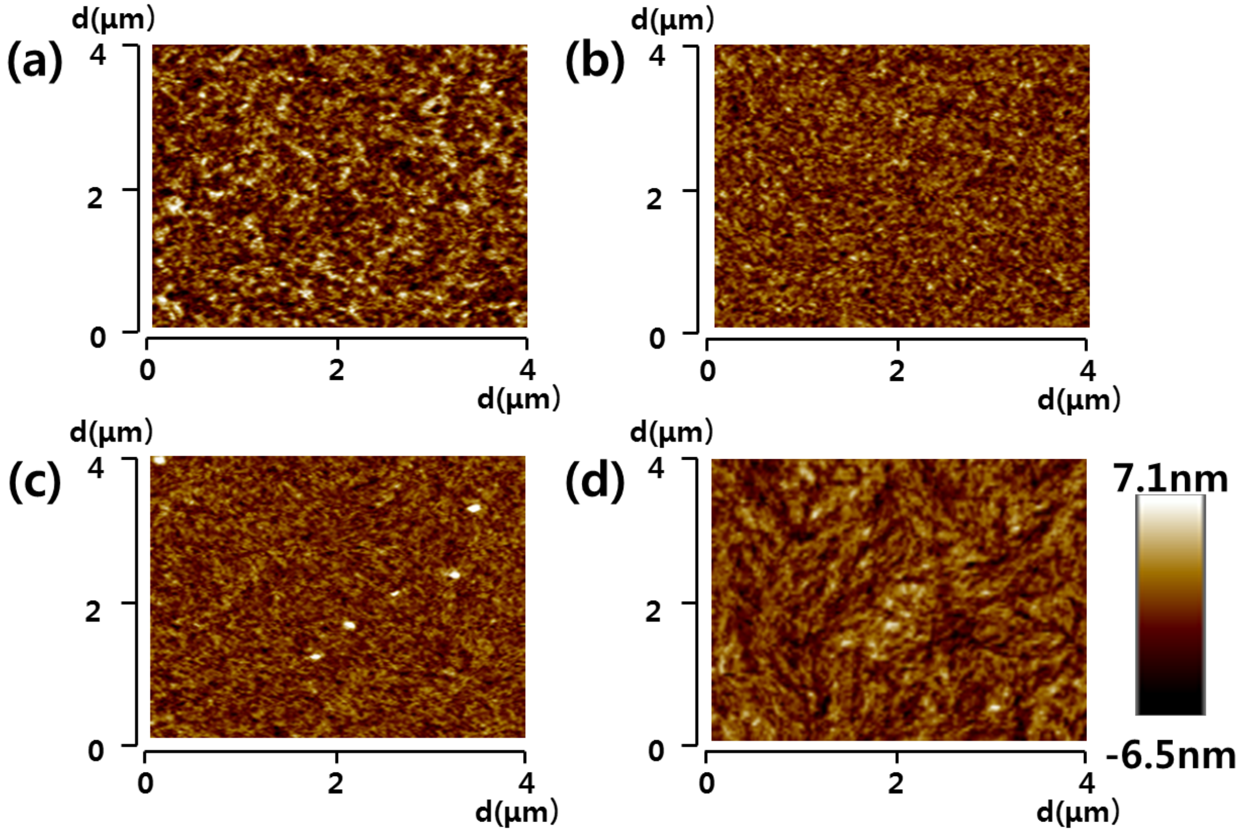


Figure S4. AFM images of (a) P-24-IID-TVT, (b) P-24-IID-SVS, (c) P-29-IID-TVT and (d) P-29-IID-SVS

Table S1.

Polymer	λ_{max}^{0-0}**sol** **(nm)**	λ_{max}^{0-1}**sol** **(nm)**	$\lambda_{max}^{0-0}film$ **(nm)**	$\lambda_{max}^{0-1}film$ **(nm)**	Eg^{opt} **(eV)**
P24-IID-TVT	707	645	699	635	1.65
P24-IID-SVS	718	656	717	651	1.6
P29-IID-TVT	725	661	713	647	1.59
P29-IID-SVS	739	685	732	663	1.55

Table S2.

Alkyl	**Oxidation onset (eV)**	**Reduction onset (eV)**	**HOMO (eV)**	**LUMO (eV)**	**Band gap (eV)**
P24-IID-SVS	**0.83**	**-0.65**	**-5.29**	**-3.81**	**1.48**
P24-IID-TVT	**0.84**	**-0.60**	**-5.30**	**-3.86**	**1.46**
P29-IID-SVS	**0.76**	**-0.59**	**-5.22**	**-3.87**	**1.37**
P29-IID-TVT	**0.79**	**-0.64**	**-5.25**	**-3.82**	**1.43**

*** Ferrocene : 4.84 - 0.38 = 4.46 eV**

Characterization

GIXD : GIXS data were measured at 3C beam line of Pohang accelerator laboratory. In GIXS, the wavelength of the incident X-ray was 1.213Å and the sample to detector distance was 209.97mm. The electrical characteristics of the transistors were measured by 4156A Precision semiconductor parameter analyzers (Agilent Technologies).

AFM : All the morphological images were obtained by using an atomic force microscope (AFM: XE-100, PISA).

Measurement : The electrical characteristics of the transistors were measured by 4156A precision semiconductor parameter analyzers (Agilent Technologies).

