Supporting Information

Synthesis of Poly(bisisoindigo) Using a Metal-free Aldol Polymerization for Thin-Film Transistor Applications

Anindya Ganguly[†], *Keqiang He*[‡], *Arthur D. Hendsbee*[‡], *Maged Abdelsamie*[§], *Raymond N. Bennett*[†], *Yuning Li*[‡], *Michael F. Toney*[§] *and Timothy L. Kelly*[†*]

[†]Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, SK, S7N 5C9, Canada.

[‡]Department of Chemical Engineering and Waterloo Institute for Nanotechnology (WIN), University of Waterloo, 200 University Avenue West, Waterloo, ON, N2L 3G1, Canada.

[§]Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA, 94025, United States of America.

* E-mail: tim.kelly@usask.ca; Fax: +1-306-966-4730; Tel: +1-306-966-4666

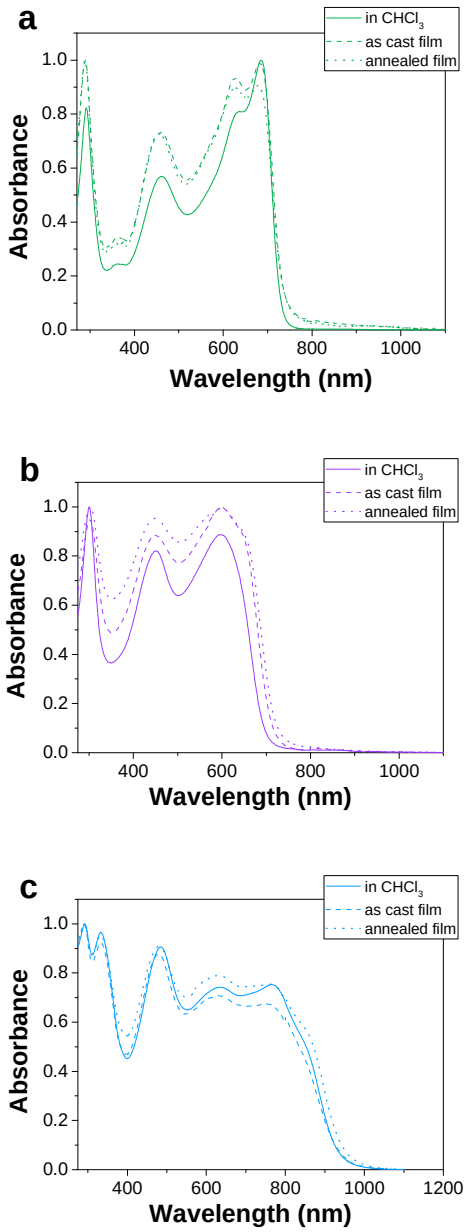


Figure S1. UV/vis spectra of: (a) polyisoindigo, (b) poly(ethynylisoindigo), and (c) poly(bisisoindigo). Thin films were drop cast from chloroform solutions (as cast) and annealed for 15 minutes at 100 °C (annealed).

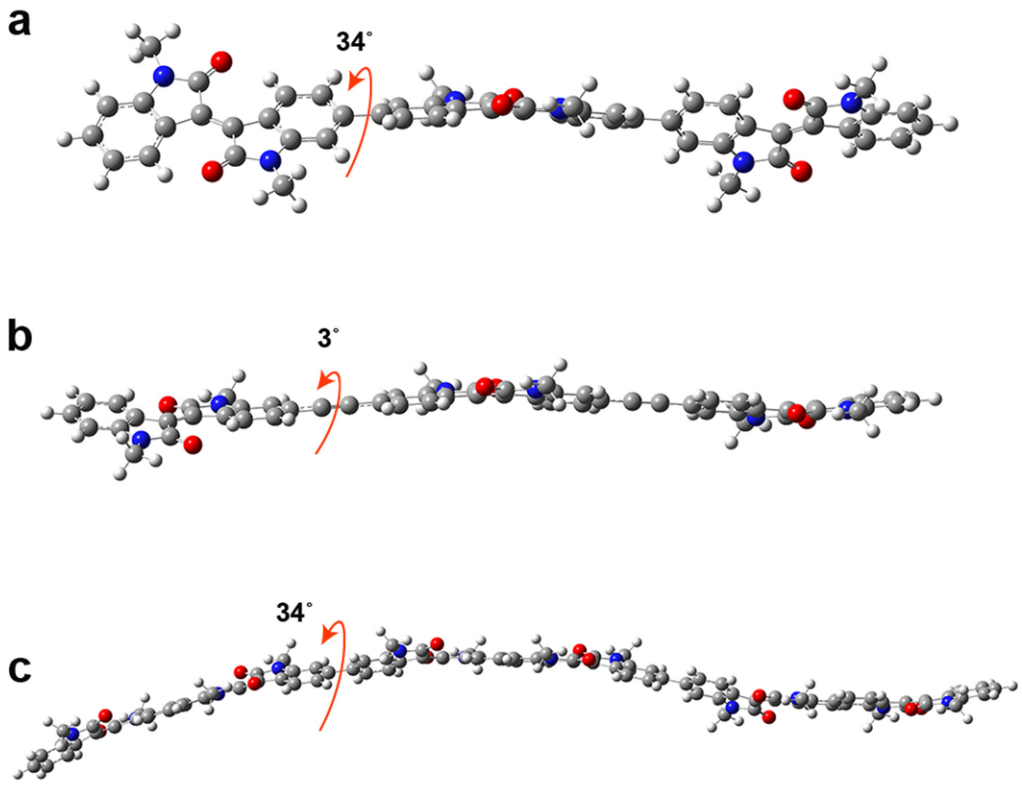


Figure S2. Optimized geometries (B3LYP/6-31G(d,p)) of: (a) polyisoindigo, (b) poly(ethynylisoindigo), and (c) poly(bisisoindigo). The torsion angles between adjacent sub-units are indicated.

Table S1. OTFT performance characteristics from five devices under each condition.

Polymer	$T_{annealing}$[a] **(°C)**		μ_e **($cm^2 V^{-1} s^{-1}$)**	I_{ON}/I_{OFF}	V_{TH} **(V)**
Polyisoindigo	room temperature	Avg.	$2.68 \times 10^{-4} \pm 1.30 \times 10^{-5}$	10^4	59
		Best	2.85×10^{-4}	-	-
	50	Avg.	$2.37 \times 10^{-4} \pm 4.48 \times 10^{-5}$	10^4	59
		Best	3.15×10^{-4}	-	-
	100	Avg.	$1.83 \times 10^{-4} \pm 4.54 \times 10^{-5}$	10^3	59
		Best	2.50×10^{-4}	-	-
	150	Avg.	$1.34 \times 10^{-4} \pm 1.25 \times 10^{-5}$	10^3	58
		Best	1.53×10^{-4}	-	-
	200	Avg.	$1.02 \times 10^{-4} \pm 1.01 \times 10^{-5}$	10^4	57
		Best	1.11×10^{-4}	-	-
Poly(ethynylisoindigo)	room temperature	Avg.	$1.33 \times 10^{-4} \pm 4.13 \times 10^{-5}$	10^3	73
		Best	1.87×10^{-4}	-	-
	50	Avg.	$1.80 \times 10^{-4} \pm 1.79 \times 10^{-5}$	10^4	65
		Best	1.96×10^{-4}	-	-
	100	Avg.	$2.60 \times 10^{-4} \pm 1.43 \times 10^{-5}$	10^4	60
		Best	2.81×10^{-4}	-	-
	150	Avg.	$3.01 \times 10^{-4} \pm 8.17 \times 10^{-5}$	10^4	58
		Best	3.59×10^{-4}	-	-
	200	Avg.	$3.71 \times 10^{-4} \pm 4.72 \times 10^{-5}$	10^4	57
		Best	4.15×10^{-4}	-	-

Table S1 (continued).

