Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Synthesis of New *n*-Type Isoindigo Copolymers.

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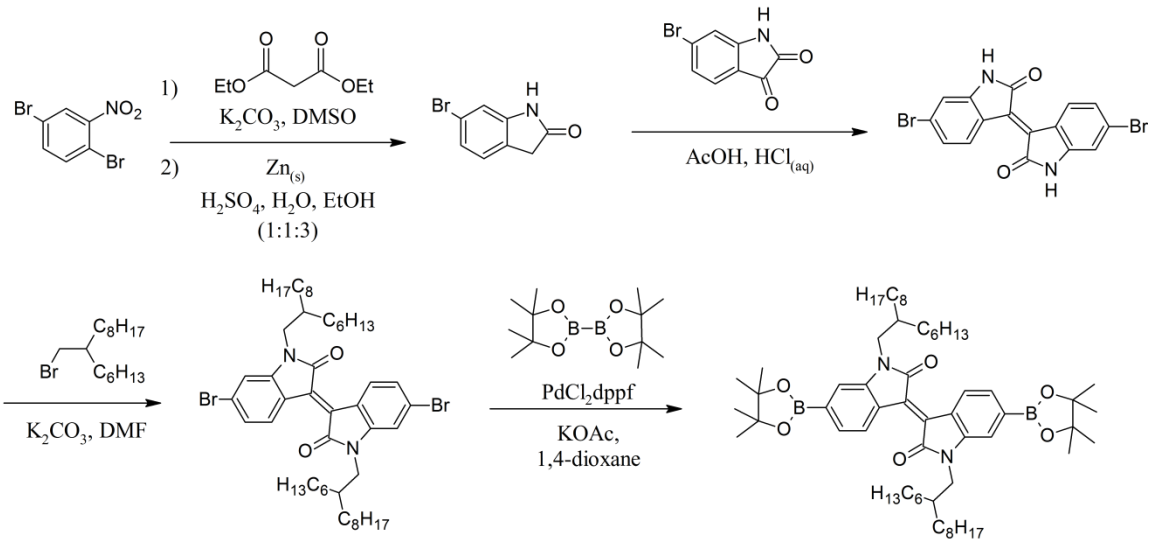
Experimental Part

Materials

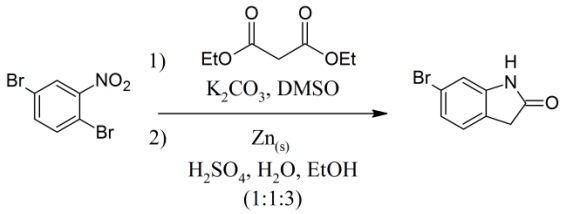
6-Bromoisatin and 2,5-dibromonitrobenzene were bought from TCI America, 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) was purchased from Boron Molecular and all other starting organic and organometallic compounds were purchased from Aldrich and used without any further purification. The reaction solvents were either distilled under inert atmosphere prior to use (THF from sodium) or bought from Aldrich as sealed anhydrous solvents (DMF, DMSO). The other solvents were usually ACS grade. 2-Hexyldecan-1-bromide[1], 5-octylthieno[3,4]pyrrole-4,6-dione[1], 1,3-dibromo-5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione[1], 5,5'-dioctyl-4*H*,4'*H*-1,1'-bithieno[3,4-*c*]pyrrole-4,4',6,6'(5*H*,5'*H*)-tetrone[2], 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-di(2-octyldodecyl)-pyrrolo[3,4c]pyrrolo-1,4-dione[3] and trans-di(μ-acetato)-bis[α(di-*o*-tolylphosphino)benzyl] dipalladium(II)[4] were prepared according to procedures reported in the literature. The synthesis of 6-bromooxindole[5, 6] and the dibromo[7] and diboronic[8] isoindigo derivatives are also based on literature. All the monomers were carefully purified prior to use in the polymerization reactions.

Synthesis of the monomers and polymers



S5: Synthesis of the isoindigo monomers.

Synthesis of 6-bromooxindole



The commercially available 2,5-dibromonitrobenzene (15.0 g, 53.4 mmol) was mixed with potassium carbonate anhydrous (73.8 g, 534 mmol) in 80 ml of dry DMSO under nitrogen atmosphere. The mixture was heated to 50 ^{o}C and diethylmalonate (44.3 g, 267 mmol) mixed in 40 mL of DMSO was added dropwise over an hour. The reaction mixture was left to react for 18h after which it was extracted with diethyl ether and the combined organic phases were washed with water. After removal of the solvents, a light yellow oil is obtained which contains the intermediate compound diethyl 2-(4-bromo-2-

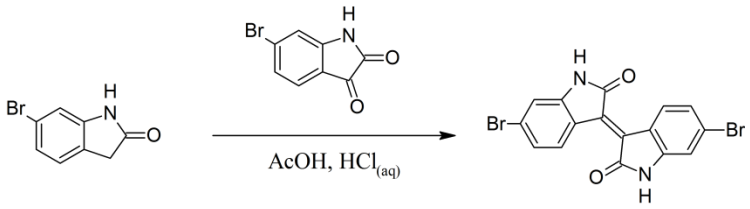
nitrophenyl)malonate mixed with diethyl malonate. This mixture was used without further purification and was solubilized in a mixture of 110 mL of water, 110 mL of sulfuric acid and 330 ml of ethanol and heated to reflux. Zinc powder (35 g, 534 mmol) was then slowly added to the reaction. The mixture was left to react for an hour before the slow addition of a second batch of zinc powder (35 g, 534 mmol). The reaction was left to react for 2 hours before being dropped in 1.5 L of water. The product was left to cristallize overnight after which it was filtered. The white solid obtained was washed with water to yield pure 6-bromooxindole (9.75 g, Y = 86%). M.P. = 214-216 ^{o}C

^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 10.50 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.10 (dd,J^1 = 8 Hz, J^2 = 1,8 Hz, 1H), 6.94 (d, *J* = 1,8 Hz, 1H), 3.44 (s, 2H)

^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 176.16, 145.11, 126.11, 125.18, 123.56, 119.80, 111.76, 35.31

HRMS (ESI)(M+H)+: Calcd: 210.9633, Found: 210.9632, diff (ppm): -0.19.