Device fabrication

Top-contact OFETs were fabricated on a common gate of highly n-doped silicon with a 100 nm thick thermally grown SiO_2 dielectric layer. The dielectric layer was further modified by OTS by dipping in toluene solution. Solutions containing the polymer semiconductors were spin-coated at 2000 rpm from 0.5 - 1 wt% solutions to form thin films with a nominal thickness of 30 nm regardless the choice of processing solvents, as confirmed using a surface profiler (Alpha Step 500, Tencor). The films were annealed at 170°C for 20 min under a nitrogen atmosphere. Gold source and drain electrodes were evaporated on top of the semiconductor layers (80 nm). For all measurements, typical channel widths (W) and lengths (L) were 1000 μm and 100 μm, respectively.

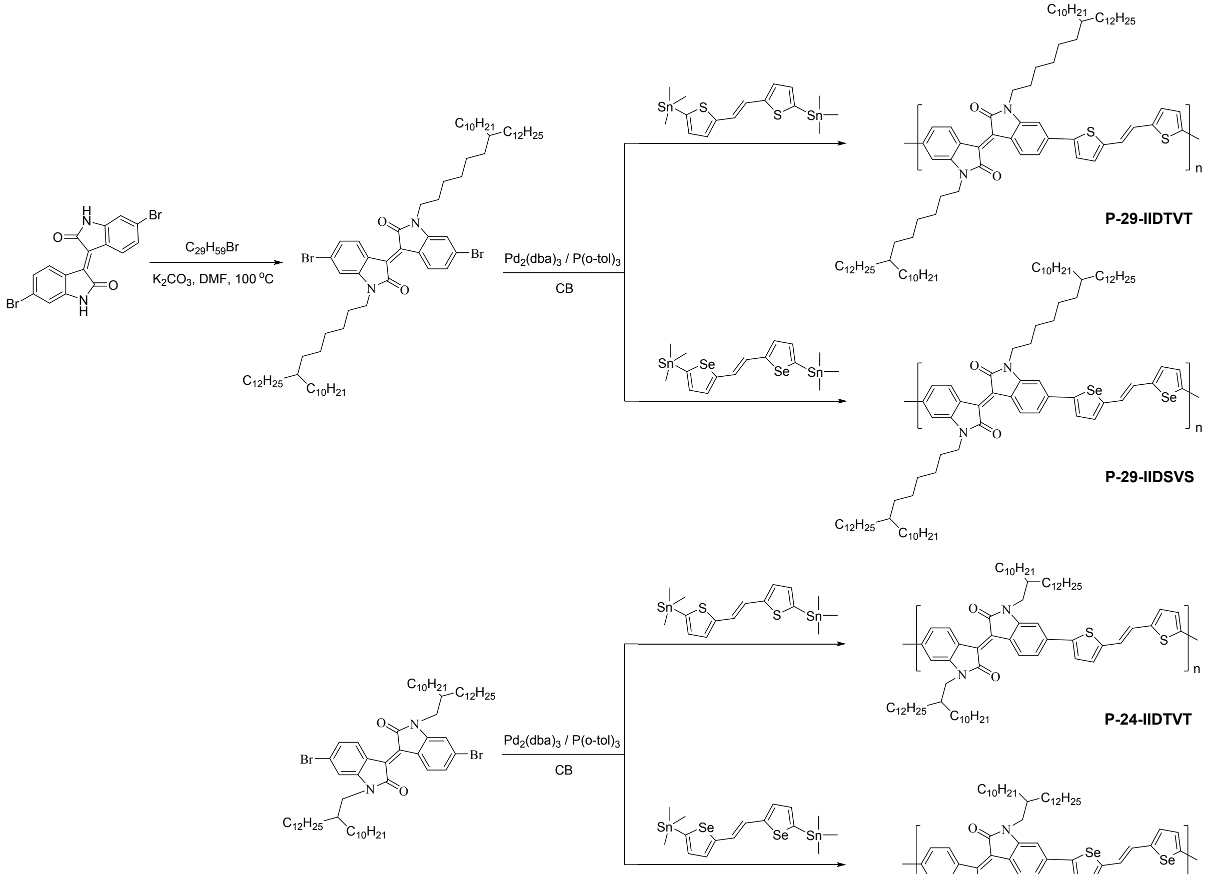
Synthesis

The polymers were prepared by Stille coupling polymerization. All polymers were purified by precipitation into methanol following subsequent Soxhlet extraction with methanol, hexane, and chloroform. The polymers showed good solubility in common organic solvent such as chloroform and chlorobenzene. Gel permeation chromatography (GPC) analysis against a polystyrene standard in chlorobenzene exhibited a number average molecular weight (Mn) of 108 kDa, 189 kDa,, 81 kDa,, and 295 kDa, and polydispersity indexes (PDI) of 2.98, 2.29, 2.72, and 2.36 for P-24-IIDTVT, P-24-IIDSVS, P-29-IIDTVT, and P-29-IIDSVS, respectively. The thermal stability of polymers was characterized by thermogravimetry analysis (TGA) (See supporting Figure S4). All of the polymers showed 5% weight loss above 400 C. The thermal transitions of the polymers were not observed in the differential scaning calorimetry (DSC) (See supporting Figure S4).

All chemicals were purchased from Aldrich and Alpha : thiophene-2-carbonitrile, Lawesson's reagent, 11-(6'-bromohexyl)tricosane,[1,2] DMF, THF, NBS, n-BuLi, and 6-bromoisatin were used without further purification and (E)-1,2-di(selenophen-2-yl)ethene[3] were synthesized via published literature procedures.