Polymer	$T_{annealing}$[a] (°C)	μ_e ($cm^2 V^{-1} s^{-1}$)		I_{ON}/I_{OFF}	V_{TH} (V)
Poly(bisisoindigo)	room temperature	Avg.	$7.04 \times 10^{-5} \pm 2.01 \times 10^{-5}$	10^3	51
		Best	9.29×10^{-5}	-	-
	50	Avg.	$6.03 \times 10^{-5} \pm 1.63 \times 10^{-5}$	10^4	51
		Best	7.67×10^{-5}	-	-
	100	Avg.	$4.37 \times 10^{-5} \pm 1.27 \times 10^{-5}$	10^3	46
		Best	5.47×10^{-5}	-	-
	150	Avg.	$3.15 \times 10^{-5} \pm 6.40 \times 10^{-5}$	10^4	42
		Best	3.83×10^{-5}	-	-
	200	Avg.	$1.86 \times 10^{-5} \pm 3.70 \times 10^{-6}$	10^4	41
		Best	2.21×10^{-5}	-	-

[a] Devices were annealed for 20 minutes at each specified temperature.

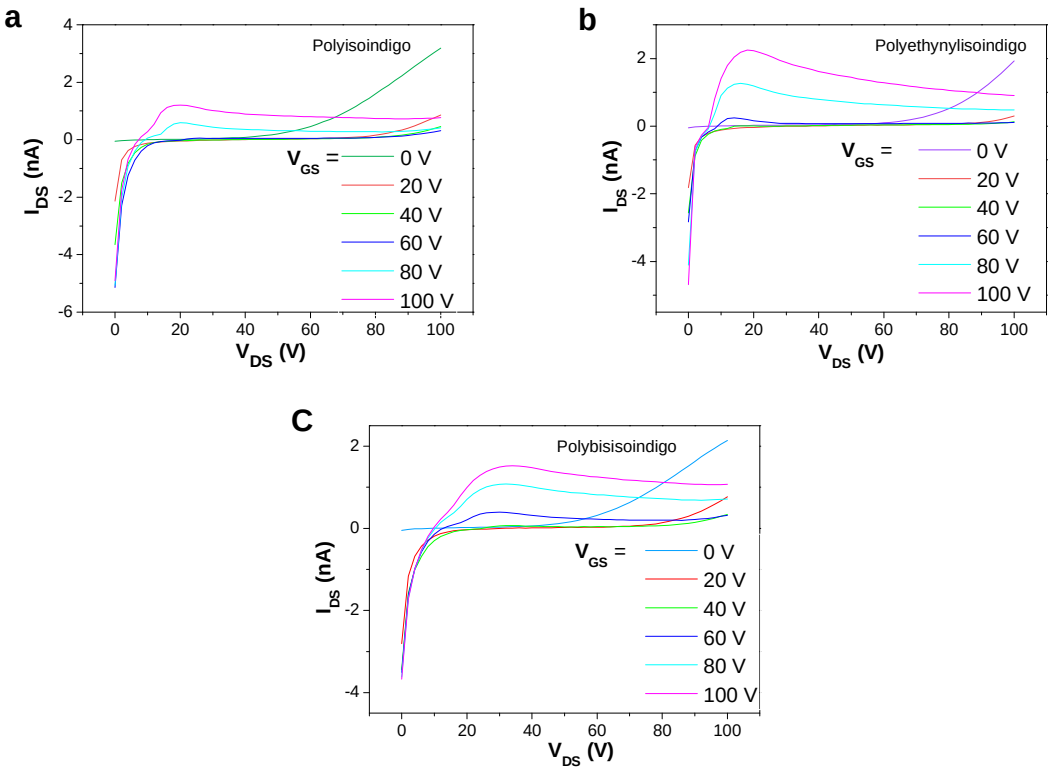


Figure S3. Output characteristics of the best performing OTFTs fabricated using: (a) polyisoindigo, (b) poly(ethynylisoindigo), and (c) poly(bisisoindigo).

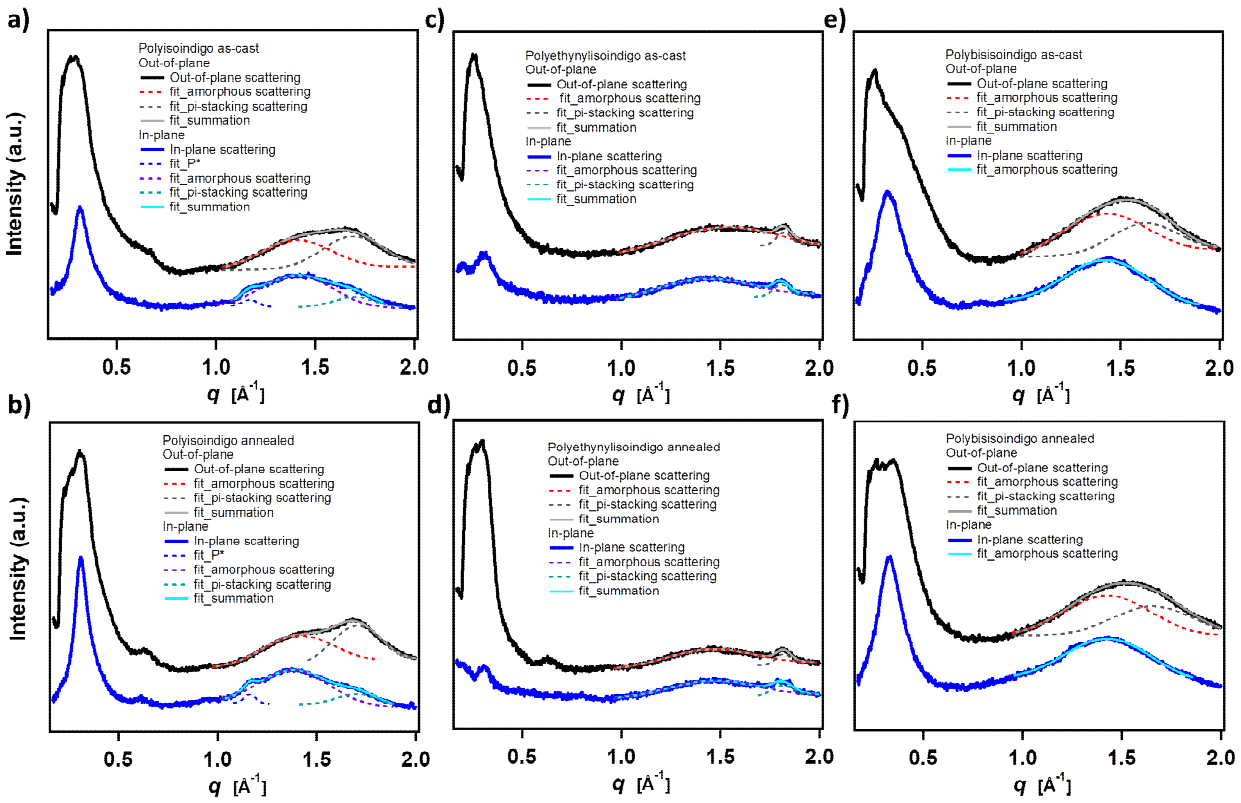


Figure S4. Fitting of the scattering peaks between q ~ 1-2 Å^{-1} for the GIWAXS patterns of polymer thin films: (a) as-cast polyisoindigo, (b) annealed polyisoindigo, (c) as-cast poly(ethynylisoindigo), (d) annealed poly(ethynylisoindigo), (e) as-cast poly(bisisoindigo), and (f) annealed poly(bisisoindigo). An amorphous scattering peak appears around q ~ 1.4-1.5 Å^{-1} for all samples, whereas the π-π stacking scattering peak appears at q ~ 1.7 ± 0.1 Å^{-1}, q ~ 1.8 ± 0.1 Å^{-1}, and q ~ 1.64 ± 0.1 Å^{-1} for polyisoindigo, poly(ethynylisoindigo), and poly(bisisoindigo), respectively. It is worth noting that there is a large uncertainty in the peak position of the π-π stacking feature in poly(bisisoindigo) due to the large overlap with amorphous scattering. We attribute this to very weak ordering of the π-π stack in poly(bisisoindigo) films. An additional scattering peak at q ~ 1.17 Å^{-1} appears in-plane for polyisoindigo films (fits marked as P*).