Synthesis of 6,6'-dibromoisoindigo



6-Bromooxindole (5.14 g, 24,3 mmol) and the commercially available 6-bromoisatin (5.50 g, 24.3mmol) were solubilised together in 160 ml of acetic acid. 1.2 mL of Hydrochloric acid 12 M was added and the mixture was refluxed for 26 hours. It was then

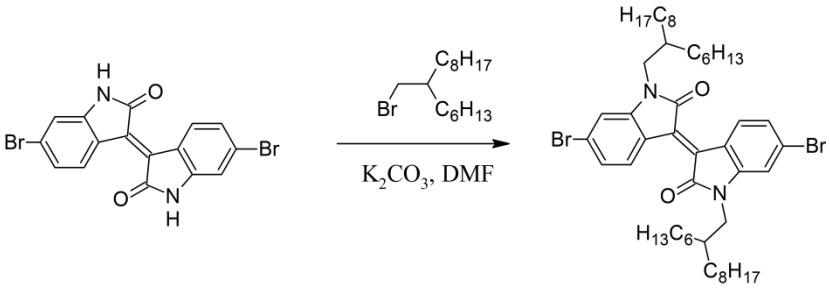
dropped in 1 L of water and filtered. The brown solid was then washed with water, methanol and ethyl acetate. The dark brown solid was then triturated in 250 ml of ethyl acetate for an hour. 6,6'-dibromoisoindigo was obtained after filtration of the solvents as a dark brown solid (9.24 g, Y = 91%). M.P. = >400°C

^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 11.10 (s, 2H), 8.99 (d, *J* = 8.8 Hz, 2H), 7.19 (dd, J^1 = 8.8 Hz, J^2 = 1,9 Hz, 2H), 6,99 (d, *J* = 1,9 Hz, 2H)

^{13}C NMR (100 MHz, $CDCl_3$, ppm) *not recorded due to low solubility*

HRMS (ESI)(M+H)+: Calcd: 417.8953, Found: 417.8938, diff (ppm): -3.5

Synthesis of 6,6'-dibromo-(*N*,*N*'-2-hexyldecyl)-isoindigo



6,6'-Dibromoisoindigo (3.65 g, 8.68 mmol) and anhydrous potassium carbonate (6.00 g, 43.4 mmol) were mixed in 175 ml of dry DMF and the mixture was heated to 100°C under nitrogen atmosphere. 2-hexyl-1-bromodecane (7.95 g, 26.0 mmol) was then added and the resulting red solution was left to react for 22 hours. The reaction mixture was then poured in water and extracted with dichloromethane. The organic phases were combined, washed with brine and dried with sodium sulfate. The solvents were evaporated under reduced pressure and a red oil was obtained. This product was then purified over a short silica column using hexane first as the eluent and then with a

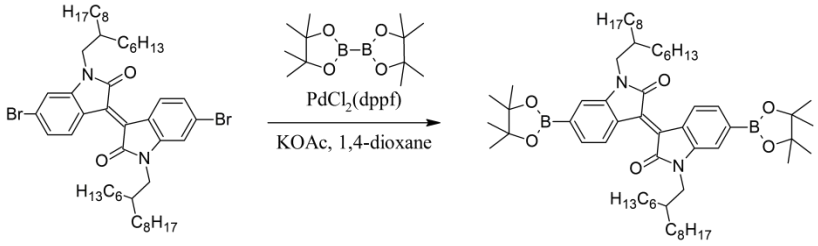
mixture of hexane and dichloromethane (1:1). A red oil was obtained which solidifies after several days. This product is further purified by column chromatography over silica gel by using methanol to remove an oily byproduct which can be observed using thin film chromatography using hexane and toluene (55:45) as the eluent and ceric ammonium molybdate stain. The product was then obtained by eluting with dichloromethane. After removal of the solvents, the red product was solubilised in dichloromethane and vacuum filtered to remove the silica which was solubilised by the methanol. After removal of the solvents, 6,6'-dibromo-*N*,*N*'-(2-hexyldecyl)-isoindigo was obtained as a pure red solid (6.21 g, Y = 82%). M.P. = 50-52^{o}C

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.06 (d, *J* = 8.9 Hz, 2H), 7.16 (dd, J^1 = 8.9 Hz, J^2 = 1.5 Hz, 2H), 6.89 (d, *J* = 1.5 Hz, 2H), 3.62 (d, *J* = 7.3 4H), 1.88 (m, 2H), 1.2-1.4 (m, 48H), 0.86 (m, 12H)

^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.29, 146.37, 132.76, 131.16, 126.82, 125.27, 120.54, 111.72, 53.58, 44.84, 36.23, 32.01, 31.94, 31.62, 30.12, 29.79, 29.68, 29.43, 26.49, 26.46, 22.81, 22.77, 14.26, 14.23.

HRMS (ESI)(M+H)+: Calcd: 866.3961, Found: 866.3935, diff (ppm): -2.96

6,6'-(*N*,*N*'-2-hexyldecyl)-pinacolatodiboronisoindigo



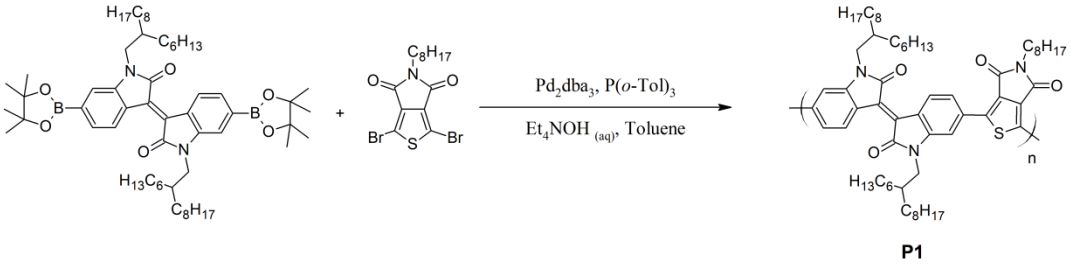
6,6'-dibromo-(*N*,*N*'-2-hexyldecyl)-isoindigo (3.00 g, 3.45 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (2.11 g, 8.29 mmol), 1,1'-Bis(diphenylphosphino)ferrocene-palladium(II)dichloride (0.151 g, 6 %mol) and potassium acetate (2.03 g, 20.7 mmol) were added to a flask under dry and inert atmosphere. 1.4 ml of dry and degassed 1,4-dioxane was added and the reaction mixture was heated to 85°C for 30 hours. The reaction mixture was then cooled to room temperature and filtered on silica using dichloromethane to recuperate the product. The solvents were evaporated to about 10 ml and the product was precipitated in methanol. The product is obtained as a dark red solid by filtration and rinsing with methanol (2.85 g, Y = 86%). M.P. = 118-120^{o}C

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.13 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.16 (s, 2H), 3.69 (d, *J* = 7.3, 4H), 1.95 (m, 2H), 1.36 (s, 24H), 1.2-1.4 (m, 48H), 0.84 (m, 12H)

^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.22, 144.57, 134.46, 128.99, 128.82, 124.35, 113.64, 84.18, 44.54, 36.20, 32.03, 31.69, 31.67, 30.14, 29.79, 29.72, 29.44, 29.30, 26.53, 26.51, 25.16, 25.00, 22.81, 22.76, 14.26, 14.25.