^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Bruker AM-300 and DRX-500 MHz spectrometers. Molecular weights and polydispersities of the copolymers were determined by gel permeation chromatography(GPC) analysis with polystyrene standard calibration (waters high-pressure GPC assembly Model M515 pump, u-Styragel columnsof HR4, HR4E, HR5E, with 500 and 100 Å , refractive index detectors, solvent chloroform). Elemental analyses were recorded using a CHNS-932 (Leco) elemental analyzer. Thermal analysis was performed using a TA TGA 2100 thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 10°C/min.

Differential scanning calorimeter (DSC) was conducted under nitrogen using a TA instrument 2100 DSC. The sample was heated at 10°C /min from 30°C to 250°C. UV–vis absorption spectra were measured using a Perkin-Elmer LAMBDA-900 UV spectrophotometer. Cyclic voltammetry (CV) was performed using an EG and G Parc model 273 Å potentiostat/galvanostat system with a three-electrode cell in a solution containing Bu_4NClO_4 (0.1 M) in acetonitrile at a scan rate of 100 mV/s. The polymer films were coated on a square carbon electrode (0.50 cm^2) by dipping the electrode into the corresponding solvents then drying in air. A Pt wire was used as the counter electrode, and an $Ag/AgNO_3$ (0.1 M) electrode was used as the reference electrode.



Scheme S1. Synthetic routes of P-29-IID-TVT, P-29-IID-SVS, P-24-IID-TVT and P-29-IID-SVS

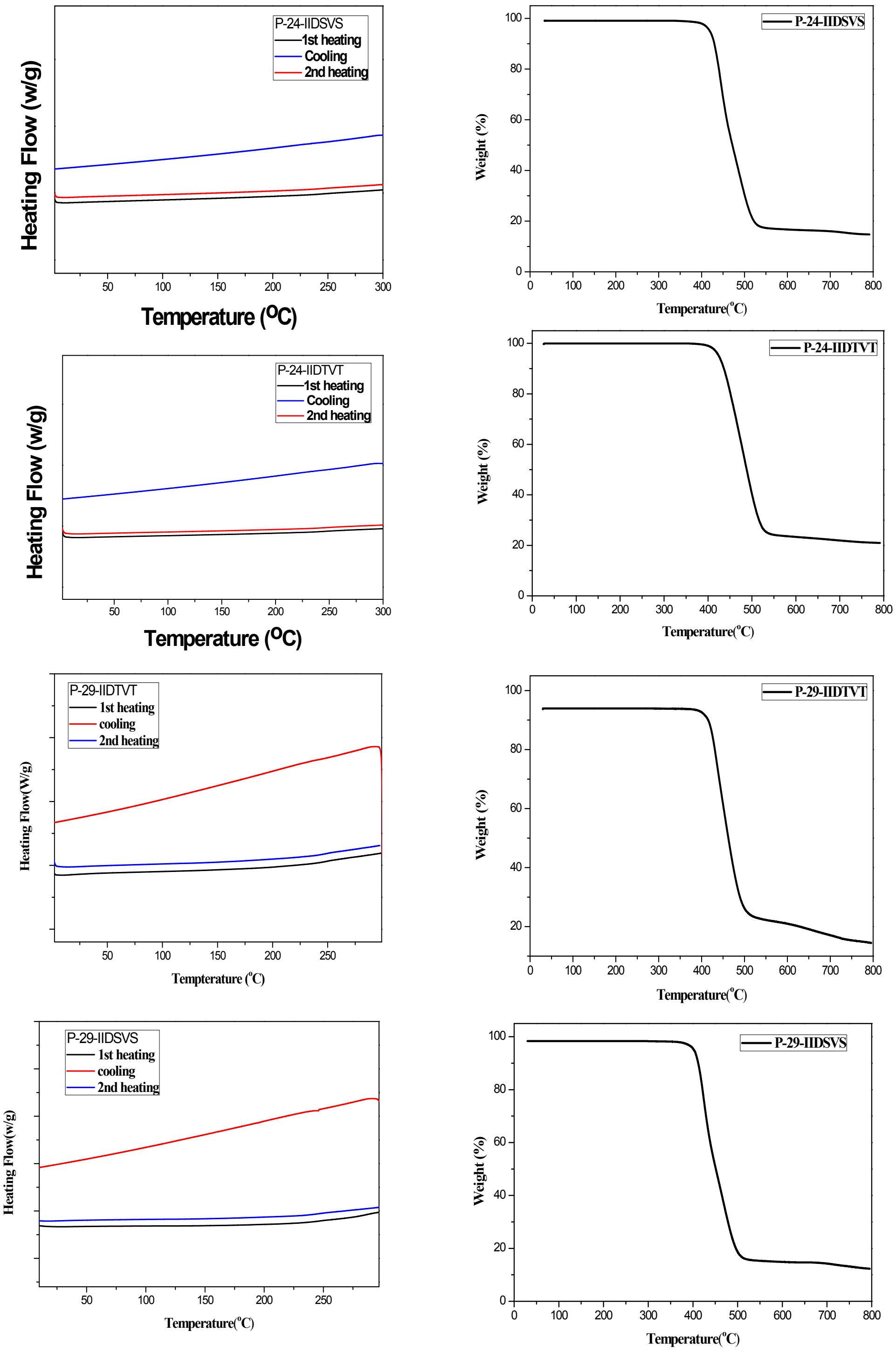


Figure S4. TGA and DSC thermograms of P-24-IID-TVT, P-24-IID-SVS, P-29-IID-TVT, P-29-IID-SVS.

Synthesis of 6,6’-dibromoisoindigo.