To isolate the π-π stacking scattering from the amorphous scattering, we fit the in-plane and out-of-plane scattering profiles separately (Figure S4), relying on the fact that amorphous scattering is isotropic in both the in-plane and out-of-plane orientations. The procedure of peak fitting in Figure S4 can be summarized as follows:

1. Fitting the out-of-plane scattering to amorphous and π-π stacking peaks.
2. Using the peak parameters of the amorphous scattering (obtained from out-of-plane scattering) as an initial guess for fitting the in-plane scattering.
3. Relying on the isotropic nature of the amorphous scattering peak, we fine-tune the choice of acceptable fitting results (i.e. the amorphous scattering peak shape in terms of position and width should be preserved in both in-plane and out-of-plane scattering).

Table S2. Summary of structural parameters and crystalline correlation length (CCL) for the polymers' lamellar stacking.

Polymer	$q_{(100)}$ **(Å^{-1})**		$d_{(100)}$ **(Å)**		**FWHM$_{(100)}$ (Å^{-1})**		**CCL$_{(100)}$ (nm)**	
	As cast	Annealed	As cast	Annealed	As cast	Annealed	As cast	Annealed
Polyisoindigo	0.3	0.31	20.9	20.3	0.08	0.068	7.9	9.2
Poly(ethynylisoindigo)	0.27	0.28	23.3	22.4	0.082	0.075	7.7	8.4
Poly(bisisoindigo)	0.32	0.33	19.6	19.0	0.12	0.1	5.2	6.3

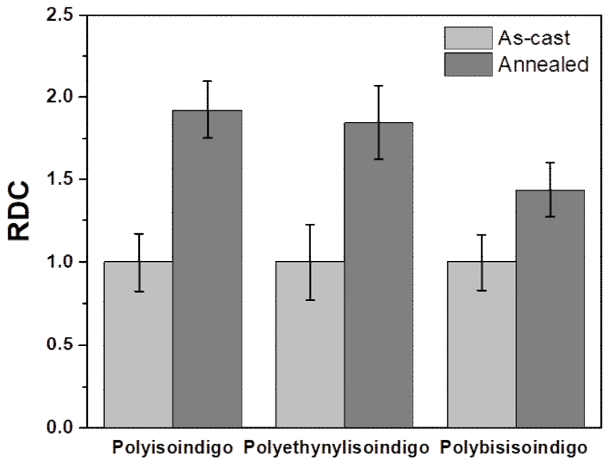
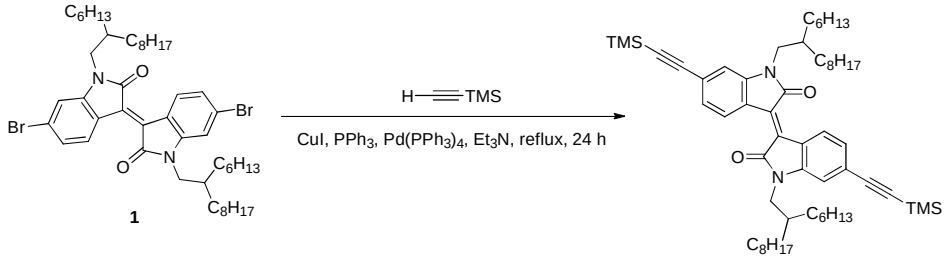


Figure S5. Relative degree of crystallinity (RDC) calculated from the lamellar stacking of polyisoindigo, poly(ethynylisoindigo), and poly(bisisoindigo), for annealed vs. as-cast films. The error bars correspond to the uncertainty in the measured materials' volume.

Synthetic Procedures

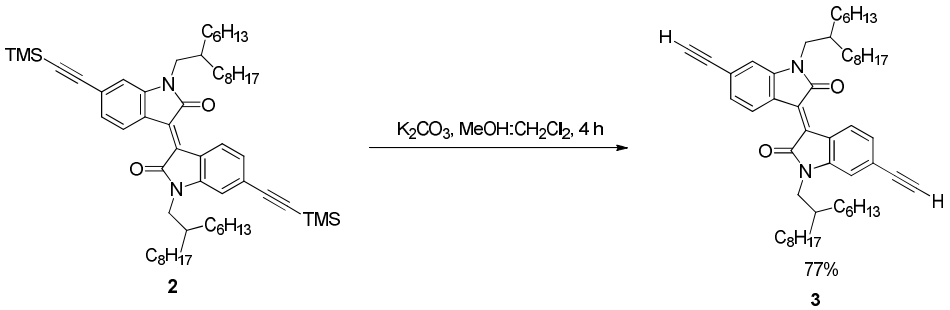
Compounds **1**,[1] **4**,[2] **6**[3] and **7**[2] were synthesized according to previously reported procedures.

Synthesis of **2**



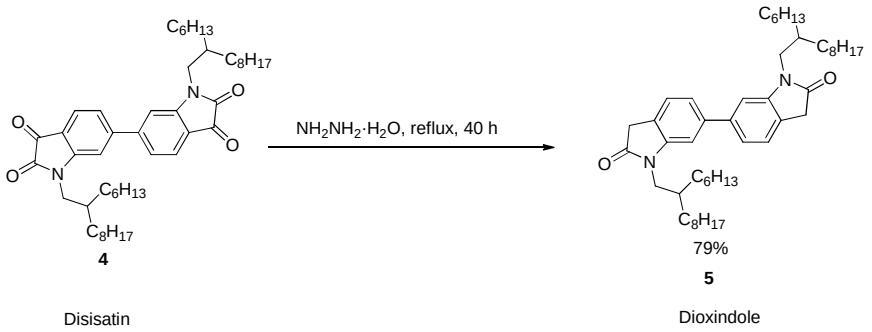
To a solution of **1** (509 mg, 0.585 mmol) in 15 mL of dry triethylamine, CuI (340 mg, 1.78 mmol) and trimethylsilylacetylene (0.28 mg, 2.88 mmol) were added. The solution was then sparged with argon for 30 min. It was followed by an addition of $Pd(PPh_3)_4$ (113 mg, 0.0978 mmol). After refluxing the solution for 24 h, the solvent was removed using a rotary evaporator to yield a brown slurry. This was dissolved in diethyl ether and washed with water (2 × 30 mL) and brine (1 × 30 mL) which was finally dried over anhydrous Na_2SO_4. After removal of the solvent, the crude was purified by flash column chromatography on silica gel, eluting with 20% CH_2Cl_2 in hexanes to yield **2** as a brown crystalline solid (290 mg, 55%). ^{1}H NMR ($CDCl_3$, 500 MHz, δ) 9.10 (d, *J* = 8.30 Hz, 1H), 7.11 (d, *J* = 8.30 Hz, 1H), 6.79 (s, 1H), 3.64 (d, *J* = 7.60 Hz, 2H), 1.92-1.90 (m, 1H), 1.33-1.25 (m, 24H), 0.88-0.84 (m, 6H), 0.27 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz, δ): 168.33, 145.13, 133.09, 129.62, 126.85, 126.28, 120.06, 111.17, 105.40, 97.95, 44.75, 36.20, 32.01, 31.95, 31.63, 30.15, 29.80, 29.69, 29.43, 26.52, 26.48, 22.81, 22.76, 22.81, 16.04, 14.23, 0.03. HRMS (*m/z*): ($M^{\bullet+}$) Cal. ($C_{58}H_{90}N_2O_2Si_2$): 902.65408 found: 902.65380. Anal. Calcd for $C_{58}H_{90}N_2O_2Si_2$: C, 77.1; H, 10.1; N, 3.1; found: C, 76.4; H, 10.8; N, 3.1.

