

Supporting Information

N-Type Conjugated Polyisoindigos

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S1. Experimental Section**S1.1. Materials and Methods**

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. The Et₄NOH (1M) aqueous solution was degassed by three freeze-pump-thaw cycles. Anhydrous solvents were obtained from an anhydrous solvent system. All ¹H NMR (300 MHz) and ¹³C NMR (75.5 MHz) spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts were referenced to residual signals from CHCl₃ (¹H 7.26 ppm and ¹³C 77.23 ppm). Elemental analyses were carried out by the CHN elementary analysis service in the Chemistry Department of the University of Florida.

Absorption spectra were recorded on a UV-vis-near-IR spectrophotometer. Thermogravimetric analysis (TGA) was performed using dynamic scans under nitrogen. Differential scanning calorimetry (DSC) analysis was performed using an instrument equipped with a controlled cooling accessory (liquid nitrogen cooling system) at 10 °C/min. Gel permeation chromatography (GPC) was performed at 40°C using a liquid chromatography system with an internal differential refractive index detector and two Styragel HR-5E columns (10 µm PD, 7.8 mm i.d., 300 mm length) using HPLC grade THF as the mobile phase at a flow rate of 1.0 mL/min.

S1.2. Electrochemical and Spectroelectrochemical Studies

Tetra-n-butylammonium hexafluorophosphate was purchased (98%, Acros) and recrystallized from ethanol. Tetraethylammonium tetrafluoroborate was purchased (Aldrich) and thoroughly dried under vacuum prior to utilization. The salts were transferred to an argon-filled drybox (OmniLab model, Vacuum Atmospheres). Acetonitrile was distilled over calcium hydride and kept under inert atmosphere before being transferred to the drybox in which the electrolyte solutions were made. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were performed using an EG&G Princeton Applied Research model 273A potentiostat/galvanostat in the argon-filled drybox. Experiments were carried out in a one compartment electrochemical cell using Ag/Ag⁺ reference electrode and platinum foil as a counter electrode; all potentials were reported vs Fc/Fc⁺ redox couple. The polymer films were dropcast from toluene solution (0.2 g/mL) onto platinum disk electrodes (0.02 cm²) and switched 10 times at a scan rate of 50 mV s⁻¹ in the corresponding range of potentials for reduction processes prior to characterization until a complete stabilization of the current responses was reached. The following setup parameters were applied for the DPV studies: a step size of 1.4

mV, a step time of 0.035 s, and amplitude of 55 mV. Spectroelectrochemistry was carried out on thin films spray coated onto ITO coated glass slides. The films were sprayed from 2mg/mL toluene solutions of the polymers, and contacts were made using copper tape. The coated ITO slides were transferred to an argon filled glovebox, in which the electrochemical cells were assembled. The cells were sealed with Teflon tape and taken out of the glovebox to perform the initial electrochemical reduction break-in cycles and the subsequent spectroelectrochemical experiments.

S1.3. *Device Fabrication*

Polymer solar cells were processed on pre-patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 20 Ω per square. First a thin layer (30 nm) of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS; Baytron AI 4083 from HC Starck) was spin-coated on ultrasonically cleaned ITO substrates, followed by backing on a hot plate at 180 °C for 10 min. An active layer of the device consisting of the blend of polymer (P3HT) and **Poly(ii)** was then spin coated from chlorobenzene solvent with a thickness 95 nm. The device was subsequently heated on a hotplate at 150 °C for 10 min. LiF (1 nm) and aluminum (100 nm) were thermally evaporated at a vacuum of ~ 0.10 nbar on top of active layer as a cathode. The area of the devices was 0.04 cm². The current density-voltage measurements of the devices were carried out using a semiconductor parameter analyzer system. The photocurrents were measured under AM 1.5G illumination at 1000 W/m² from a solar simulator. Device fabrication was done under nitrogen atmosphere and characterizations were performed in an ambient environment without any encapsulation.

S2. Synthetic Procedures and Characterizations of Products

6,6'-(N,N'-2-hexyldecyl)-dibromoisoidindigo (1).¹ To a suspension of 6,6'-dibromoisoidindigo (4.20 g, 10.0 mmol) and potassium carbonate (8.29 g, 60 mmol) in DMF (45 mL), 2-hexyl-bromodecane (9.16 g, 30 mmol) was injected through a septum under nitrogen. The mixture was stirred for 15 h at 100 °C and then poured into water (200 mL). The organic phase was extracted by CH₂Cl₂, washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the dark red liquids were purified by silica chromatography, eluting with (CH₂Cl₂: Hexane = 1:2) to give 6,6'-dibromo-N,N'-(2-hexyldecyl)-isoidindigo (6.1 g, 70 %) as dark red solids. ¹H-NMR (CDCl₃) δ: 9.04 (d, J = 9 Hz, 2H), 7.14 (dd, J₁ = 9Hz, J₂ = 1.8 Hz, 2H), 6.83 (d, J = 1.8 Hz, 2H), 3.56 (d, J = 7.5 Hz, 4H), 1.83 (bs, 2H), 1.40-1.24 (m, 48H), 0.88-0.84 (m, 12H); ¹³C-NMR (CDCl₃) δ: 168.2, 146.3, 132.6, 131.3, 126.9, 125.2, 120.6, 112.7, 44.9, 36.3, 32.1, 32.0, 31.7, 30.2, 29.87, 29.77, 29.5, 26.6, 22.89, 22.87, 14.34, 14.31.

6,6'-(N,N'-2-hexyldecyl)-pinacoldiboronisoidindigo (2). 6,6'-(N,N'-2-hexyldecyl)-dibromoisoidindigo (4.35 g, 5.0 mmol), pinacol ester of diboron (3.05 g, 12 mmol), [PdCl₂(dppf)] (220 mg), and potassium acetate (2.95 g, 30 mmol) were mixed at room temperature under an argon atmosphere. Anhydrous 1,4-dioxane (2 mL) was injected with a syringe through a septum. The solution was heated at 80 °C for 30 h and then cooled to room temperature. The reaction mixture was filtered by passing through a short pad of silica gel, and washed by a mixture of methylene chloride and hexane (1:1). The collected filtration was concentrated and precipitated into cold methanol (100 mL). The precipitates was filtered and dried to give a dark red shiny powder (3.6 g, 75%). ¹H-NMR (CDCl₃) δ: 9.15 (d, J = 7.2 Hz, 2H), 7.48 (d, J₁ = 8.1Hz, J₂ = 0.6 Hz, 2H), 7.15 (d, J = 0.6 Hz, 2H), 3.69 (d, J = 7.5 Hz, 2H), 1.95 (bs, 2H), 1.59-1.19 (m, 72H), 0.85 (t, J = 6.6 Hz, 6H); ¹³C-NMR (CDCl₃) δ: 168.3, 144.7, 134.5, 129.0, 128.9, 124.4, 113.7, 84.2, 44.6, 36.3, 32.1, 32.0, 31.8, 31.2, 29.8, 29.78, 29.5, 26.6, 25.1, 22.9, 22.8, 14.32, 14.30.