The reaction was carried out by literature method.[4] A solution of 6-bromoisatin (5.0 g, 22.1 mmol) and Lawesson's Reagent (4.4 g, 11.0 mmol) in 100 mL *o*-xylene were stirred at 50 ^{o}C for 3 h. The reaction mixture was then cooled down to room temperature. After removal of solvent, the crude product was filtrated and washed with hot methanol.

Synthesis of 6,6’-dibromo-(N,N’-2-decyltetradecyl)-isoindigo.

After 6,6′-dibromoisoindigo (1.0 g, 2.3 mmol) was dissolved in *N,N’*-dimethylformamide (70 mL), potassium carbonate (1.3 g, 9.5 mmol) and 11-(bromomethyl)tricosane (7.9 g, 19.0 mmol) were added under nitrogen. The mixture was stirred for 22 h at 100 ^{o}C. After cooling down, the mixture was poured into water and extracted with CH_2Cl_2 and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified via chromatography with silica (Hexane: DCM = 1:5) and recrystallized from dichloromethane, hexane, and methanol. Yield: 0.7 g (28%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 9.1 (d, 2H), 7.20-7.16 (d, 2s), 6.92 (d, 2H), 3.65-3.63 (t, 4H), 1.96-1.84 (m, 2H), 1.31-1.22 (m, 80H), 0.91-0.87 (t, 12H). Element Anal. $C_{64}H_{104}Br_2N_2O_2$ Cal: C, 70.31; H, 9.59; Br, 14.62; N, 2.56; Found: C, 70.38; H, 9.54; N, 2.53.

Synthesis of 6,6’-dibromo-(N,N’-2-decylnonadecyl)-isoindigo.

After 6,6′-dibromoisoindigo (1.0 g, 2.3 mmol) was dissolved in *N,N’*-dimethylformamide (70 mL), potassium carbonate (1.3 g, 9.5 mmol) and 11-(6-bromohexyl)tricosane (9.2 g, 19.0 mmol) were added under nitrogen. The mixture was stirred for 22 h at 100 ^{o}C. After cooling down, the mixture was poured into water and extracted with CH_2Cl_2 and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified via chromatography with silica (Hexane: DCM = 1:5) and recrystallized from dichloromethane, hexane, and methanol. Yield : 0.6 g (25%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 9.12 (d, 2H), 7.20-7.17 (d, 2s), 6.95 (d, 2H), 3.77-3.72 (t, 4H), 1.73-1.67 (m, 4H), 1.27-1.22 (m, 98H), 0.91-0.87 (t, 12H). ^{13}C-NMR (500 MHz, $CDCl_3$): 167.749, 145.800, 132.672, 131.222, 126.750, 125.142, 120.430, 111.324, 37.366, 33.634, 31.940, 30.167, 29.733, 29.676, 29.380, 27.416, 27.040, 26.696, 22.708, 14.141. Element Anal. $C_{74}H_{124}Br_2N_2O_2$ Cal: C, 72.05; H, 10.13; Br, 12.95; N, 2.27; Found: C, 72.22; H, 10.20; N, 2.30.

Synthesis of poly[6,6’-dibromo-(N,N’-2-decyltetradecyl)-isoindigo-(E)-1,2-di(thiophen-2-yl)ethene] (P-24-IID-TVT).

To a Schlenk flask was added 6,6’-dibromo-(N,N’-2-decyltetradecyl)-isoindigo (0.3000 g, 0.274 mmol), (E)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (0.142 g, 0.274 mmol) and chlorobenzene (5 mL) under nitrogen. After degassing under nitrogen for 30 min, $Pd_2(dba)_3$ (5.0 mg, 0.005 mmol) and $P(o\text{-}tol)_3$ (6.6 mg, 0.021 mmol) were added to the mixture, which was then stirred for 48 h at 140 ^{o}C. 2-Bromothiophene and tributyl(thiophen-2-yl)stannane were injected sequentially into the reaction mixture for end-capping, and the solution was stirred for 6 h after each addition. After cooling to room temperature, the polymer was precipitated in 100 mL methanol. The crude polymer was collected by filtration and purified by Soxhlet extraction with methanol, acetone, hexane and chloroform successively. The final product IID_{24} -TVT was obtained by precipitation in methanol. Yield : 0.20 g. Element Anal. $C_{74}H_{110}N_2O_2S_2$ Cal: C, 79.14; H, 9.80; N, 2.49; S, 5.70; Found: C, 79.36; H, 10.00; N, 2.49; S, 5.52.

Synthesis of poly[6,6'-dibromo-(N,N'-2-decyltetradecyl)-isoindigo-(E)-1,2-di(selenophen-2-yl)ethene] (P-24-IID-SVS).

To a Schlenk flask was added 6,6'-dibromo-(N,N'-2-decyltetradecyl)-isoindigo (0.3000 g, 0.274 mmol), (E)-1,2-bis(5-(trimethylstannyl)selenophen-2-yl)ethene (0.1678 g, 0.274 mmol) and chlorobenzene (5 mL) under nitrogen. After degassing under nitrogen for 30 min, $Pd_2(dba)_3$ (5.0 mg, 0.005 mmol) and $P(o\text{-}tol)_3$ (6.6 mg, 0.021 mmol) were added to the mixture, which was then stirred for 48 h at 140 ^{o}C. 2-Bromothiophene and tributyl(thiophen-2-yl)stannane were injected sequentially into the reaction mixture for end-capping, and the solution was stirred for 6 h after each addition. After cooling to room temperature, the polymer was precipitated in 100 mL methanol. The crude polymer was collected by filtration and purified by Soxhlet extraction with methanol, acetone, hexane and chloroform successively. The final product IID_{24} -SVS was obtained by precipitation in methanol. Yield : 0.22 g, ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 9.15$ (br, 2H), 7.62-6.92 (br, 4H), 3.73 (s, 2H), 1.25 (br, 84H), 0.87 (br, 12H). Element Anal. $C_{74}H_{110}N_2O_2Se_2$ Cal: C, 73.02; H, 9.04; N, 2.30; Se, 12.99; Found: C, 72.23; H, 9.08; N, 2.27.