Synthesis of **3**



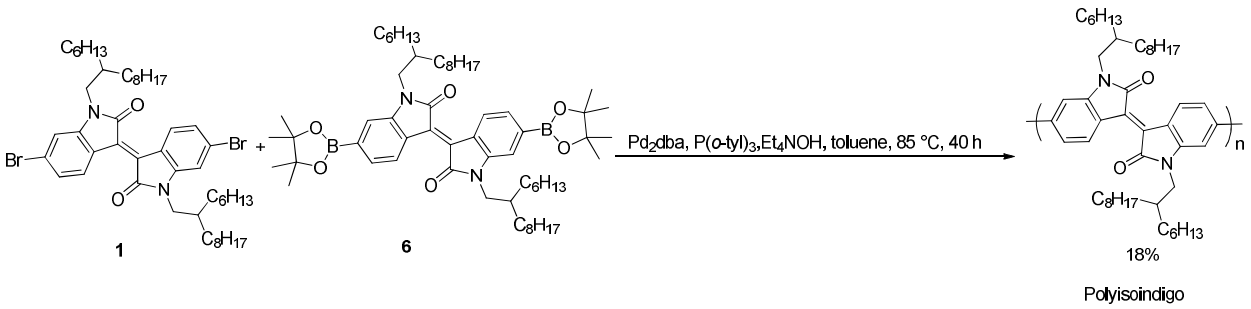
To a solution of **2** (100 mg, 0.1 mmol) in a mixture of dry CH_2Cl_2 and MeOH (1:1), K_2CO_3 (42 mg, 0.30 mmol) was added. After stirring the solution at room temperature for 4 h, the organic layer was extracted with ether (20 mL). This organic layer was washed with water (2 × 30 mL) and brine (1 × 30 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to yield a dark-brown solid (**3**), which was dissolved in a mixture of CH_2Cl_2:hexanes (1:1) and filtered through a short silica-gel pad. The solvent was removed by evaporation under reduced pressure to yield **3** as a brown solid (65 mg, 77%). ^{1}H NMR (CD_2Cl_2, 500 MHz, δ) 9.13 (d, *J* = 8.25 Hz, 1H), 7.12 (d, *J* = 8.30 Hz, 1H), 6.86 (s, 1H), 3.61 (d, *J* = 7.50 Hz, 2H), 3.30 (s, 1H), 1.90-1.87 (s, 1H), 1.31-1.23 (m, 24H), 0.84-0.82 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, δ): 168.23, 145.25, 133.25, 129.81, 126.39, 125.86, 122.21, 111.39, 84.03, 80.14, 44.82, 36.25, 32.01, 31.95, 31.66, 30.14, 29.81, 29.69, 29.43, 26.53, 26.50, 22.81, 22.78, 16.16, 14.26, 14.23. HRMS (*m/z*): ($M^{\bullet+}$) Cal. ($C_{52}H_{74}N_2O_2$): 758.57503 found: 758.57474. Anal. Calcd for $C_{52}H_{74}N_2O_2$: C, 82.3; H, 9.8; N, 3.7; found: C, 82.2; H, 10.1; N, 3.8.

Synthesis of **5**



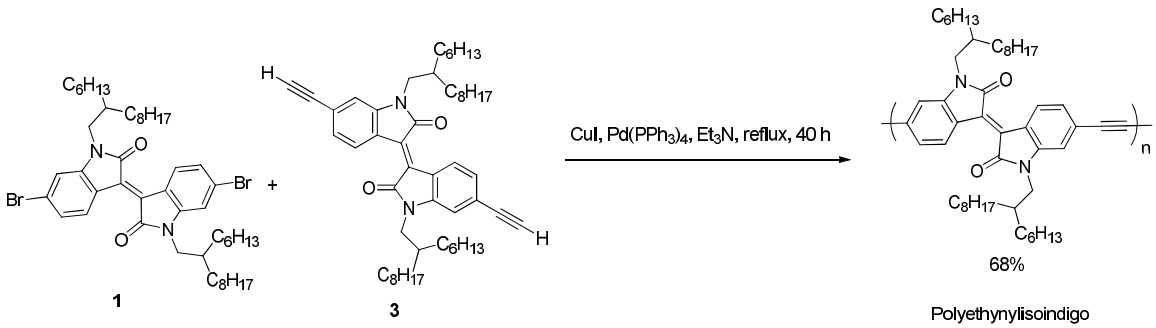
This procedure was adapted from a previous literature report.[2] Compound **4** (1.21 g, 1.63 mmol) was suspended in 50.0 mL of hydrazine and heated to reflux for 48 h. After cooling the mixture down to room temperature, the organic layer was extracted with dichloromethane (2 × 40 mL). The organic layer was washed with water (5 × 50 mL) and brine (1 × 50 mL), dried over anhydrous $MgSO_4$, and finally condensed to yield a brown oil. The oil was precipitated in a mixture (3:1) of isopropanol and hexanes (10 mL) to yield a grey solid. This was isolated by vacuum filtration to yield **5** (921 mg, 79%). ^{1}H NMR ($CDCl_3$, 600 MHz, δ) 7.32 (d, *J* = 7.68 Hz, 1H), 7.21 (d, *J* = 7.23 Hz, 1H), 6.96 (s, 1H), 3.64 (d, *J* = 7.44 Hz, 2H), 3.57 (s, 1H), 1.91-1.89 (s, 1H), 1.32-1.21 (m, 24H), 0.86-0.83 (m, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz, δ): 175.56, 145.90, 141.52, 147.76, 124.09, 121.10, 107.61, 44.67, 36.30, 35.70, 32.01, 31.97, 31.76, 30.20, 29.87, 29.72, 29.47, 27.23, 26.69, 26.64, 22.81, 16.04, 14.26, 14.23. HRMS (*m/z*): ($M^{\bullet+}$) Cal. ($C_{48}H_{76}N_2O_2$): 712.59068 found: 712.59158. Anal. Calcd for $C_{48}H_{76}N_2O_2$: C, 80.8; H, 10.7; N, 3.9; found: C, 80.2; H, 10.4; N, 4.4.

Synthesis of **polyisoindigo**



Polyisoindigo was synthesized according to literature procedures.[3] Compounds **1** (448 mg, 0.515 mmol) and **6** (495 mg, 0.515 mmol) were dissolved in dry toluene under argon and the solution was degassed for 30 minutes. It was followed by the addition of $Pd_2(dba)_3$ (47.3 mg, 0.051 mmol), $P(o\text{-tyl})_3$ (22.4 mg, 0.072 mmol), and tetraethylammonium hydroxide (3.12 mmol, 25% in H_2O). After heating the resulting solution at 85 ˚C for 40 h, it was cooled to room temperature. Diethylammonium diethyldithiocarbamate (20.0 mg, 0.089 mmol) was subsequently added and stirred at room temperature for 2 h to scavenge the residual palladium in the solution. The resulting solution was then slowly precipitated in methanol and the crude polymer was collected by filtration. This was purified by sequential Soxhlet extraction with methanol (24 h), acetone (24 h), and hexanes (24 h). The remaining insoluble fraction was extracted into chloroform and precipitated from methanol. The resulting dark bluish-green solid was isolated by vacuum filtration and dried under high vacuum (131 mg, 18%). ^{1}H NMR ($CDCl_3$, 500 MHz, δ) 8.98-8.70 (br), 7.40-6.80 (br), 4.25-3.61 (br), 2.07-0.81 (br). M_w = 43.9 kDa, M_n = 21.9 kDa, $Đ$ = 2.0. Anal. Calcd for $C_{50}H_{72}N_2O_2$: C, 81.30; H, 10.23; N, 3.95; found: C, 81.12; H, 10.47; N, 3.83.