HRMS (MALDI-TOF) Calculated for $C_{60}H_{96}B_2N_2O_6$ ($M+Na$)⁺: 963.7548 Found: m/z 963.7583.

Anal. Calcd for $C_{60}H_{96}B_2N_2O_6$: C, 74.83; H,10.05; N,2.91. Found: C, 74.91; H,10.75; N, 2.80.

P(isoI). In a flame-dried Schlenk flask (50 mL), **1** (434.45 mg, 0.5 mmol) and **2** (481.52 mg, 0.5 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (18 mg) and $P(o\text{-}t\text{-}yl)_3$ (12 mg) were added. The flask was evacuated and back-filled with argon three times, after which degassed toluene (15 mL) and tetraethylammonium hydroxide (3 mmol, 1M) was transferred to the mixture through a septum. The resulting solution was heated up to 85 °C under argon and stirred for 36 h. The mixture was cooled to room temperature and poured slowly in methanol (300 mL). The precipitates were collected through a 0.45 μ m PTFE filter. The crude polymer (711 mg of dark solids) was purified with Soxhlet extraction with methanol, hexane to remove low molecular species and catalyst residues. From the hexanes fraction, 150 mg of lower molecular weight species were collected. Last, the higher molecular weight fraction was extracted with chloroform, to which diethylammonium diethyldithiocarbamate (as palladium scavenger, ~30 mg) was subsequently added in one portion. The latter mixture was then stirred for two hours at room temperature, and then poured slowly in methanol (300mL). The precipitates were filtered and dissolved in a minimum amount of chloroform, and precipitated a second time in methanol (100mL). The precipitates were collected via vacuum filtration through a 0.45 μ m PTFE filter and dried, yielding dark blue solids (523 mg, 74%). ¹H-NMR ($CDCl_3$) δ : 8.98-8.70 (M, 2H), 7.40-6.80 (m, 4H), 3.60-3.25 (m, 4H), 2.20-0.60 (m, 62H). GPC: M_n = 28.7 kDa, PDI = 2.4. Anal. Calcd for $C_{48}H_{72}N_2O_2$: C, 81.30; H,10.23; N,3.95. Found: C, 80.47; H, 10.52; N, 3.84.

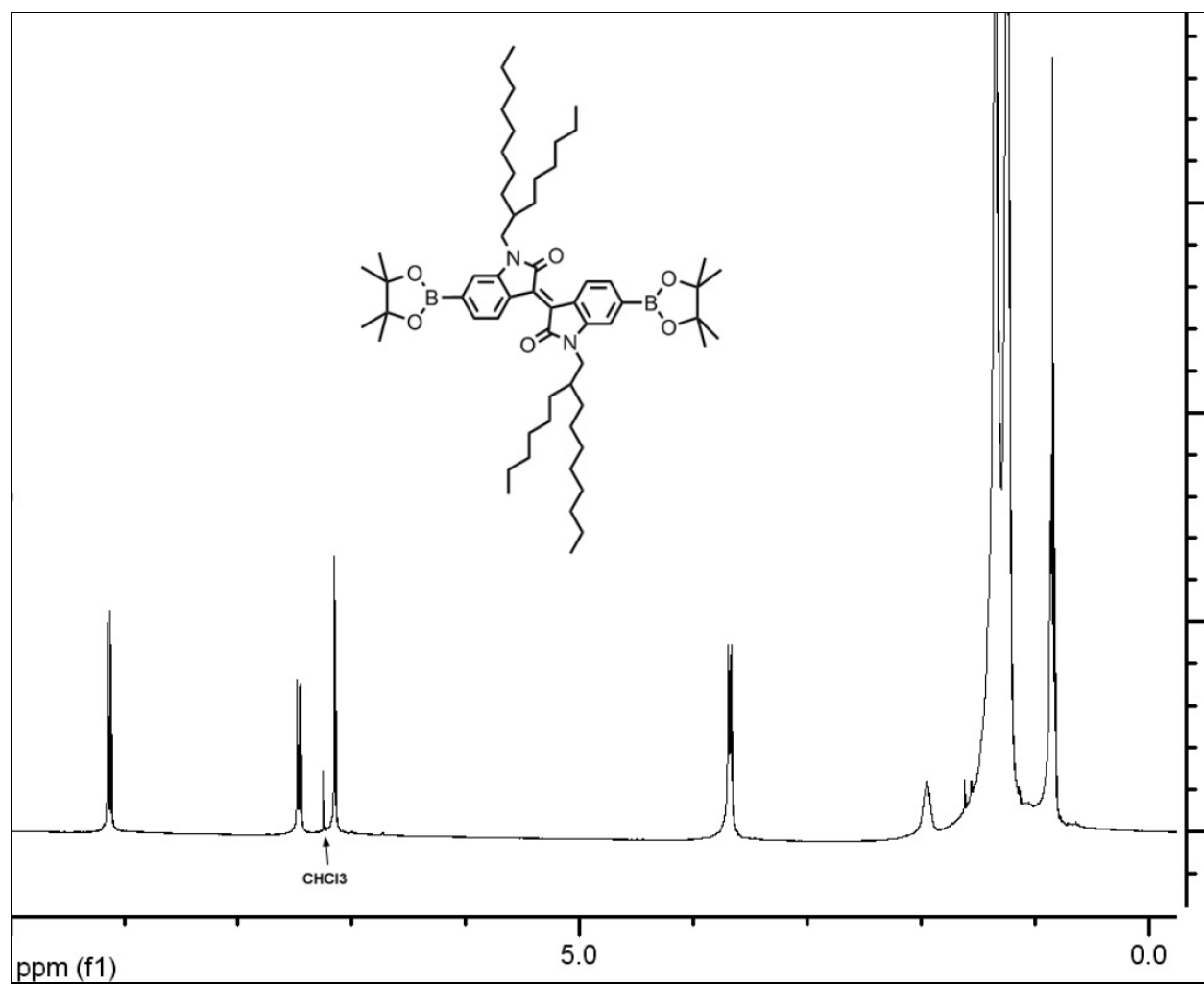
P(isoI-BTD). In a flame-dried Schlenk flask (50 mL), 4,7-dibromobenzothiadiazole (73.49 mg, 0.25 mmol) and **2** (240.76, 0.25 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (9 mg) and $P(o\text{-}t\text{-}yl)_3$ (6 mg) were added. The flask was evacuated and back-filled with argon three times, after which

degassed toluene (15 mL) and tetraethylammonium hydroxide (2 mmol, 1M) was transferred to the mixture through a septum. The resulting solution was heated up to 85 °C under argon and stirred for 36 h. The mixture was cooled to room temperature and poured slowly in methanol (300 mL). The precipitates were collected through a 0.45 µm PTFE filter. The crude polymer (220 mg of dark solids) was purified with Soxhlet extraction with methanol to remove catalyst residues. The polymer was extracted with chloroform, to which fraction diethylammonium diethyldithiocarbamate (as palladium scavenger, ~20 mg) was added in one portion. The mixture was stirred for two hours at room temperature, and then poured slowly in methanol (300mL). The precipitates were filtered and dissolved in a minimum amount of chloroform, and precipitated a second time in methanol (100mL). The precipitates were collected via vacuum filtration through a 0.45 µm PTFE filter and dried, yielding dark brown solids (202 mg, 95%).