Synthesis of poly[6,6'-dibromo-(N,N'-2-decylnonadecyl)-isoindigo-(E)-1,2-di(thiophen-2-yl)ethene] (P-29-IID-TVT).

To a Schlenk flask was added 6,6'-dibromo-(N,N'-2-decylnonadecyl)-isoindigo (0.3000 g, 0.243 mmol), (E)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (0.1259 g, 0.243 mmol) and chlorobenzene (5 mL) under nitrogen. After degassing under nitrogen for 30 min, $Pd_2(dba)_3$ (4.4 mg, 0.004 mmol) and $P(o\text{-}tol)_3$ (5.9 mg, 0.019 mmol) were added to the mixture, which was then stirred for 48 h at 140 ^{o}C. 2-Bromothiophene and tributyl(thiophen-2-yl)stannane were injected sequentially into the reaction mixture for end-capping, and the solution was stirred for 6 h after each addition. After cooling to room temperature, the polymer was precipitated in 100 mL methanol. The crude polymer was collected by filtration and purified by Soxhlet extraction with methanol, acetone, hexane and chloroform successively. The final product IID_{29} -TVT was obtained by precipitation in methanol. Yield : 0.26 g, ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 9.12$ (s, 2H), 7.39-6.90 (br, 4H), 3.75 (s, 2H), 3.32 (s, 2H), 1.29-0.79 (br, 114H). FT-IR (cm^{-1}): 3122 (aromatic), 2922-2854 (aliphatic, C-H), 1684-1611 (C=C). Element Anal. Cal. $C_{84}H_{130}N_2O_2S_2$: C, 79.87; H, 10.30; N, 2.21; S, 5.07; Found: C, 79.62; H, 10.41; N, 2.23; S, 5.06.

Synthesis of poly[6,6'-dibromo-(N,N'-2-decylnonadecyl)-isoindigo-(E)-1,2-di(selenophen-2-yl)ethene] (P-29-IID-SVS).

To a Schlenk flask was added 6,6'-dibromo-(N,N'-2-decylnonadecyl)-isoindigo (0.3000 g, 0.243 mmol), (E)-1,2-bis(5-(trimethylstannyl)selenophen-2-yl)ethene (0.1487 g, 0.243 mmol) and chlorobenzene (5 mL) under nitrogen. After degassing under nitrogen for 30 min, $Pd_2(dba)_3$ (4.4 mg, 0.004 mmol) and $P(o\text{-}tol)_3$ (5.9 mg, 0.019 mmol) were added to the mixture, which was then stirred for 48 h at 140 ^{o}C. 2-Bromothiophene and tributyl(thiophen-2-yl)stannane were injected sequentially into the reaction mixture for end-capping, and the solution was stirred for 6 h after each addition. After cooling to room temperature, the polymer was precipitated in 100 mL methanol. The crude polymer was collected by filtration and purified by Soxhlet extraction with methanol, acetone, hexane and chloroform successively. The final product IID$_{29}$ -SVS was obtained by precipitation in methanol. Yield : 0.24 g, ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 8.82$ (br, 2H), 7.49-7.07 (br, 4H), 3.43 (br, 4H), 1.34-0.89 (br, 114H). FT-IR (cm^{-1}): 3126 (aromatic), 2922-2844 (aliphatic, C-H), 1684-1606 (C=C). Element Anal. $C_{84}H_{130}N_2O_2Se_2$ Cal: C, 74.33; H, 9.58; N, 2.06; Se, 11.65; Found: C, 74.16; H, 9.62; N, 2.16.