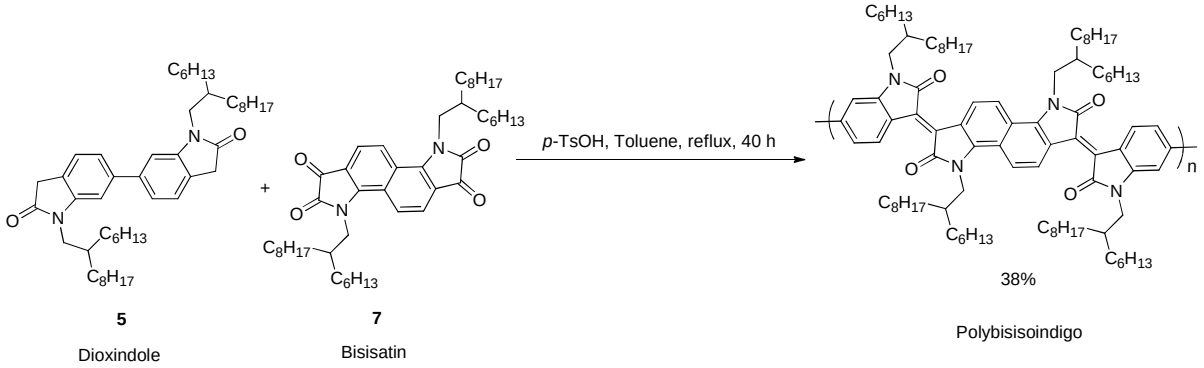
Synthesis of **poly(ethynylisoindigo)**



1 3

Compound **1** (112.0 mg, 0.128 mmol) and **3** (96.1 mg, 0.128 mmol) were dissolved in dry triethylamine (12.0 mL), followed by the addition of CuI (91.2 mg, 0.478 mmol). The solution was degassed by sparging argon for 30 min and further followed by the addition of $Pd(PPh_3)_4$ (18.0 mg, 0.015 mmol). After refluxing the solution for 40 h, it was allowed to cool to room temperature. Diethylammonium diethyldithiocarbamate (10.0 mg, 0.045 mmol) was then added and the mixture was stirred for 3 h to remove any residual catalyst. It was then precipitated in methanol (100 mL) and filtered to yield a green solid. This was purified via Soxhlet extraction consecutively with methanol, acetone, and hexanes for 24 h for each solvent. The remaining insoluble fraction was extracted into chloroform and precipitated from methanol. The precipitate was isolated by vacuum filtration and dried under high vacuum to yield poly(ethynylisoindigo) as a dark green solid (130 mg, 68%). ^{1}H NMR ($CDCl_3$, 500 MHz, δ) 9.18-8.99 (br), 7.00-6.54 (br), 3.69-3.67 (br), 1.96-0.85 (br). M_w = 40.4 kDa, M_n = 15.4 kDa, $Đ$ = 2.6. Anal. Calcd for $C_{50}H_{72}N_2O_2$: C, 81.92; H, 9.90; N, 3.82; found: C, 72.02; H, 9.22; N, 3.40.

Synthesis of **poly(bisisoindigo)**



To a solution of **5** (60.9 mg, 0.0853), and **7** (61.1 mg, 0.0853 mmol) in 10.0 mL dry toluene, *p*-toluene sulfonic acid was added (5 mg, 0.03 mmol). The solution was refluxed for 40 h with a Dean-Stark apparatus to distill out the water generated over the course of reaction. The resulting suspension was cooled to room temperature and precipitated in cold methanol (50.0 mL). The precipitate was filtered off and then washed by sequential Soxhlet extraction with methanol (24 h), acetone (24 h), and hexanes (12 h). The remaining insoluble fraction was extracted in chloroform and precipitated from methanol. The precipitate was isolated by vacuum filtration and dried under high vacuum to yield poly(bisisoindigo) as a dark green solid (45 mg, 38%). ^{1}H NMR ($CDCl_3$, 500 MHz, δ) 9.16 (brs), 8.89-8.79 (brd), 7.67 (brs), 7.08-6.90 (br), 5.14-5.12 (brs), 4.72-3.63 (br), 1.99-0.67 (br). M_w = 38.0 kDa, M_n = 15.5 kDa, $Đ$ = 2.4. Anal. Calcd for $C_{50}H_{72}N_2O_2$: C, 81.10; H, 10.28; N, 4.02; found: C, 80.88; H, 9.97; N, 4.14.

^{1}H NMR and ^{13}C NMR Spectra

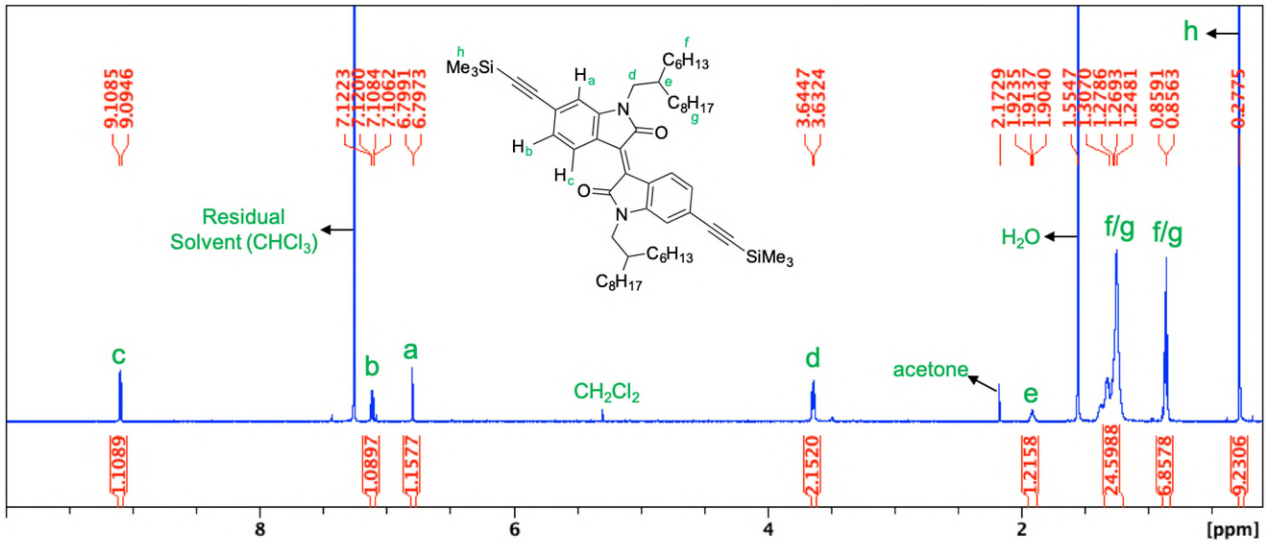


Figure S6. ^{1}H NMR spectrum of **2** in $CDCl_3$.

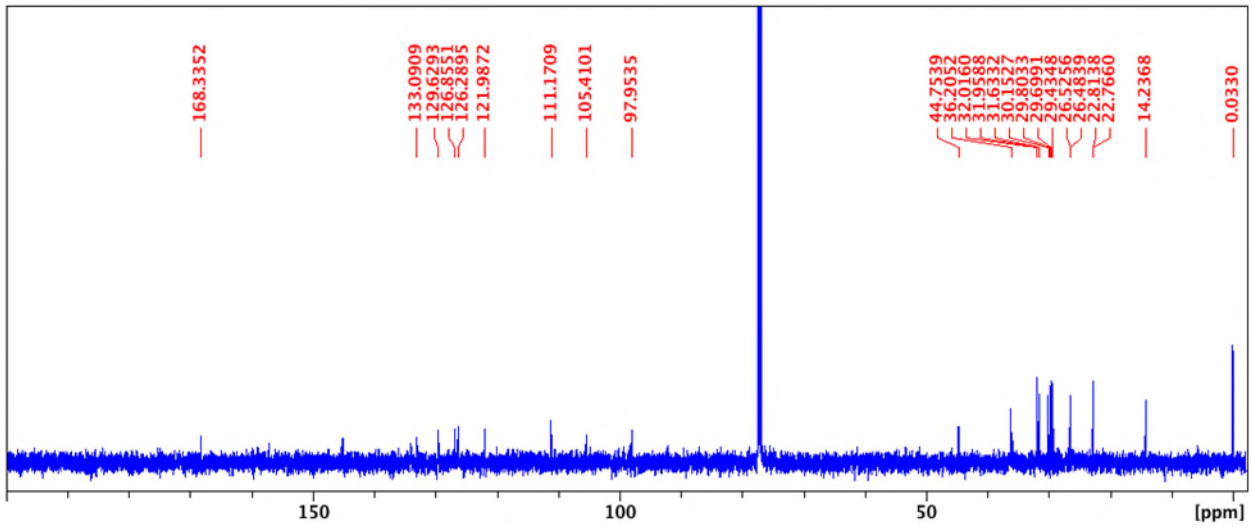


Figure S7. ^{13}C NMR spectrum of **2** in $CDCl_3$.