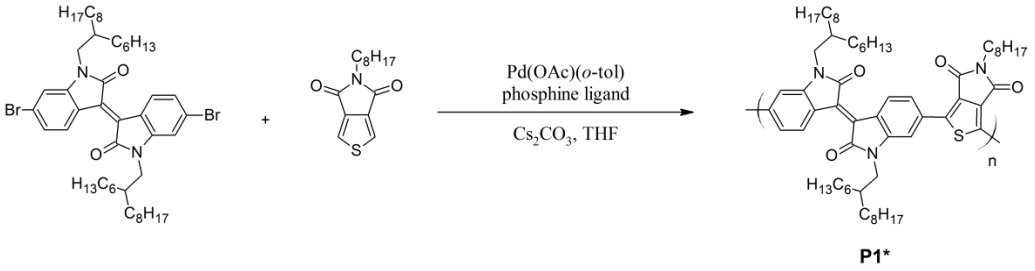
HRMS (ESI)(M+H)+: Calcd: 960.7527, Found: 960.7557, diff (ppm): 3.08

Synthesis of P1



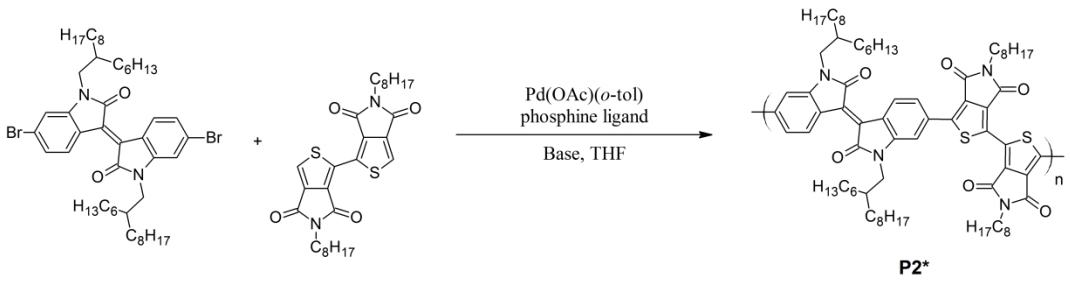
1,3-Dibromo-5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione (44.0 mg, 0.104 mmol), 6,6'-dibromo-*N*,*N*'-(2-hexyldecyl)-isoindigo (100 mg, 0.104 mmol), tris(dibenzylideneacetone)dipalladium(0) (3.3 mg, 3.5% mol) and tri(*o*-tolyl)phosphine (2.2 mg, 7% mol) were put in a reaction flask under N_2 atmosphere. 3 mL of toluene and 0.6 ml of a 1M aqueous solution of tetraethylammonium hydroxide were added and the reaction was heated with an oil bath at 85^{o}C for 48 hours. The whole mixture was cooled to room temperature and poured in 500 mL of a 9:1 mixture of methanol and water. The precipitate was filtered. Soxhlet extractions with acetone removed catalytic residues and low molecular weight materials. Polymers were then extracted with hexanes. The solvents were reduced to about 10 mL and the mixtures were poured into methanol. The precipitates were filtered. **P1** was obtained in 16% yield. M_n of 13 kDa and M_w of 17 kDa.

Synthesis of P1*



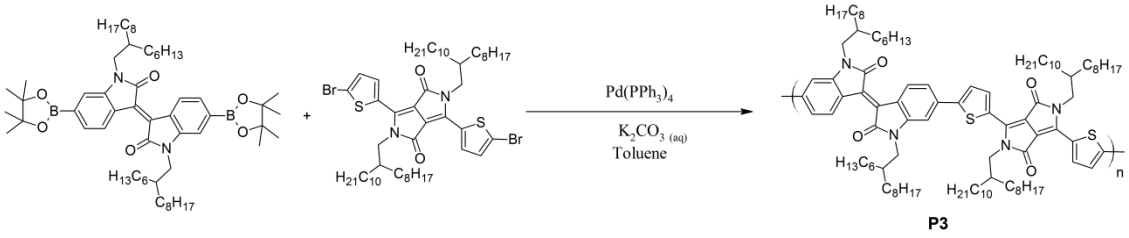
General procedure for the synthesis of **P1***: 5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione (53.1 mg, 0.2 mmol), 6,6'-dibromo-*N*,*N*'-(2-hexyldecyl)-isoindigo (173.8 mg, 0.20mmol), *trans*-di(μ-acetato)bis[*o*-(di-*o*-tolyl-phosphino)benzyl]dipalladium(II) **(**9,4 mg, 5% mol), phosphine ligand (20% mol) and Cs_2CO_3 (130 mg, 0.40 mmol) were put in a Biotage microwave vial (size 2 to 5 mL) with a magnetic stirring bar. The vial was sealed with a cap and put under vacuum for 20 minutes. It was then purged with nitrogen to remove the oxygen. 1 ml of THF was added and the reaction was heated with an oil bath at 120^{o}C for 20 hours. At the end of the reaction time, the reaction was cooled and 5-alkyl[3,4-c]pyrrole-4,6-dione was added as a capping agent (50 mg in 1 mL). The solution was heated again at 120^{o}C to complete the end-capping procedure. After an additional hour of reaction, the whole mixture was cooled to room temperature and poured in 500 mL of a 9:1 mixture of methanol and water. The precipitate was filtered. Soxhlet extractions with acetone followed by hexanes removed catalytic residues and low molecular weight materials. Polymers were then extracted with chloroform. The solvent was reduced to about 10 mL and the mixture was poured into methanol. The precipitate was filtered to obtain **P1*** as a black solid. Molecular weights obtained are shown in Table 1 of the main article.

Synthesis of P2*



The same general procedure utilized for **P1*** was used for **P2***. 5,5'-dioctyl-4*H*,4'*H*-1,1'-bithieno[3,4-*c*]pyrrole-4,4',6,6'(5*H*,5'*H*)-tetrone (52.9 mg, 0.1 mmol), 6,6'-dibromo-N,N'-(2-hexyldecyl)-isoindigo (86.9 mg, 0.10 mmol), *trans*-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) **(**1,9 mg, 2% mol), phosphine ligand (8% mol), 2 equivalents of base, 0.5 ml of THF. Pivalic acid additive (30% mol) was added in some reactions, in which case 2.3 equivalents of base were used instead of 2 equivalents. The reaction was carried out for 22 hours. Molecular weights obtained are shown in Table 1 of the main article.

Synthesis of P3



3,6-Bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-di(2-octyldodecyl)-pyrrolo[3,4c]pyrrolo-1,4-dione (105 mg, 0.104 mmol), 6,6'-dibromo-N,N'-(2-hexyldecyl)-isoindigo (100 mg, 0.104 mmol), Tetrakis(triphenylphosphine)palladium(0) (12,0 mg, 10% mol) and K_2CO_3

(30.1 mg, 0.218 mmol) were put in a reaction vessel under N_2 atmosphere. 3 mL of toluene and 0.6 ml of water were added and the reaction was heated with an oil bath at 120^{o}C for 7 days. The whole mixture was cooled to room temperature and poured in 500 mL of a 9:1 mixture of methanol and water. The precipitate was filtered. Soxhlet extractions with acetone removed catalytic residues and low molecular weight materials. Polymers were then extracted with hexanes and chloroform. The solvents were reduced to about 10 mL and the mixtures were poured into methanol. The precipitates were filtered. The hexanes and chloroform fractions yielded identical molecular weights and were combined. **P3** was obtained in 70% yield. M_n of 44 kDa and M_w of 132 kDa.