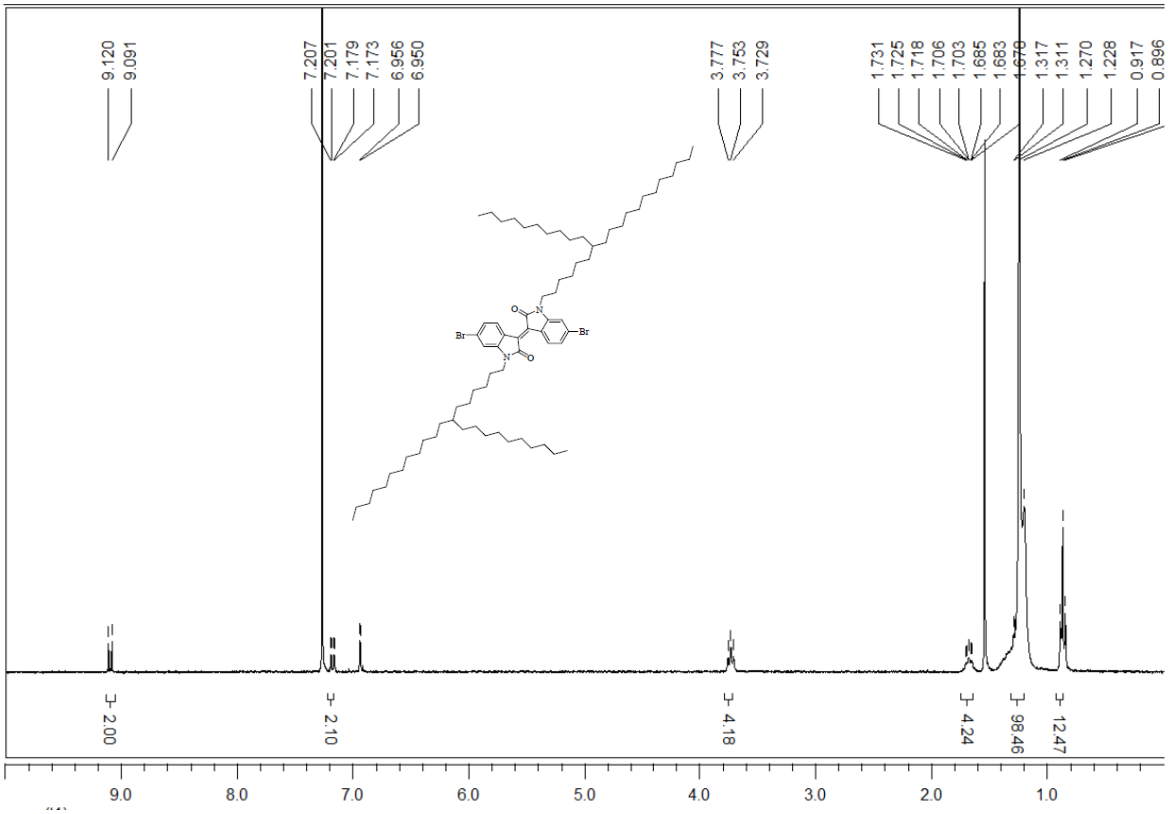


Figure S5. 1H-NMR of 6,6’-dibromo-(N,N’-2-decylnonadecyl)-isoindigo

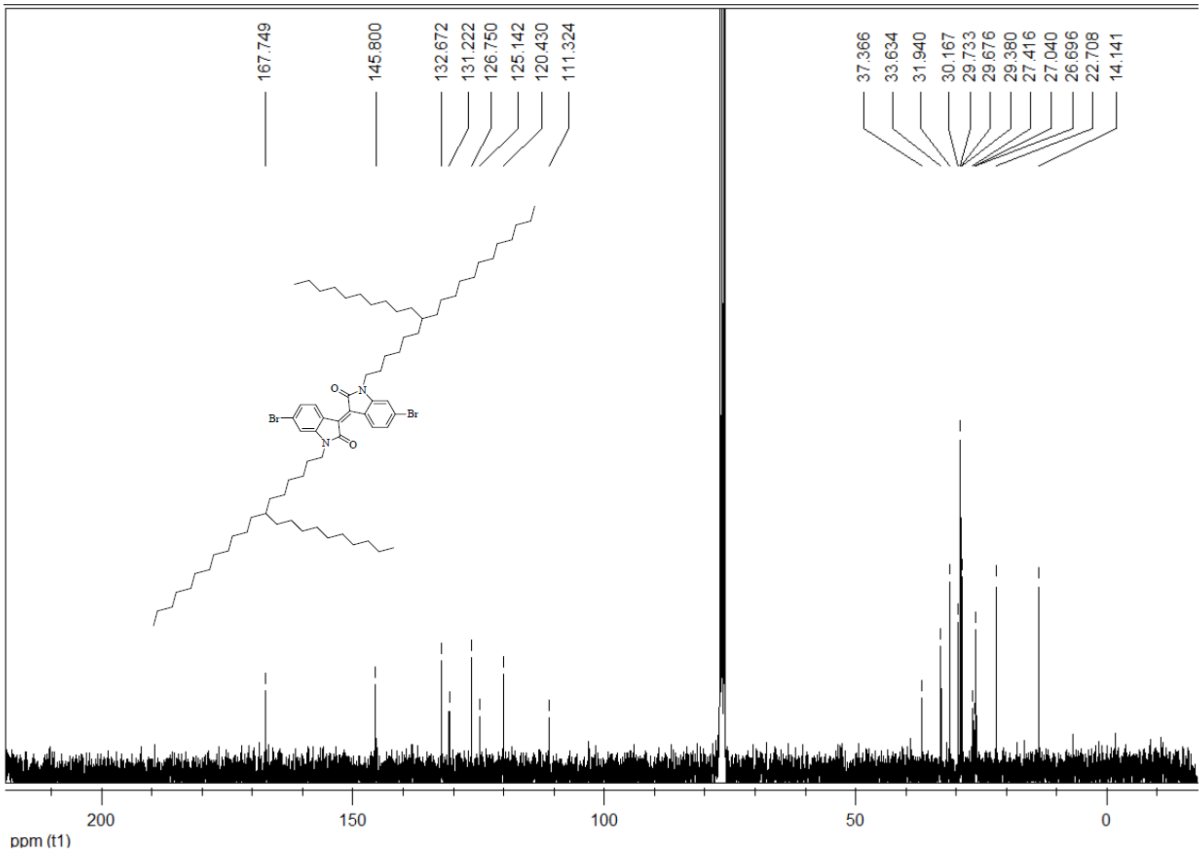


Figure S6. 