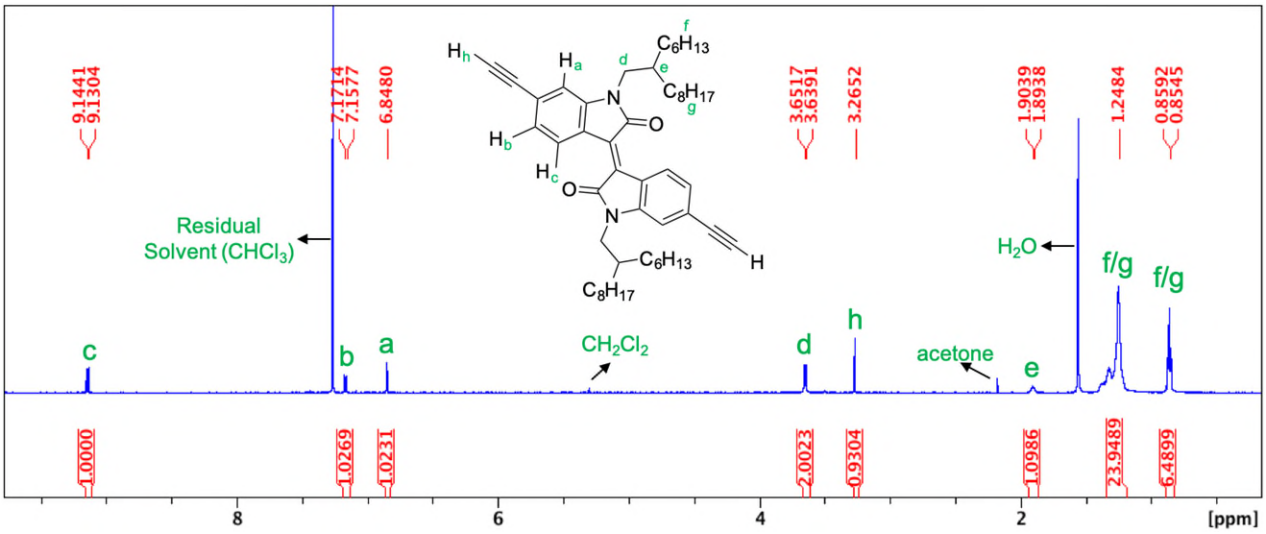


Figure S8. ^{1}H NMR spectrum of **3** in $CDCl_3$.

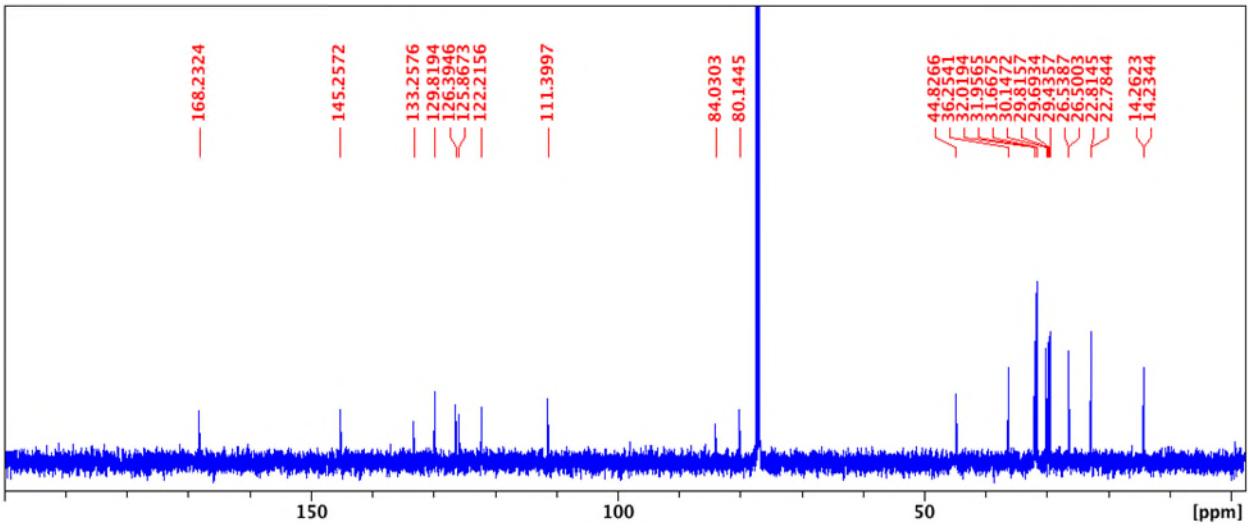


Figure S9. ^{13}C NMR spectrum of **3** in $CDCl_3$.

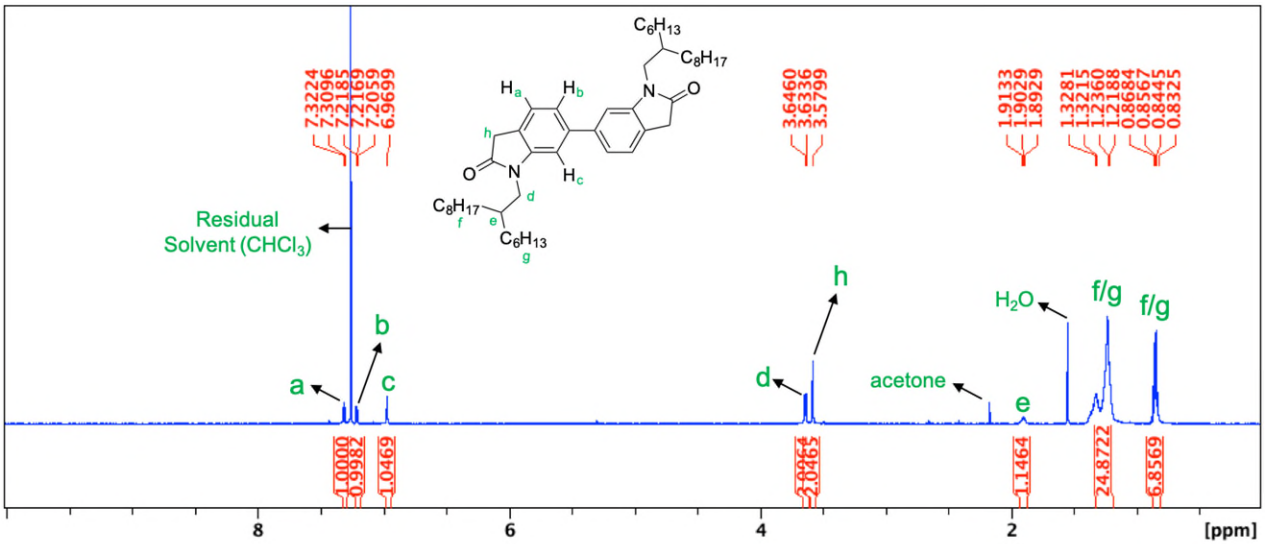


Figure S10. ^{1}H NMR spectrum of **5** in $CDCl_3$.