¹H-NMR (CDCl₃) δ: 9.42-8.95 (m, 2H), 7.78-5.98 (m, 8H), 3.60-3.20 (m, 4H), 2.20-0.45 (m, 62H). GPC: M_n = 16.3 kDa, PDI = 3.5. Calcd for C₅₄H₇₄N₄O₂S: C, 76.91; H, 8.85; N, 6.64. Found: C, 76.55; H, 8.86; N, 6.30.

1. Wang, E.; Ma, Z.; Zhang, Z.; Henriksson, P.; Inganas, O.; Zhang, F.; Andersson, M. R. Chem. Commun. 2011, 47, 4908-4910.

S3. Supporting Figures and Tables

**Figure S1:** ^1H NMR spectrum of diborylated isoindigo compound **2** in CDCl_3 .

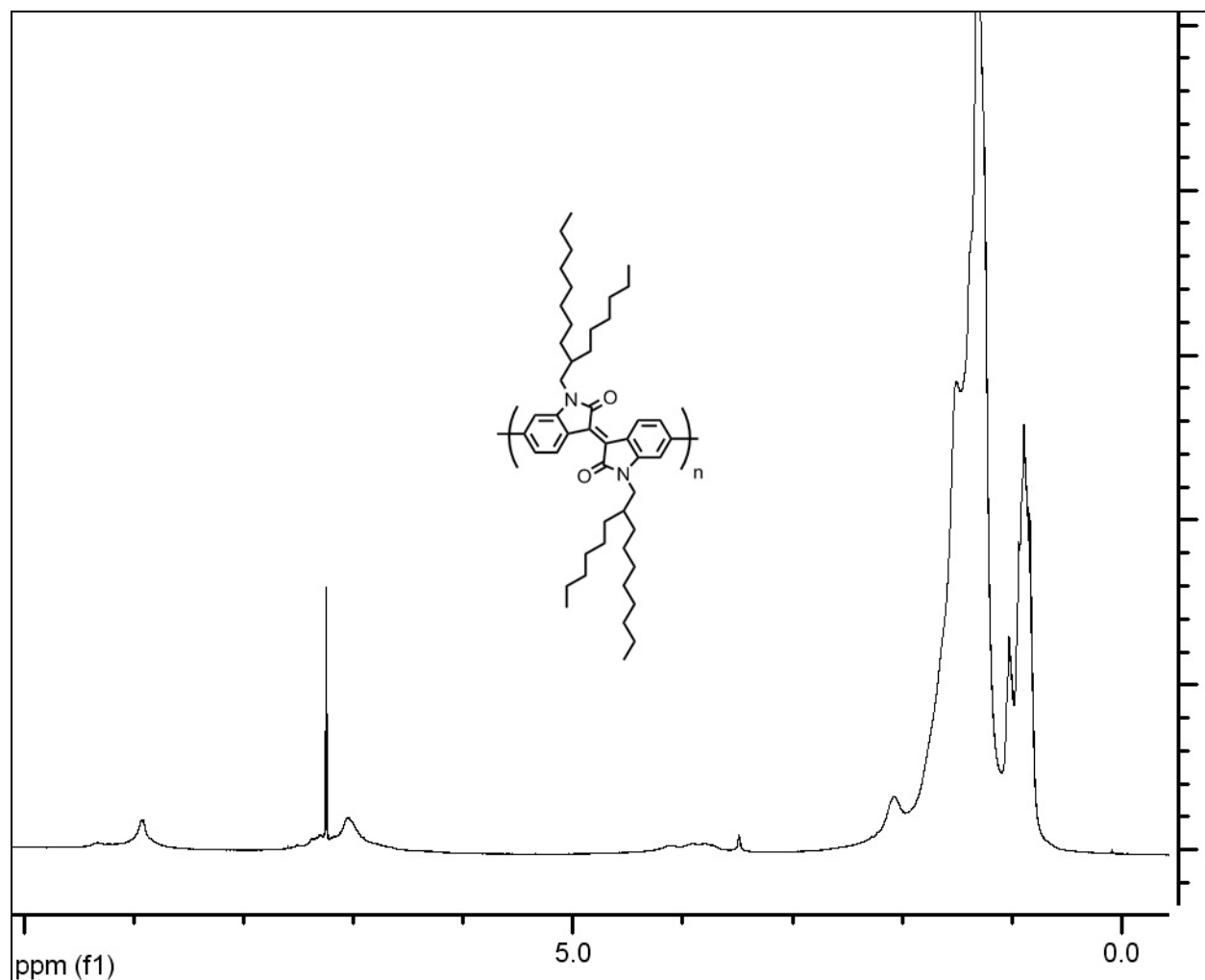


Figure S2: ^1H NMR spectrum of **Poly(iI)** in CDCl_3 .