Characterization:

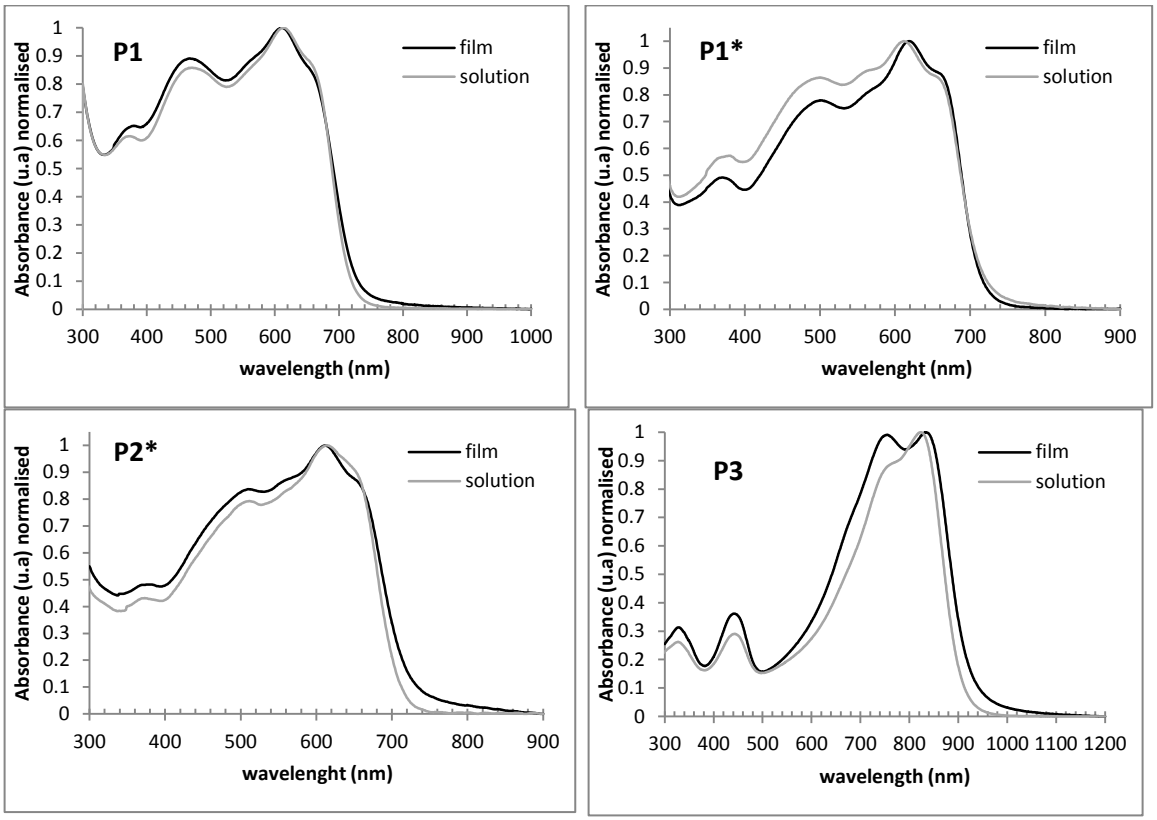
^{1}H and ^{13}C NMR spectra were recorded using a Varian AS400 in deuterated chloroform or dimethylsulfoxide solution at 298 K.

Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) using a Varian Polymer Laboratories GPC220 with two PLgel Mixed C (300 x 7.5 mm) columns. 1,2,4-trichlorobenzene was used as the eluent with a flow rate of 1.0 ml/min. The analyses were made at 110 °C and a refraction index detector was used. For the calibration curve, a series of monodisperse polystyrene standards (Shodex) was used.

UV-vis-NIR absorption spectra were recorded using a Varian Cary 500. Quartz cuvettes with an internal width of 1 cm were used for solution measurements and dropcast films on VWR Vistavision microscope glass slides or on quartz plates were used for solid-state measurements. Optical bandgaps were determined from the onset of the absorption band. Results are shown in figure S1

Cyclic voltammograms (CV) were recorded on a Solartron 1287 potentiostat using platinum wires as working electrode and counter-electrode at a scan rate of 50 mV/s. The reference electrode was Ag/Ag+ (0.1 M of AgNO3 in acetonitrile) and the electrolyte was a solution of 0.1 M of tetrabutylammonium tetrafluoborate in dry acetonitrile. The Ag/Ag+ reference electrode was calibrated against the ferrocene-

ferrocenium redox couple using a SCE and the voltammograms were represented against SCE. In these conditions, the oxidation potential of ferrocene was 0.16 V versus Ag/Ag+, whereas the oxidation potential of ferrocene was 0.41 V versus SCE. The HOMO and LUMO energy levels were determined from the oxidation and reduction onsets (where the current differs from the baseline) assuming that SCE electrode is -4.71 eV from vacuum.



S1. UV-vis spectra of isoindigo copolymers **P1, P1***, **P2*** and **P3** as thin films and in solution in chloroform.