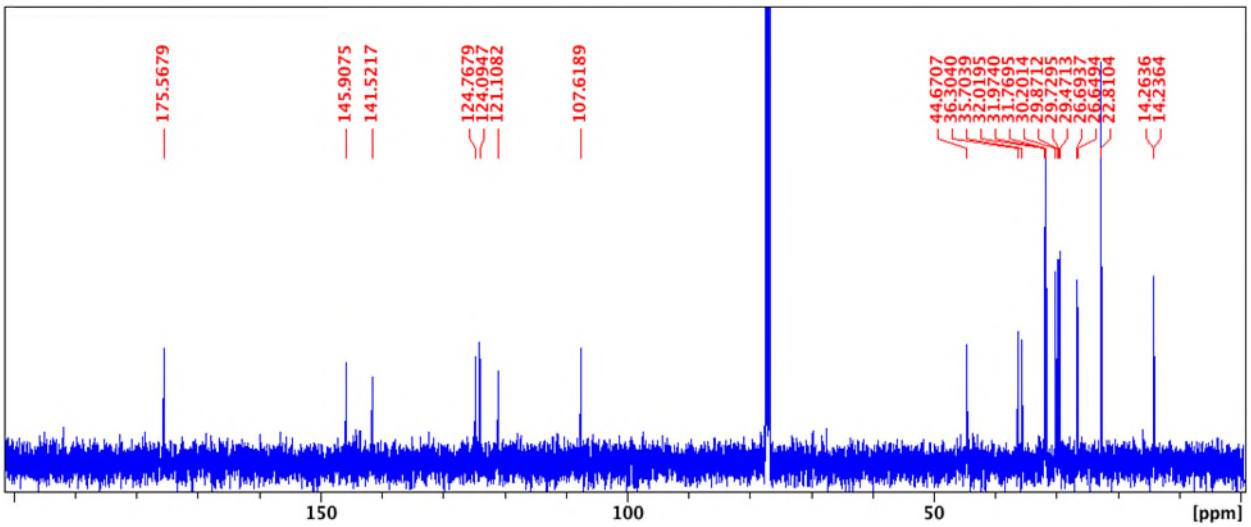


Figure S11. ^{13}C NMR spectrum of **5** in $CDCl_3$.

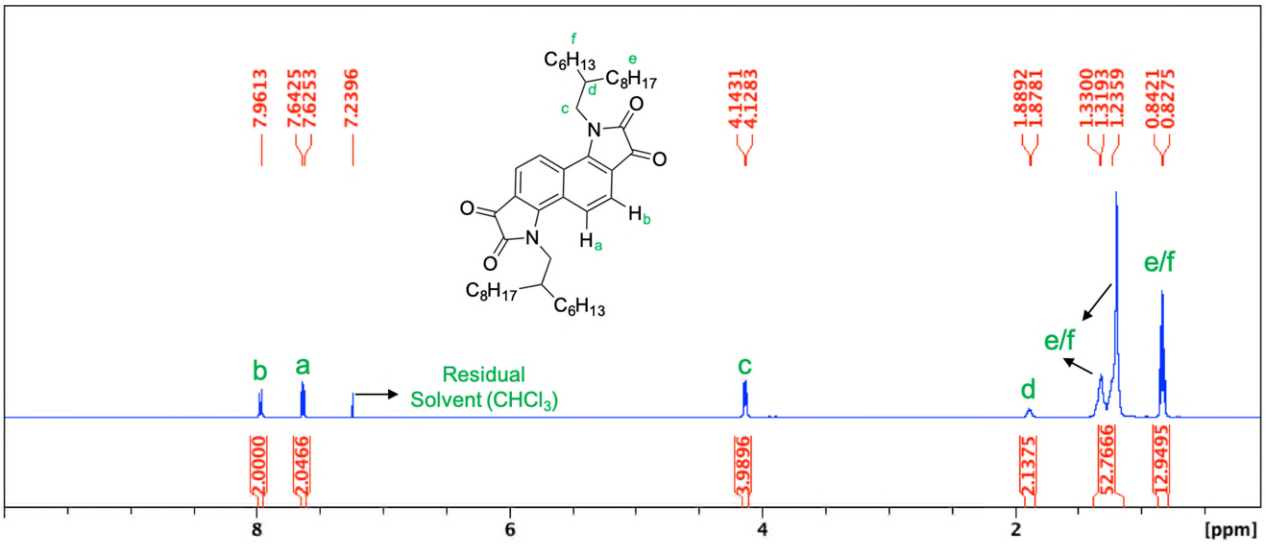


Figure S12. ^{1}H NMR spectrum of **7** in $CDCl_3$.

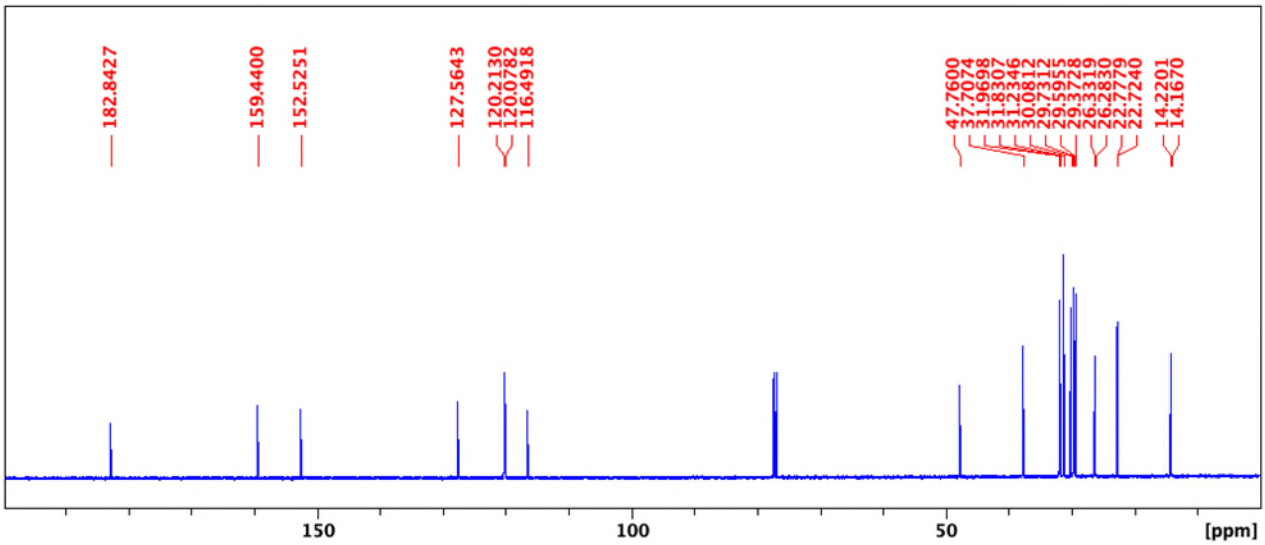


Figure S13. ^{13}C NMR spectrum of **7** in $CDCl_3$.