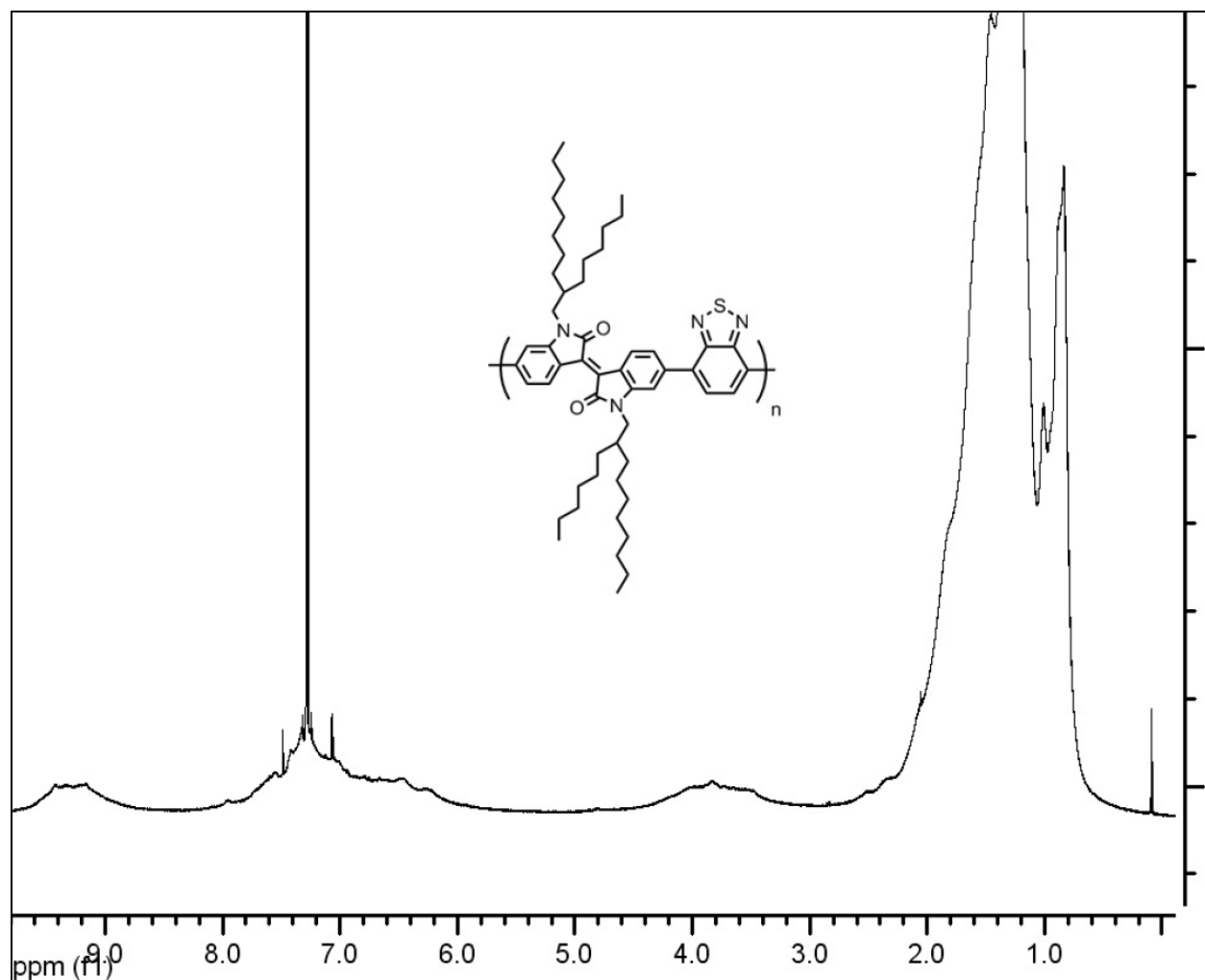


Figure S3: ^1H NMR spectrum of **Poly(iI-BTD)** in CDCl_3 .

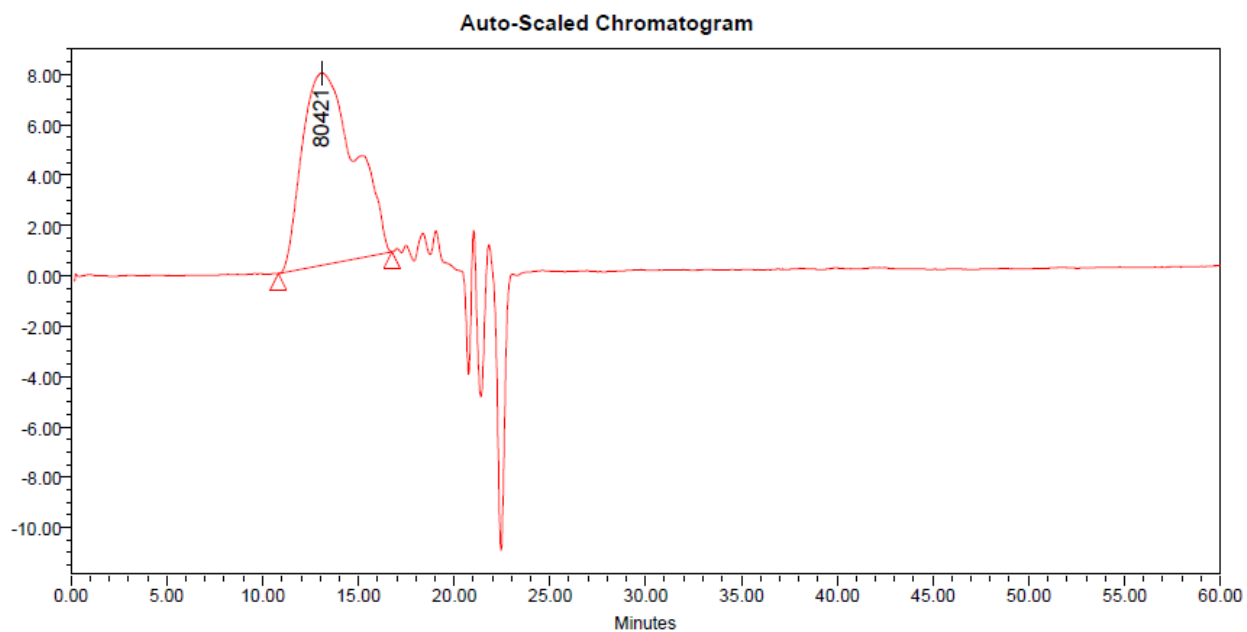


Figure S4: GPC trace for **Poly(II)** at 40°C in THF, against polystyrene standards.