13C-NMR of 6,6'-dibromo-(N,N'-2-decylnonadecyl)-isoindigo

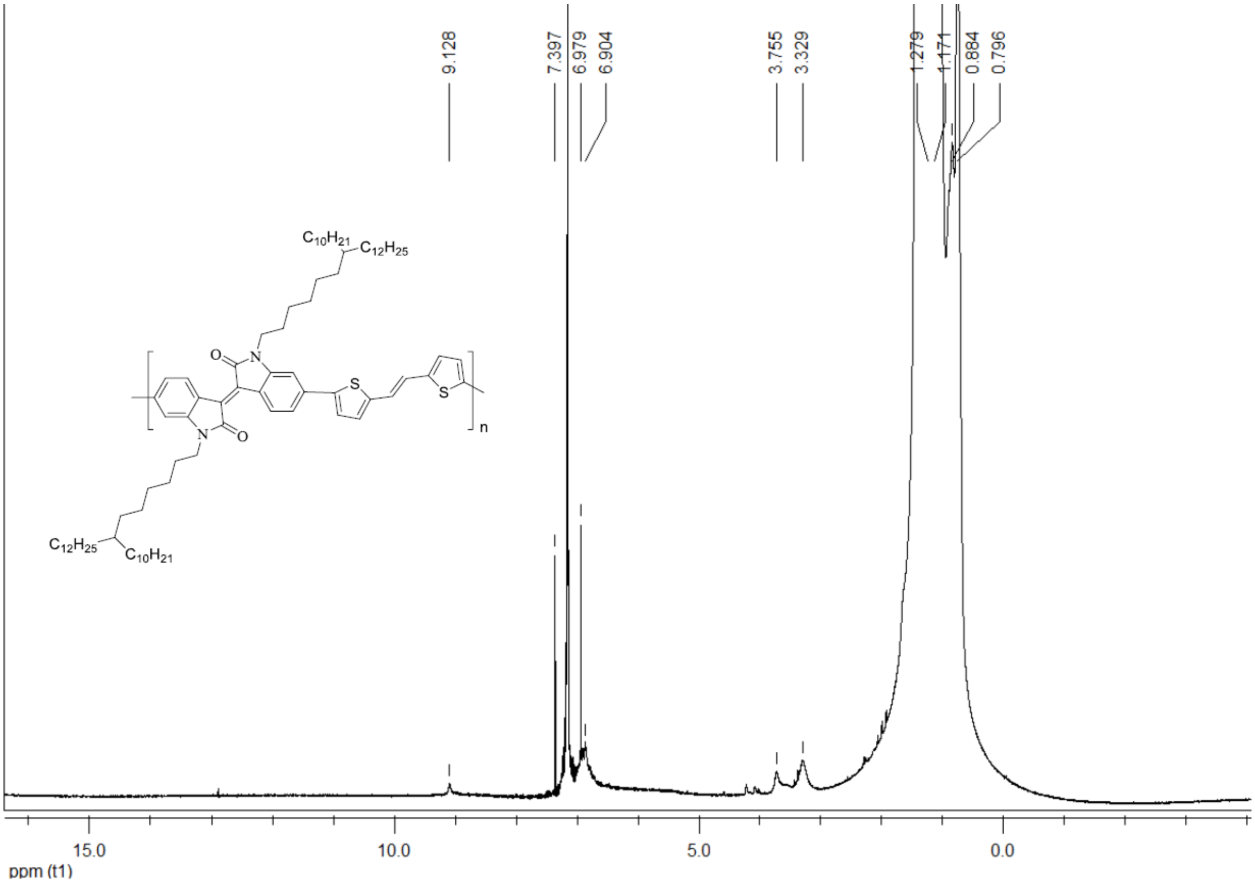


Figure S7. 1H-NMR of poly[6,6’-dibromo-(N,N’-2-decylnonadecyl)-isoindigo-(E)-1,2-di(thiophen-2-yl)ethene] (P-29-IIDTVT).