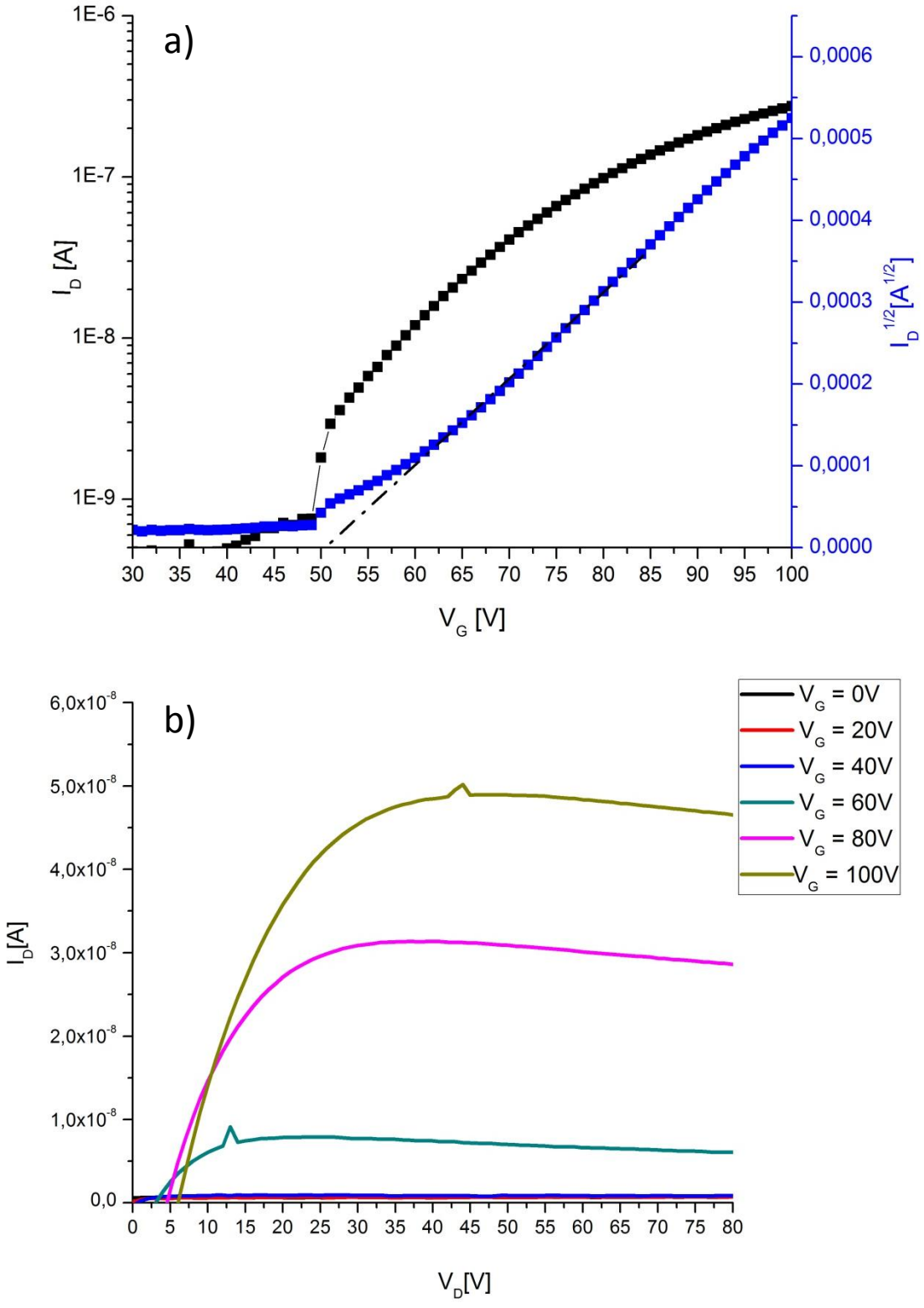
Thin film transistor measurements

Bottom gate, bottom contact field effect transistors with the architecture "Si (500 μm) / SiO_2 (200nm) / Au (50nm) / Decyltricholosilane / copolymer" were fabricated by drop casting without filtering. The pre-patterned substrates (Si/SiO_2/Au) were first cleaned by ultra-sonication in acetone and in isopropanol for 3 minutes and were then dried at 120°C for 10 minutes. The samples were then surface-activated with acid hydrolysis and dried again at 120°C for 10 minutes. After treatment by UVO_3 for 15 minutes, the substrates were passivated in a 1 vol% solution of decyltricholosilane in toluene solution at 80°C for 25 minutes. The samples were rinsed with toluene, dried under nitrogen flow before casting the polymer semiconductors.

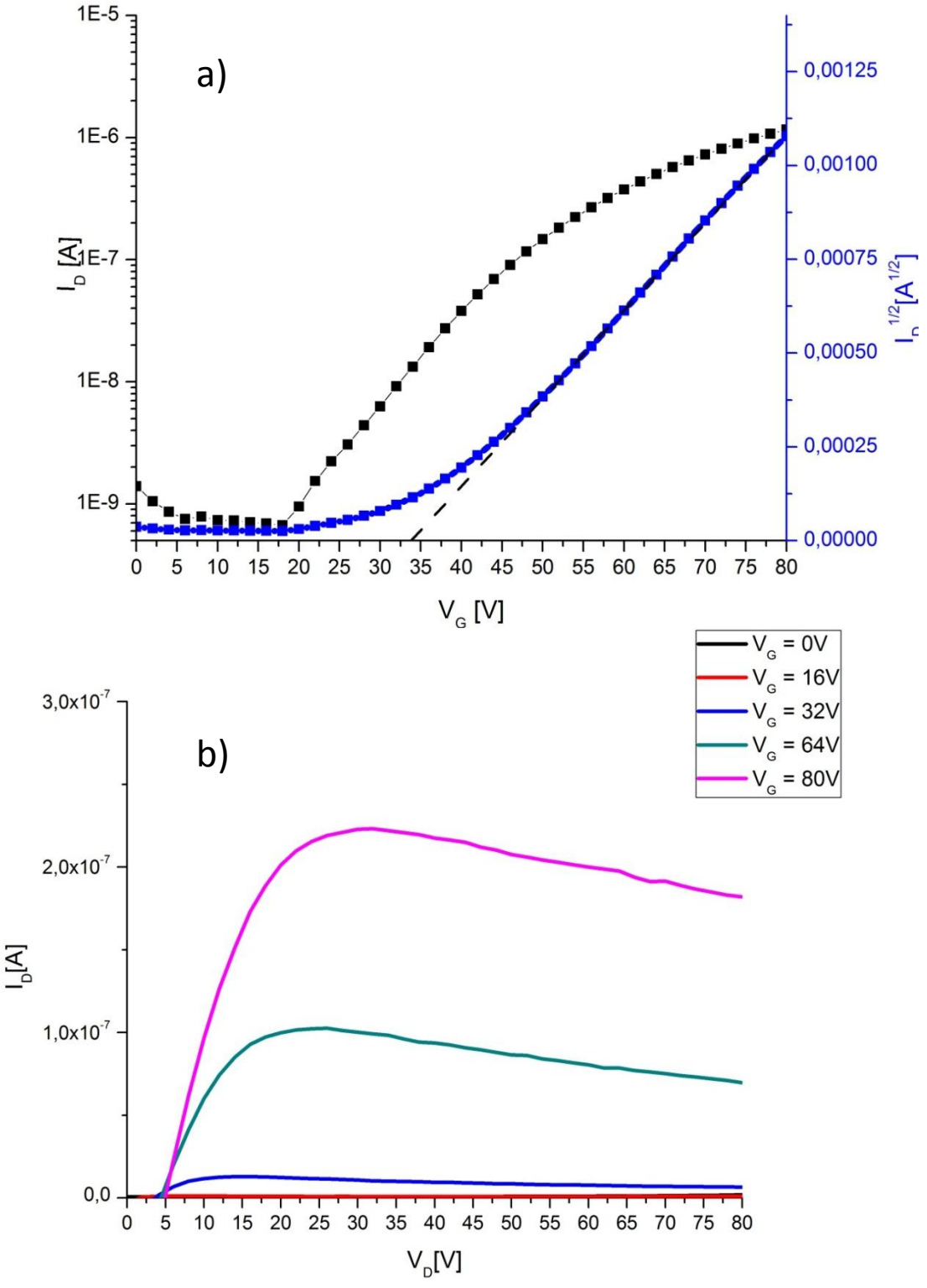
For **P1** and **P2**, the drop casting solution was made of 1 mg of polymer dissolved in 3 mL of 1,2-dichlorobenzene by heating at 120°C for 1 hour. After casting, solvents were slowly dried over 2 h at 40°C in a petri dish with a lid. The lid was then removed and the film was allowed to dry for one more hour. Thermal annealing at 200°C was done for 10 minutes. The channel length varied from 10 μm to 80 μm with channel width of 1 mm. The mobility data in this work mostly came from the devices with 20 μm. The average data were taken from 10 devices.

For **P3**, the drop casting solution was made of 2 mg of polymer dissolved in 3 mL of 1,2-dichlorobenzene by heating at 60°C overnight. After casting, solvents were slowly dried over 2 h at 60°C in a petri dish with a lid. The lid was then removed and the film was allowed to dry for one more hour. Thermal annealing at 200°C was done for 10 minutes. The thin film transistors made had a channel length of 20 μm with a channel width of 1 mm. The average data were taken from 10 devices.