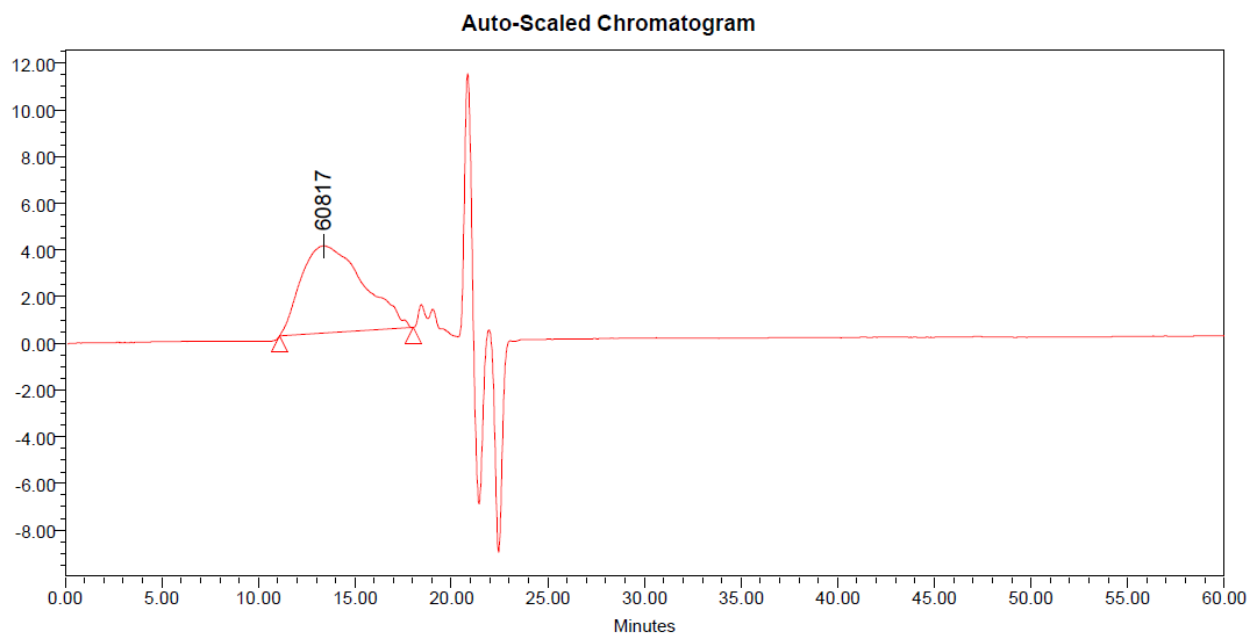


Figure S5: GPC trace for **Poly(II-BTD)** at 40°C in THF, against polystyrene standards.

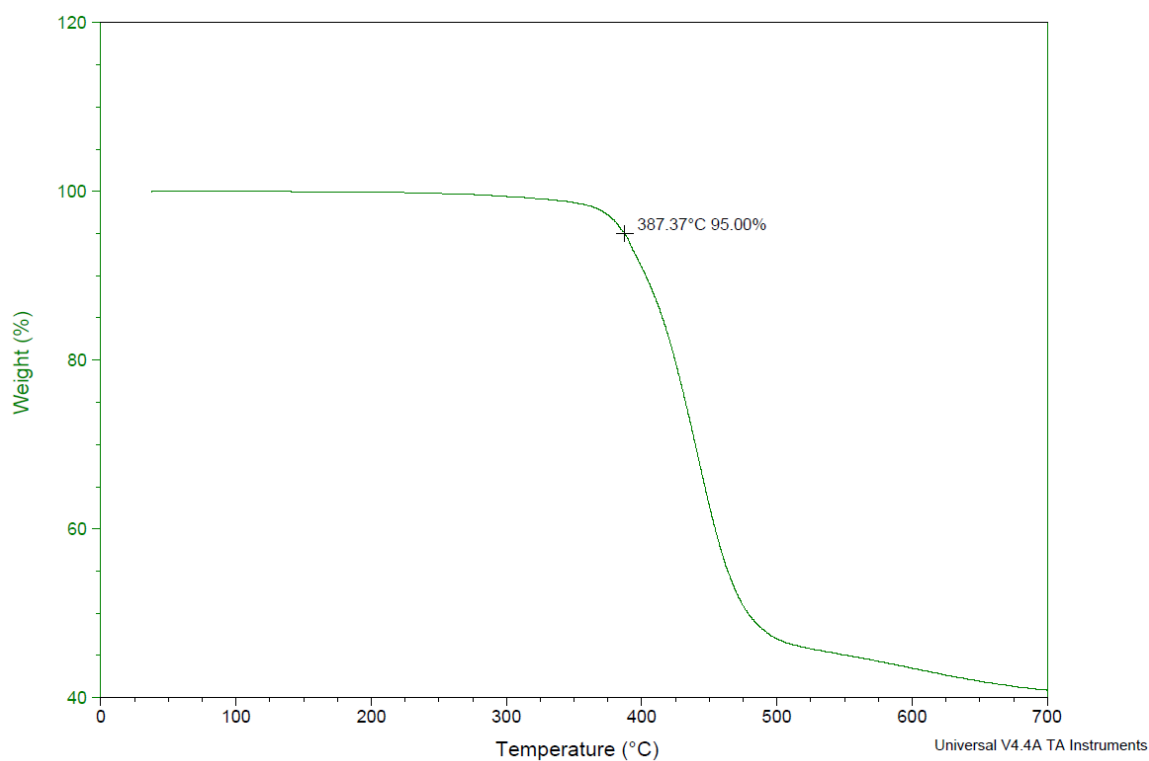


Figure S6: TGA thermogram of **Poly(iI-BTD)** under nitrogen flow.

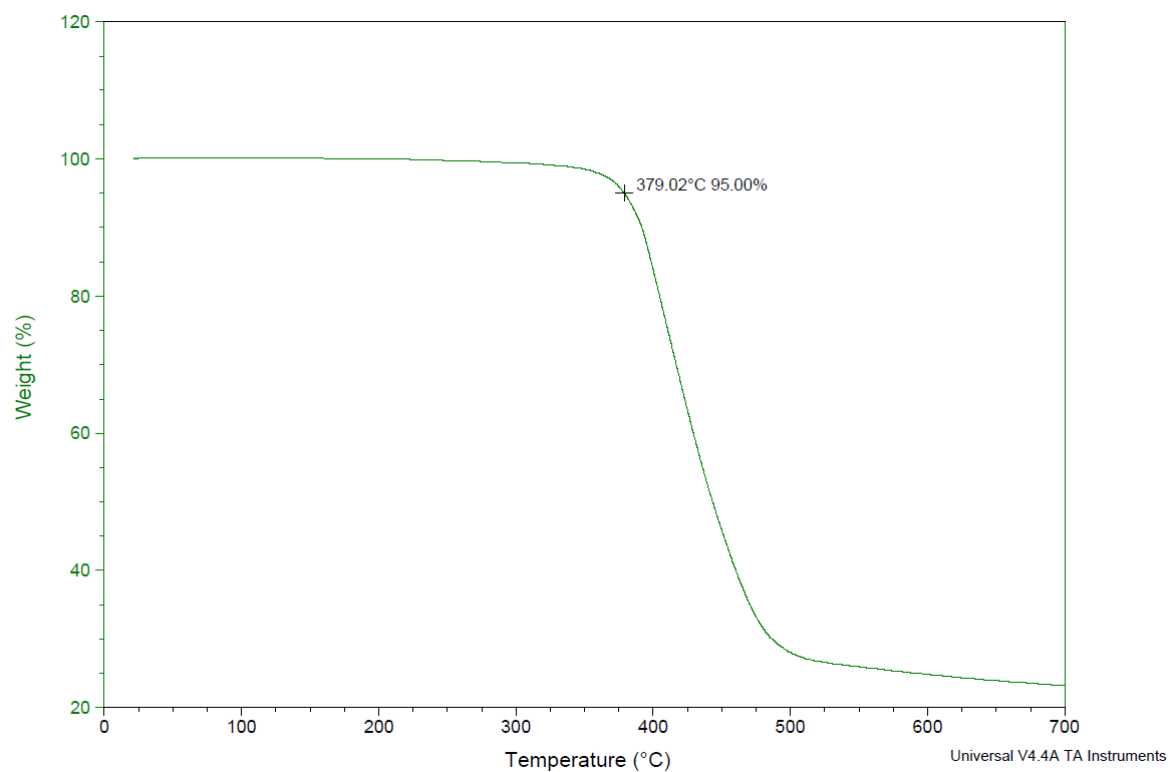


Figure S7: TGA thermogram of **Poly(iI)** under nitrogen flow.