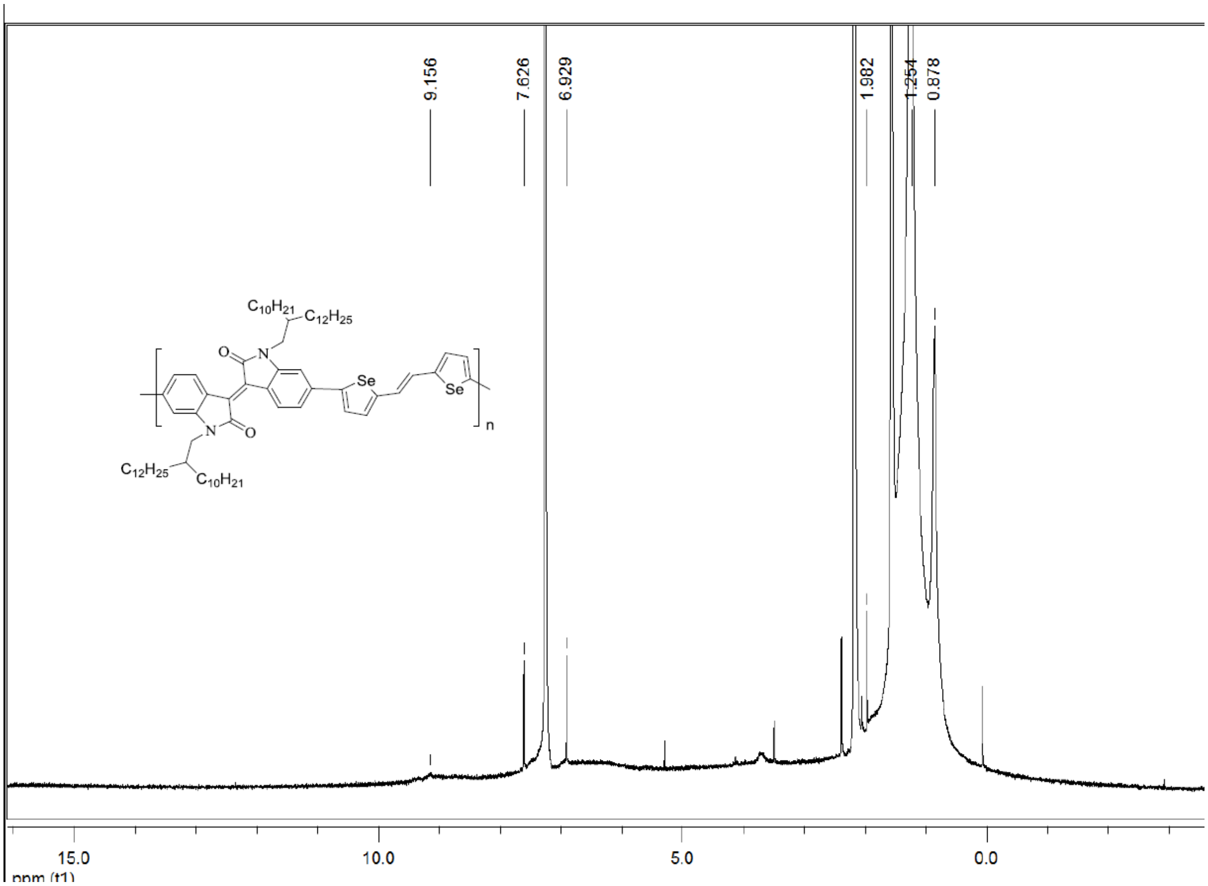


Figure S8. 1H-NMR of poly[6,6'-dibromo-(N,N'-2-decylnonadecyl)-isoindigo-(E)-1,2-di(thiophen-2-yl)ethene] (P-24-IIDSVS).

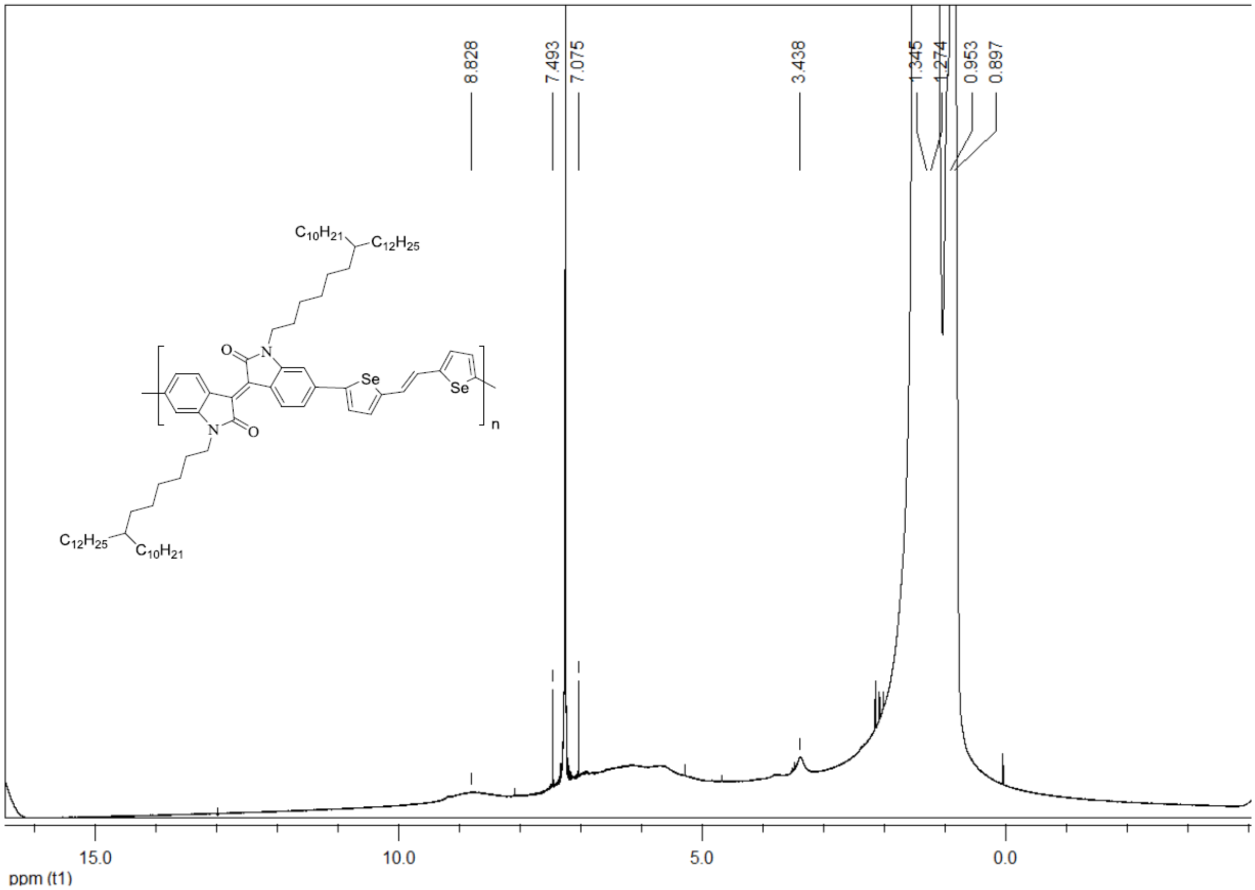


Figure S9. 1H-NMR of poly[6,6'-dibromo-(N,N'-2-decylnonadecyl)-isoindigo-(E)-1,2-di(thiophen-2-yl)ethene] (P-29-IIDSVS).

Reference

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