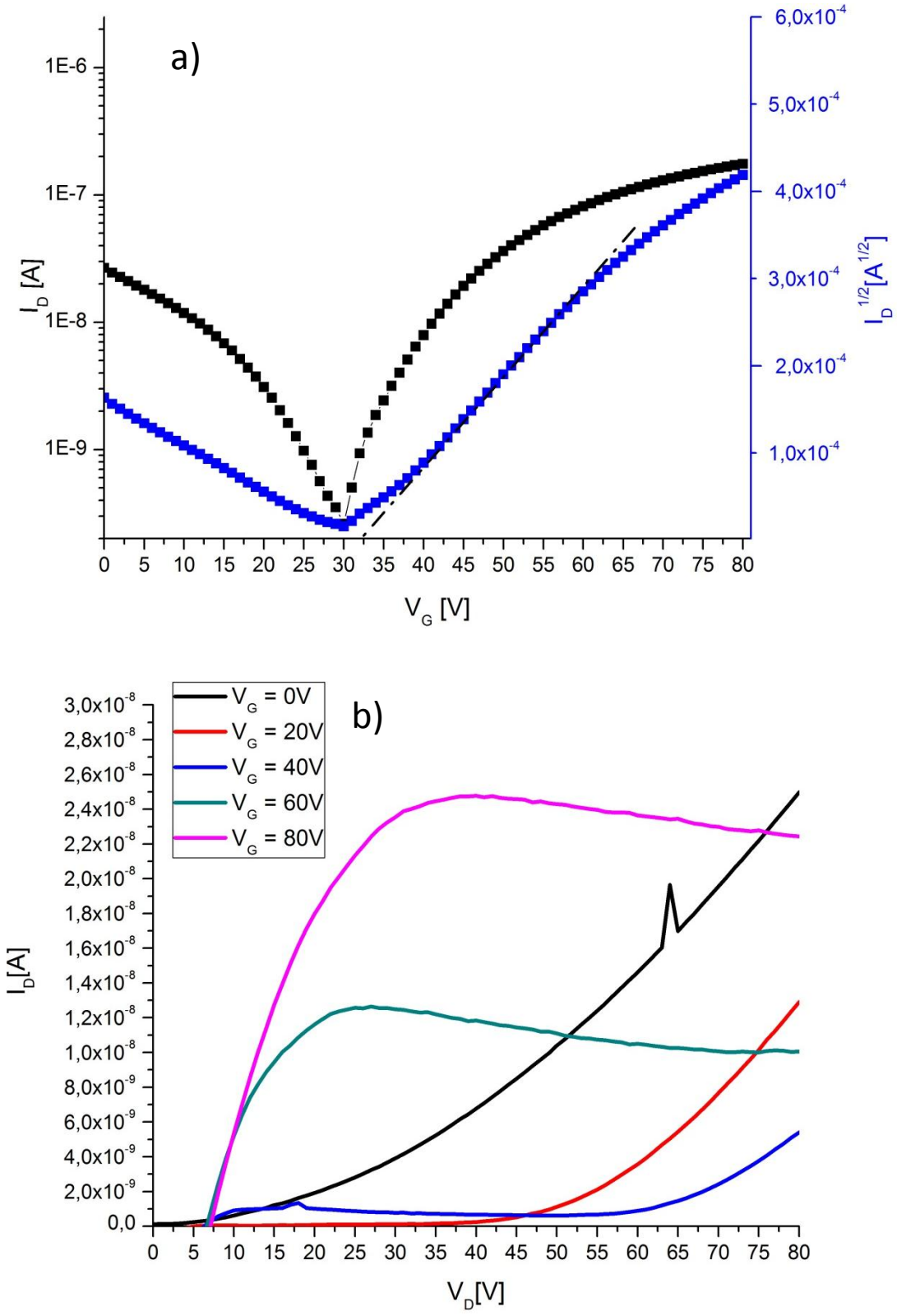
The film deposition, annealing, and I-V characterization were done in nitrogen environment. All the annealing processes were done for 10 minutes. The field-effect mobility is calculated from equation: $I_{DS} = (W/2L)\ Ci\ \mu\ (V_{GS}–V_{th})^2$ where W/L is the channel width/length, *Ci* is the gate dielectric layer capacitance per unit area, and V_{GS} and V_{th} are the gate voltage and threshold voltage.



S2. a) Electron transfer and b) output characteristics of a **P1*** device annealed at 200°C.



S3. a) Electron transfer and b) output characteristics of a **P2*** device after 200°C annealing.