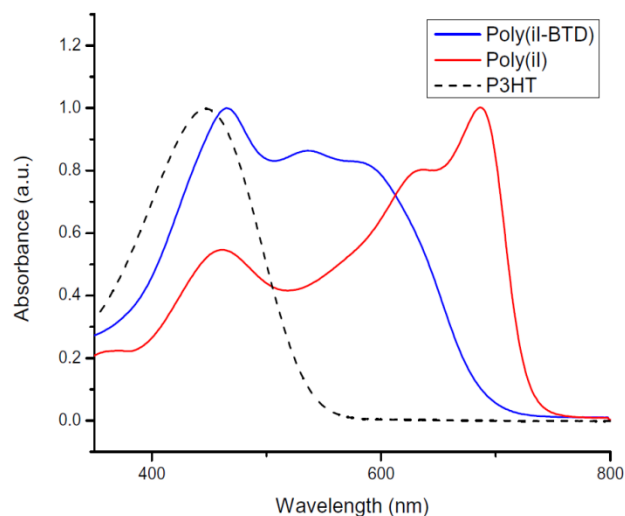


Figure S8: Normalized absorption of P3HT (dashed line), **Poly(iI)** (red line) and **Poly(iI-BTD)** (blue line) in toluene solution.

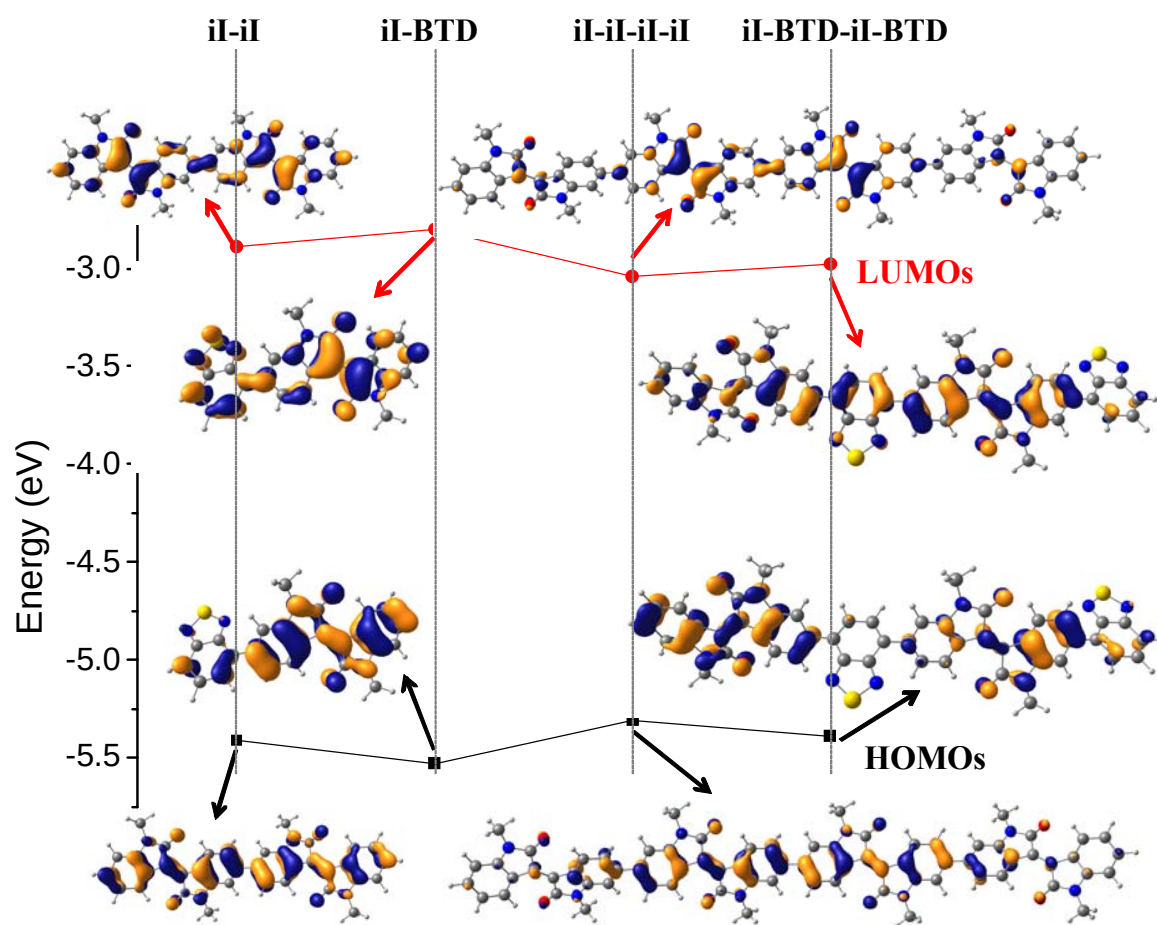
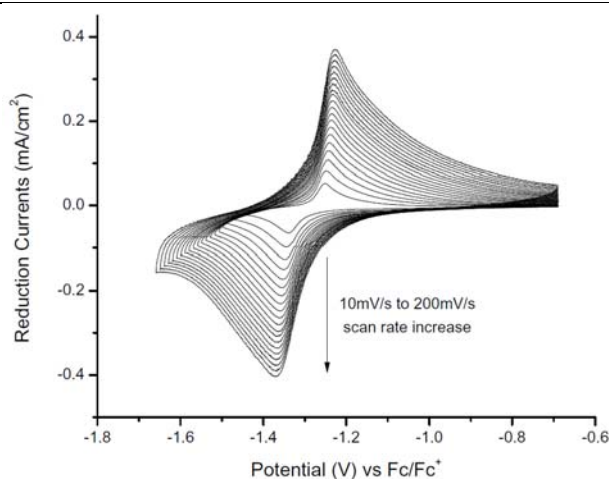
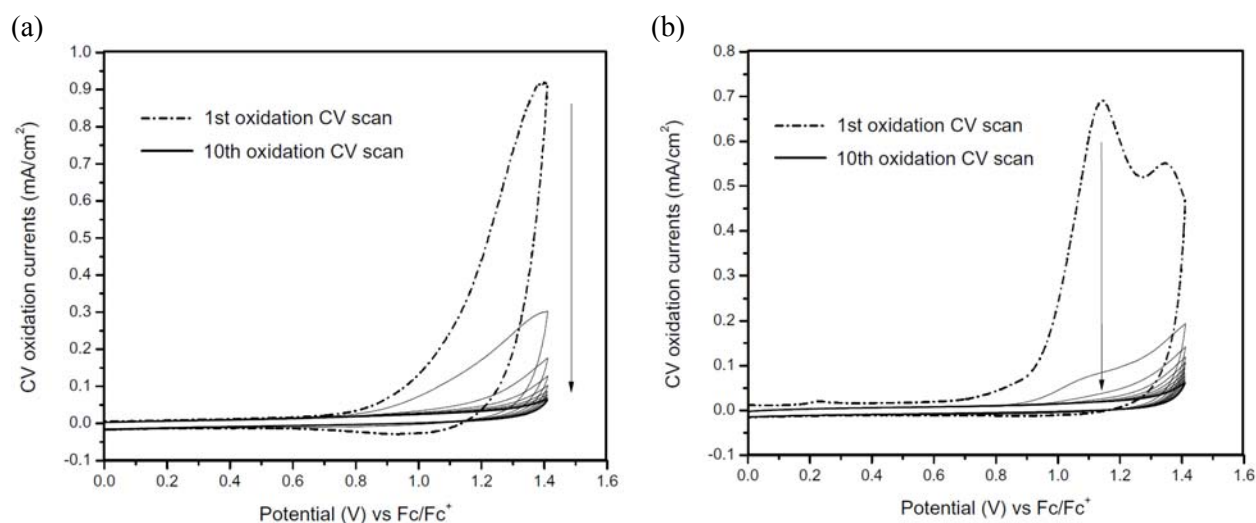