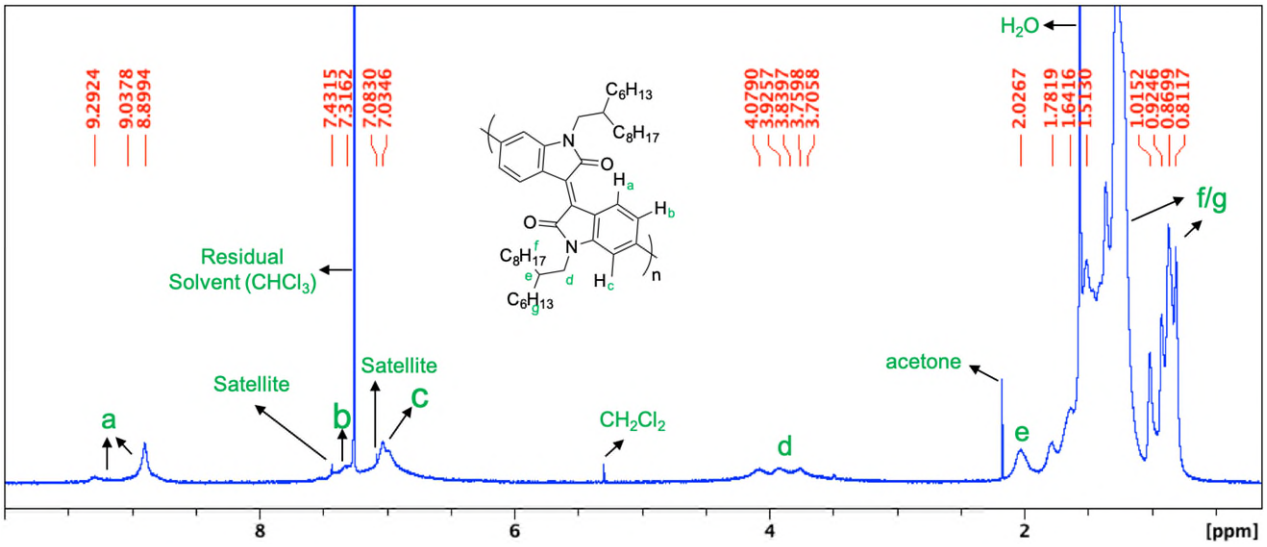


Figure S14. ^{1}H NMR spectrum of **polyisoindigo** in $CDCl_3$.

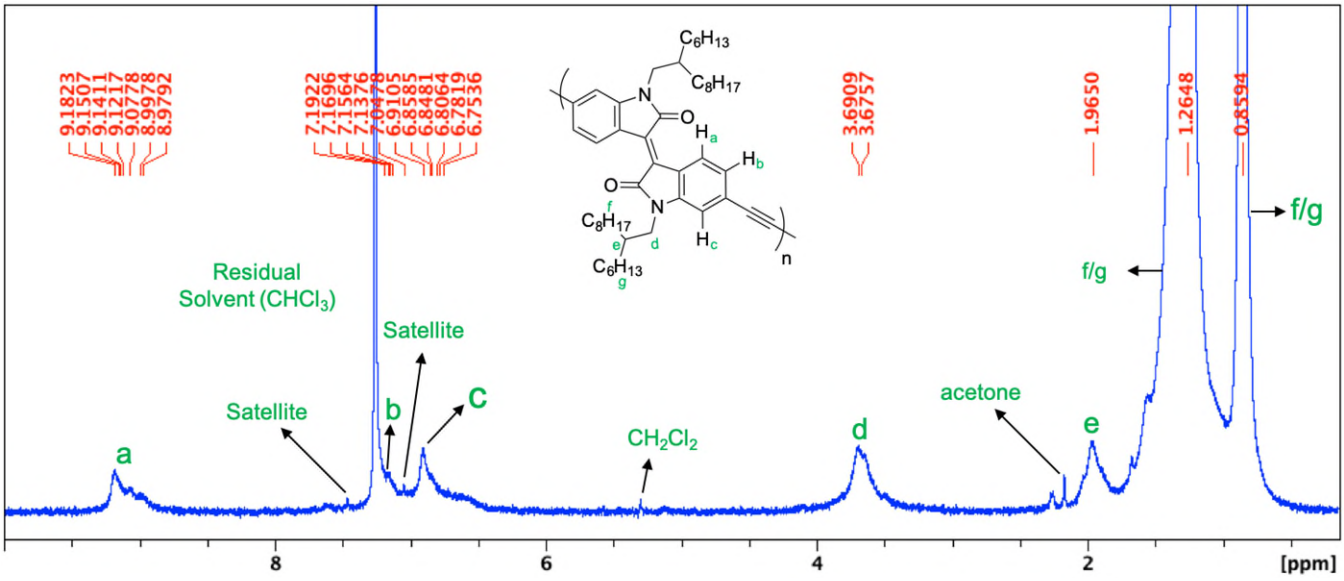


Figure S15. ^{1}H NMR spectrum of **poly(ethynylisoindigo)** in $CDCl_3$.

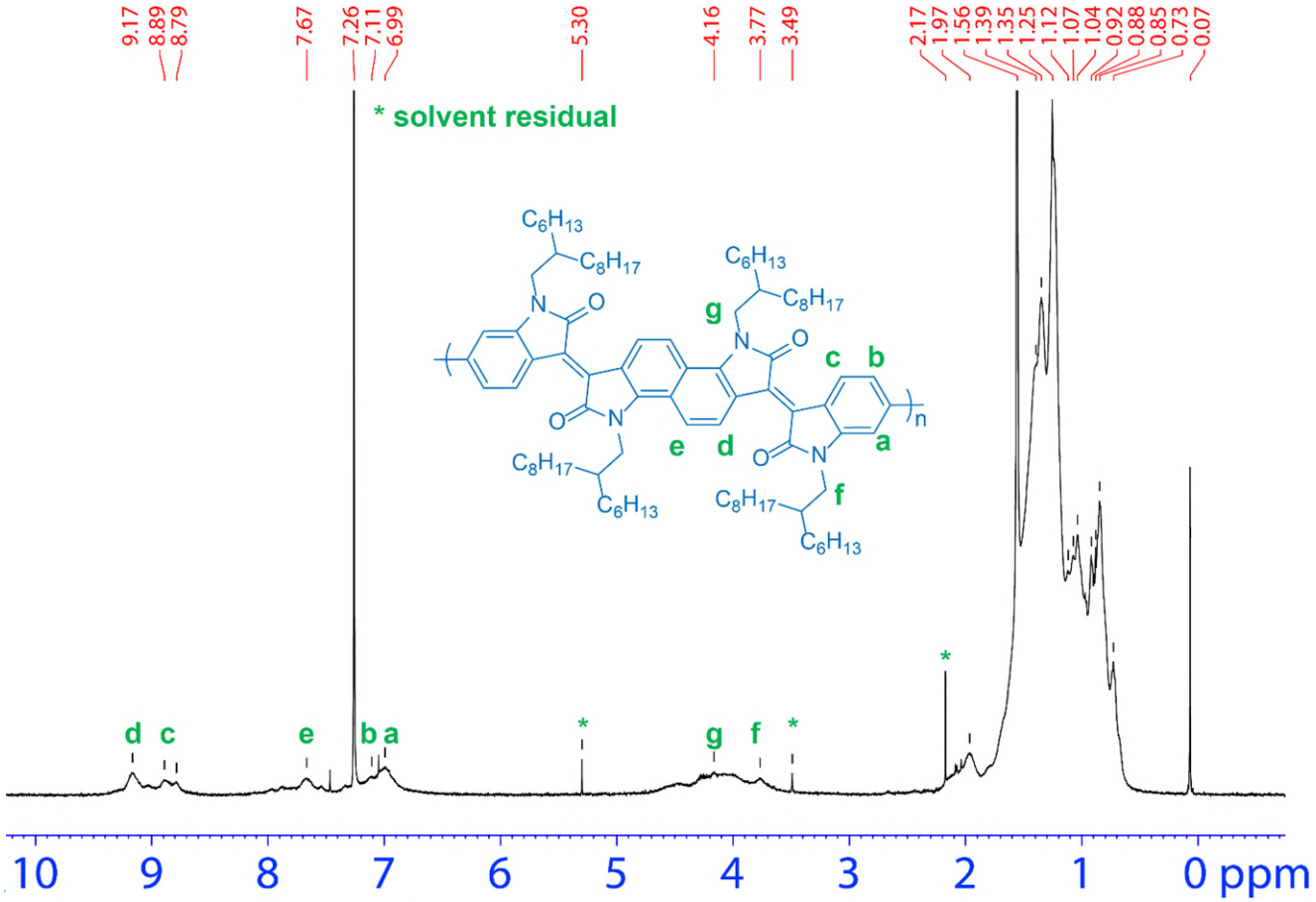


Figure S16. ^{1}H NMR spectrum of **poly(bisisoindigo)** in $CDCl_3$.

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