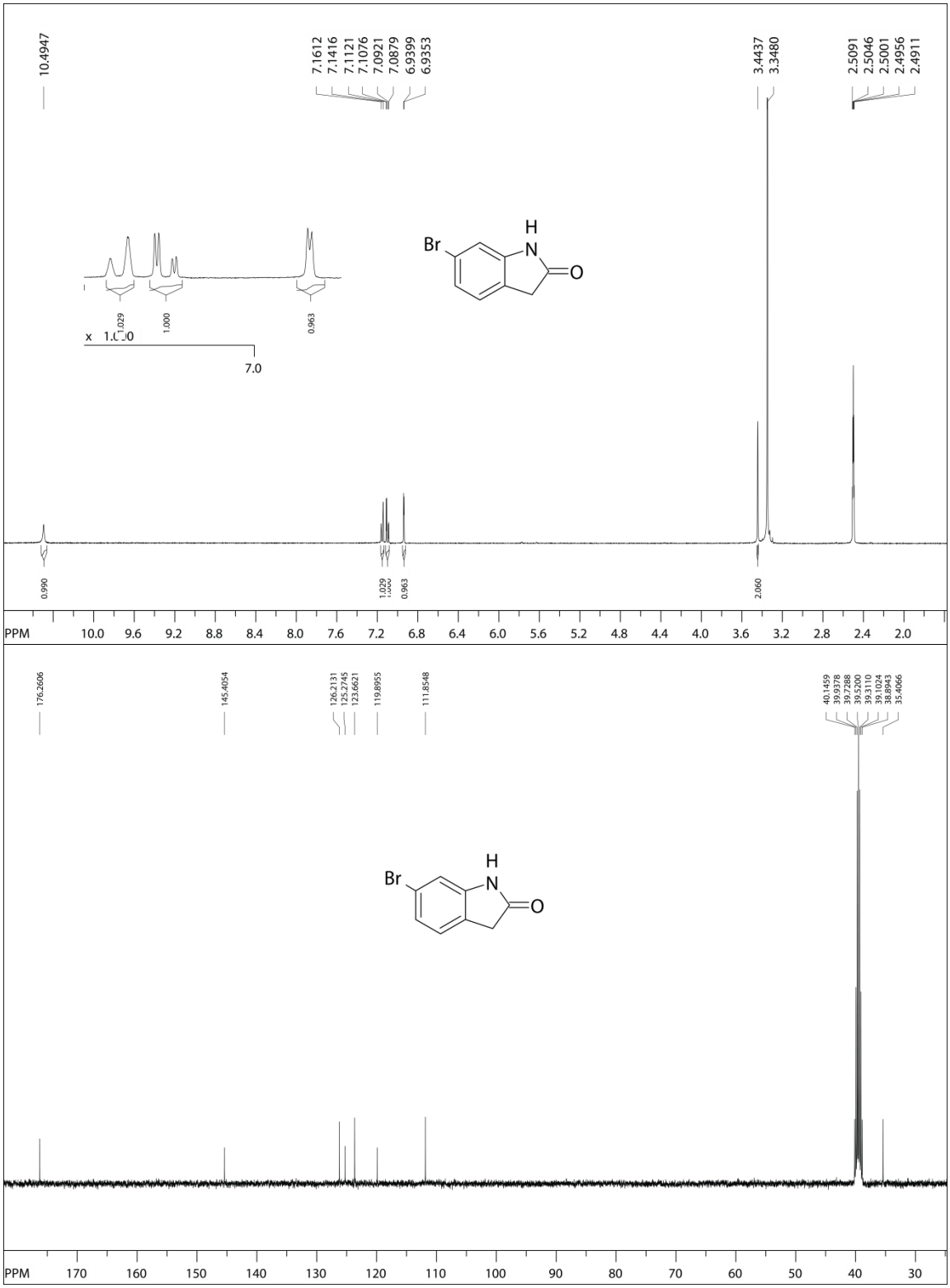


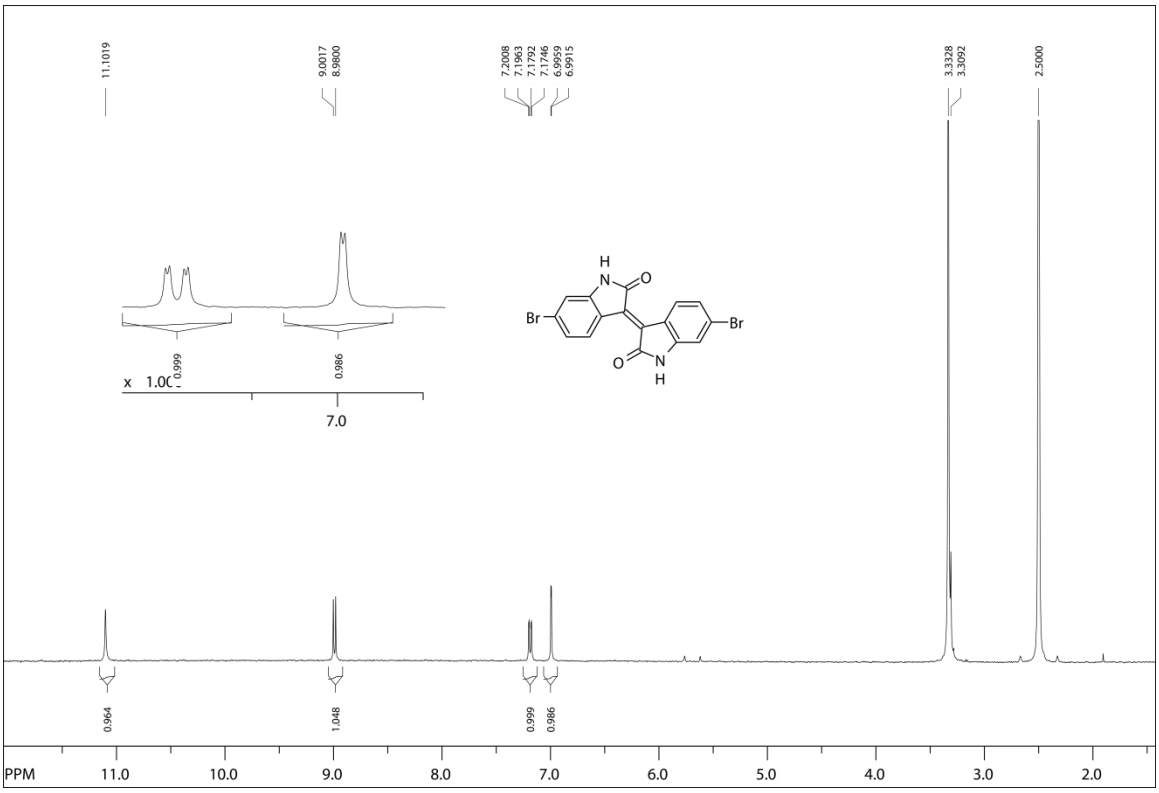
S4. a) Electron transfer and b) output characteristics of a **P3** device after annealing at 200°C.

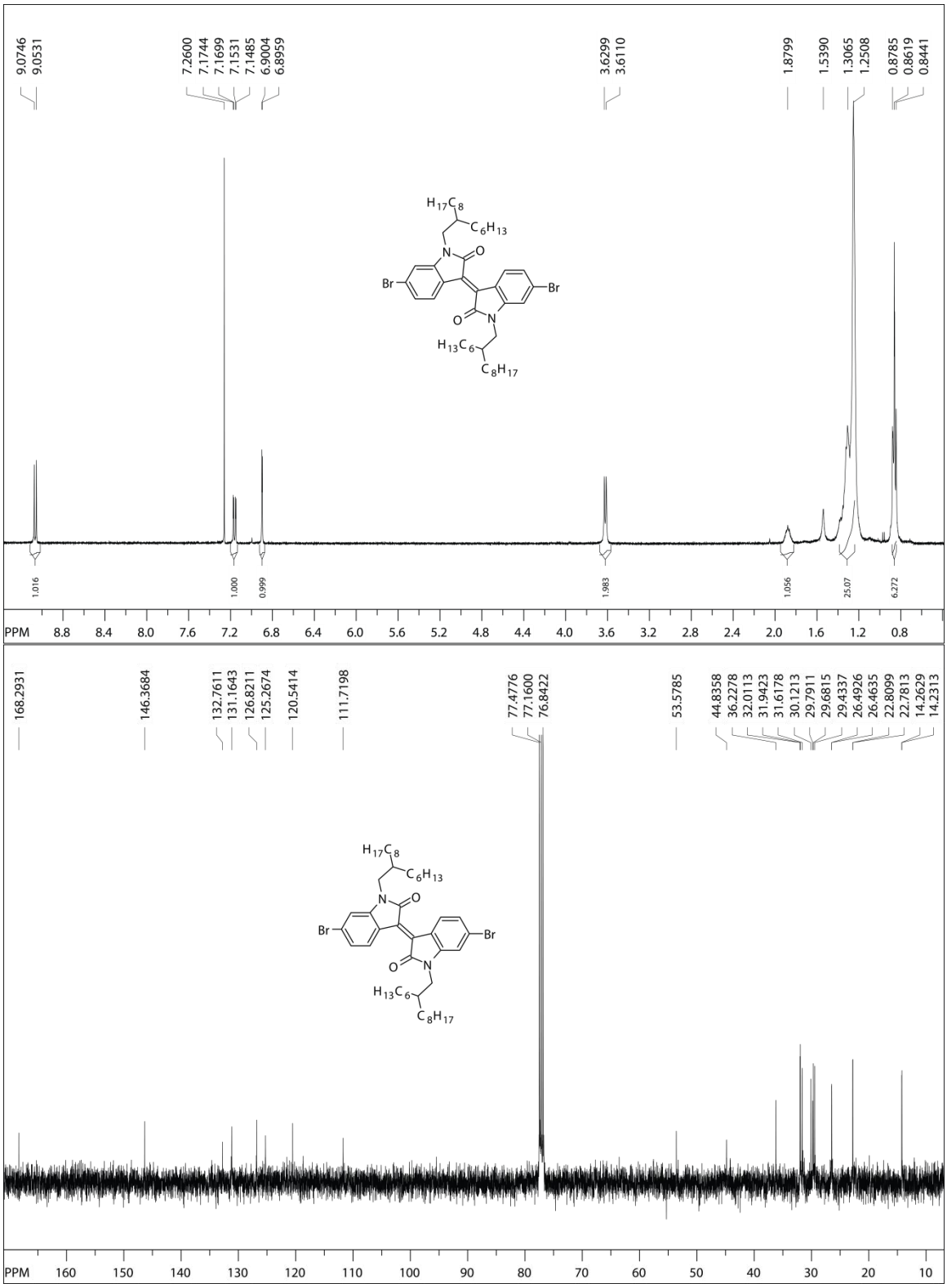
Table S1: Thin film transistor results of **P1***, **P2*** and **P3** isoindigo copolymers