Figure S9. Pictorial representation of the Kohn-Sham frontier orbital energies plus orbital maps for iI-iI and iI-BTD dimers, as well as iI-iI-iI-iI and iI-BTD-iI-BTD tetramers.

Table S1: Dihedral angles for selected model oligomers of isoindigo (iI) and iI-BTD dyads, calculated by DFT.

Compound	Dihedral angles			
	Bond1 (deg.)	Bond2 (deg.)	Bond3 (deg.)	Bond4 (deg.)
iI	--	--	--	--
BTD-iI	145.8471	--	--	--
iI₂	145.7653	--	--	--
BTD-iI-BTD	145.9689	145.9694	--	--
iI-BTD-iI	144.7874	146.4945	--	--
iI₃	146.4204	145.9176	--	--
BTD-iI-BTD-iI	144.3267	145.7010	145.5114	--
iI₄	145.9390	145.5817	145.9399	--
iI₅	146.1148	145.6261	146.1992	145.5239

**Figure S10:** Overlaid CVs of **Poly(iI)** recorded in 0.1M TBAPF₆/ACN, at increasing scan rates from 10mV/s to 200 mV/s with a 10mV/s rate increment.**Figure S11:** Overlaid ten first oxidation CVs of (a) **Poly(iI)** and (b) **Poly(iI-BTD)** recorded in 0.1M TBAPF₆/ACN, at 50mV/s scan rate.

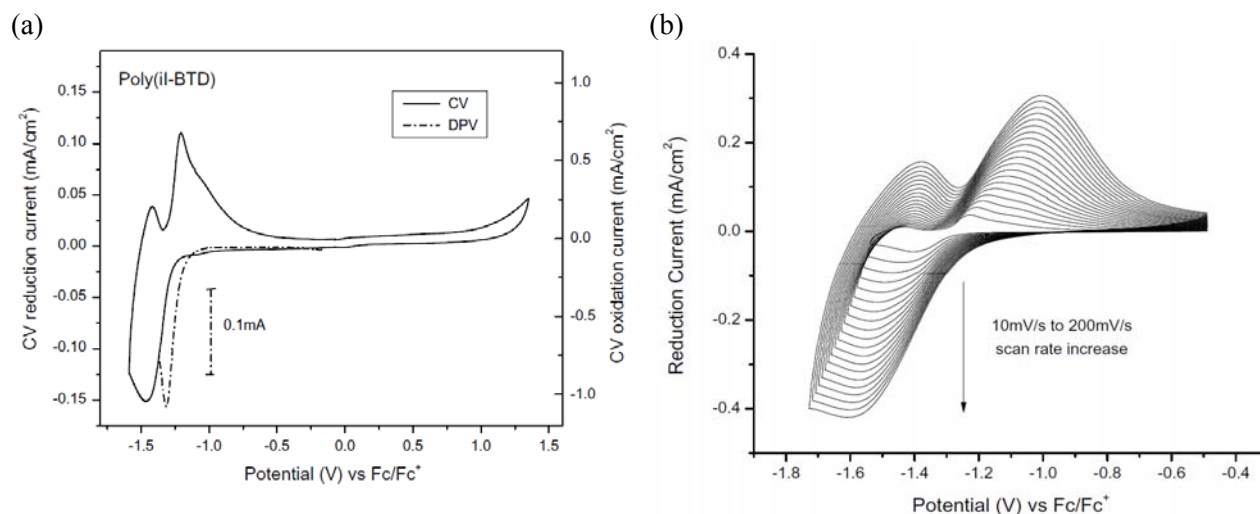


Figure S12: (a) Cyclic (solid line) and differential pulse (dashed line) voltammograms of **Poly(iI-BTD)** recorded from thin films on Pt-button electrodes, in 0.1M TBAPF₆/ACN electrolyte versus Fc/Fc⁺. (b) Overlaid CVs of **Poly(iI-BTD)** recorded in 0.1M TBAPF₆/ACN, at increasing scan rates from 10mV/s to 200 mV/s with a 10mV/s rate increment.

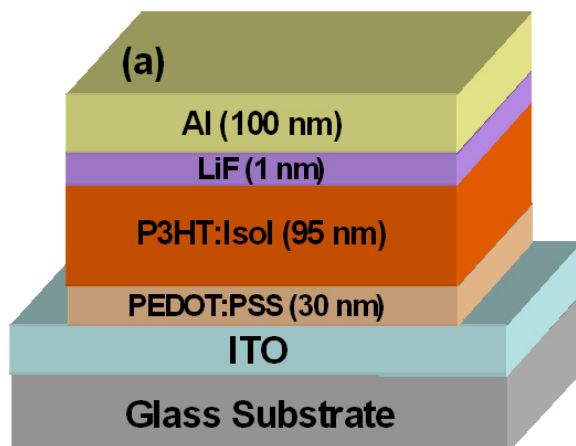


Figure S13 Schematic diagram of the all-polymer solar cell with conventional device geometry.