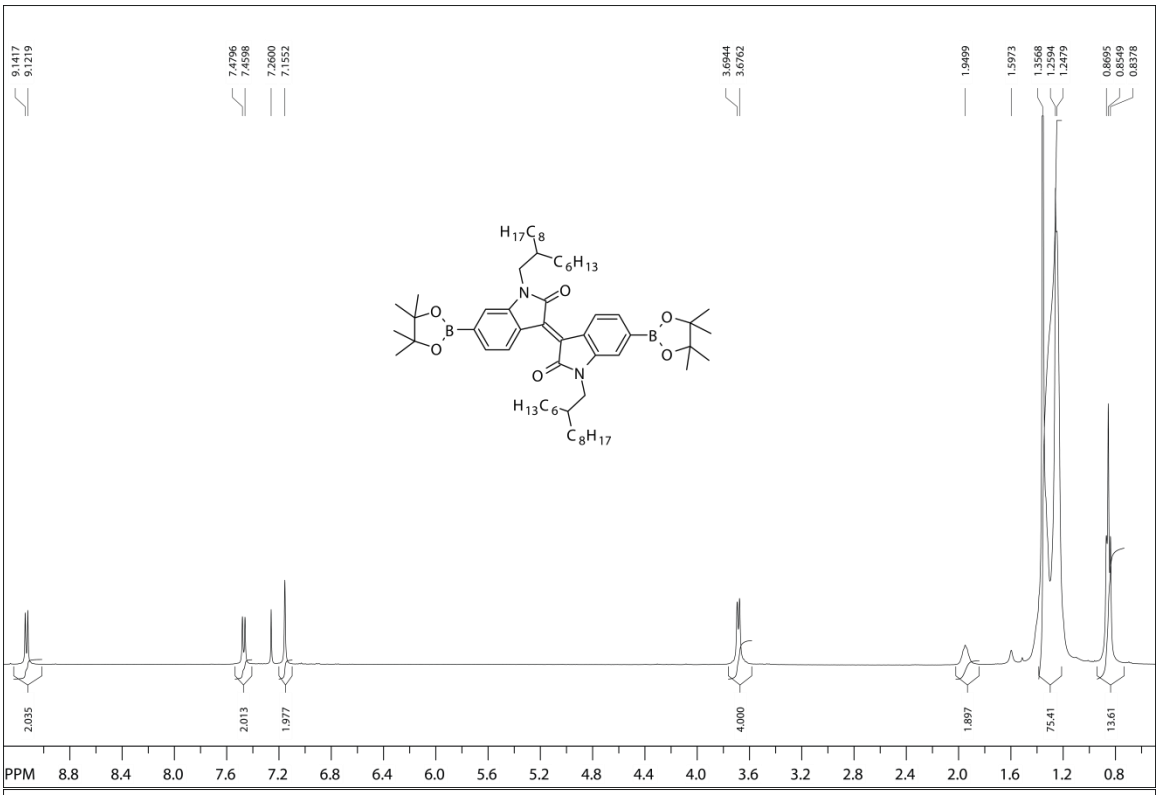
Polymer	Electron mobility		
	Annealing conditions	μ_e	$I_{on/off}$
	°C	$cm^2\ s^{-1}\ V^{-1}$	---
P1*	200	$3.0 \pm 0.7 \times 10^{-4}$	10^2
P2*	200	$2.5 \pm 0.7 \times 10^{-3}$	10^3
P3	200	$1.6 \pm 0.6 \times 10^{-4}$	10^3

NMR spectra:





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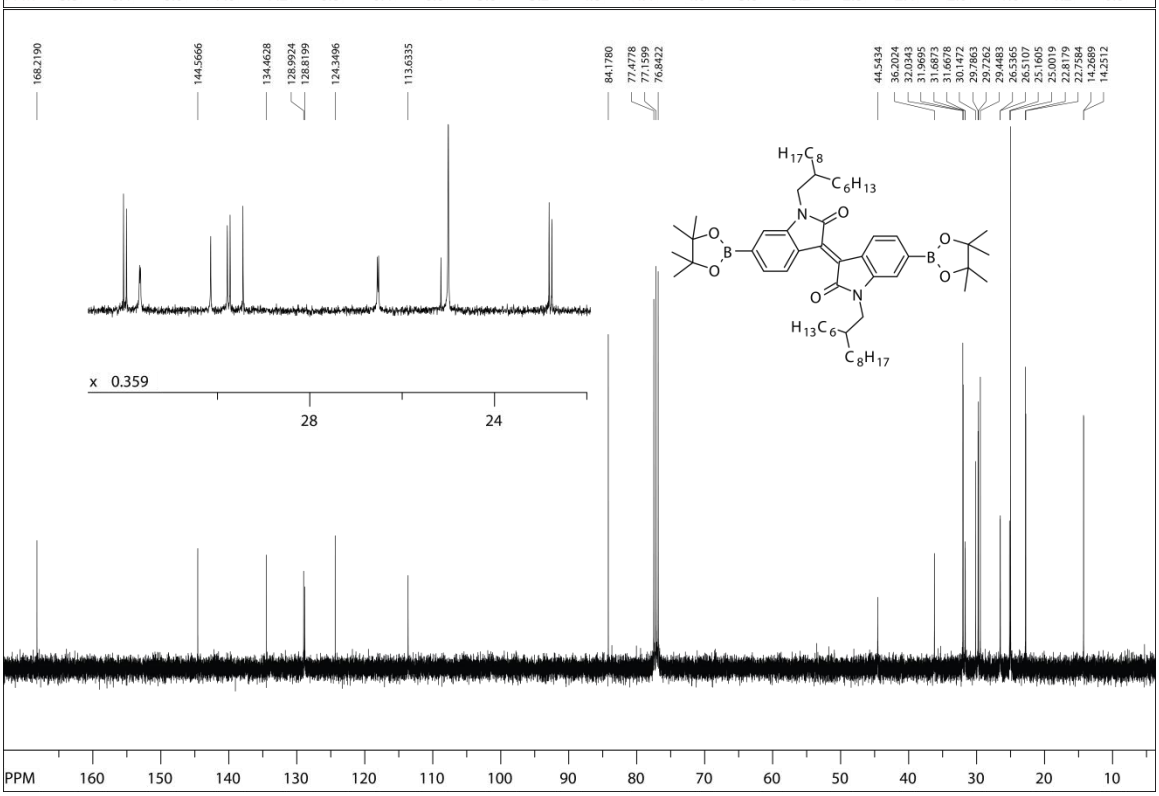
PPM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28
24
PPM

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