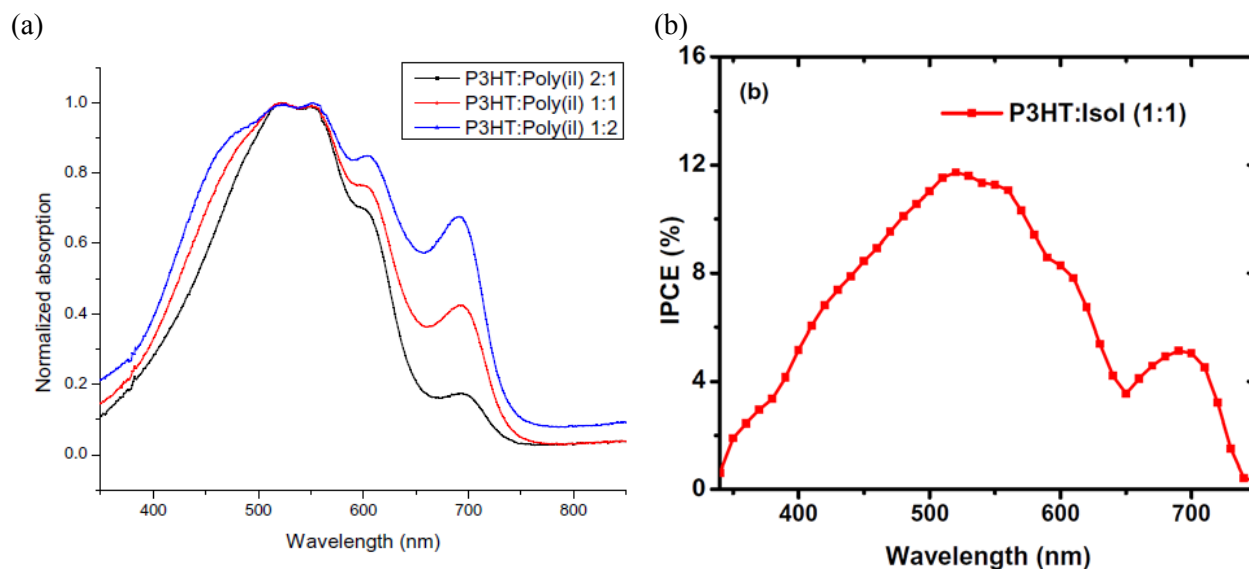


Figure S14: (a) Normalized absorption of blend films of P3HT and Poly(II) at ratios used in the solar cells. (b) External quantum efficiency of the 1:1 P3HT:Poly(II) device.

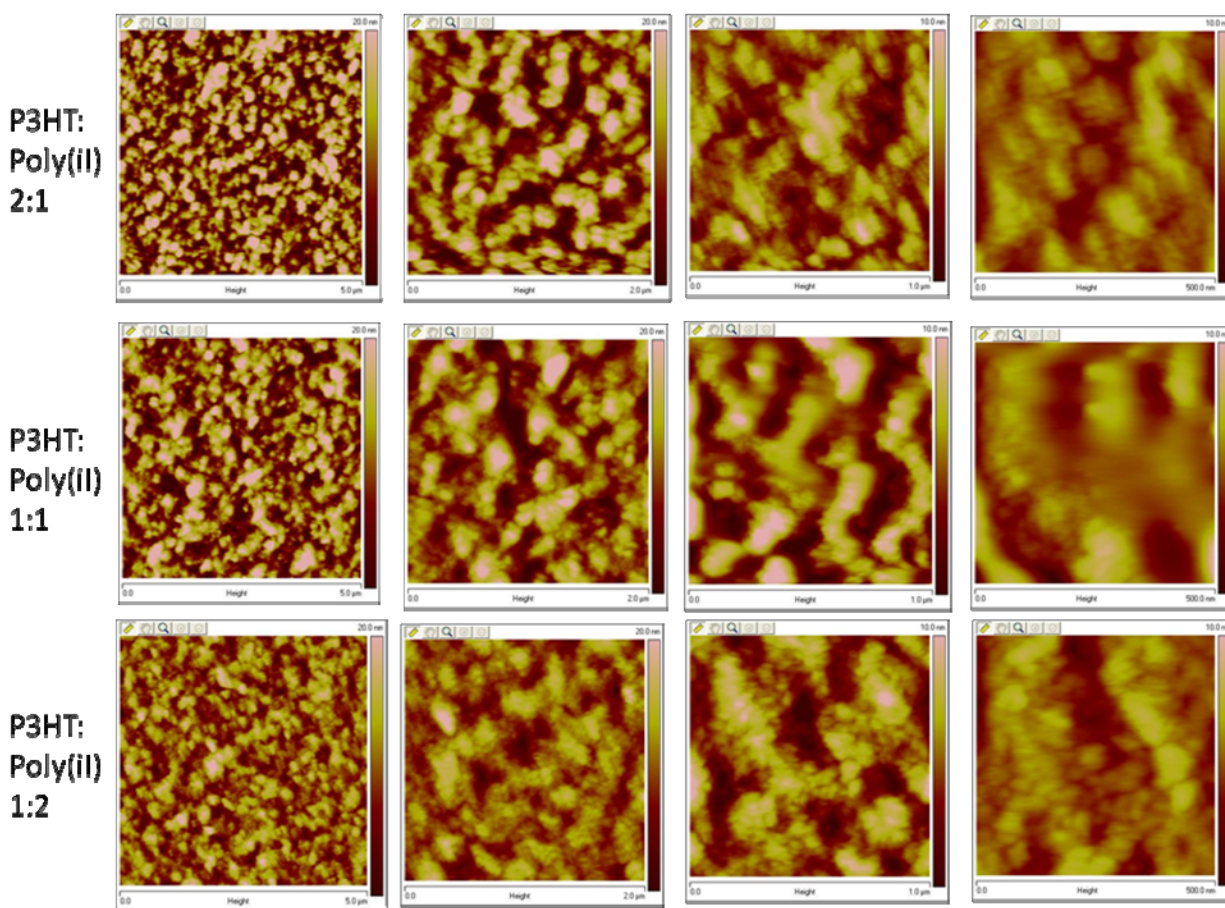


Figure S15: AFM height images of P3HT:Poly(II) blend films at three different blend ratios. For each blend ratio (row), images are 5 × 5 μm (20 nm height scale), 2 × 2 μm (20 nm height scale), 1 × 1 μm (10 nm height scale), and 0.5 × 0.5 μm (10 nm height scale), from left to right respectively.

S3. DFT Calculations

The Gaussian03 program package was used to perform all the presented calculations.¹ The unconstrained geometries of the il-based oligomers in gas phase were optimized by Density Functional Theory (DFT) using the Becke's three-parameter functional² hybridized with the Lee-Yang-Parr correlation functional³ and the 6-31G* split-valence basis set.⁴ The solubilizing alkyl groups from isoindigo were replaced for methyl to speed up the computations.

Cartesian coordinates of optimized geometries and relevant orbitals for vertical transitions.

A. il₂

C01	8.37361	0.83885	-0.37703	C25	-2.90919	-1.05030	-0.31942	H49	7.17792	3.99637	-0.42601
C02	7.56911	-0.31741	-0.19700	C26	-3.58457	0.12099	0.05262	H50	8.54964	3.49367	-1.45296
C03	6.17247	0.13523	-0.08374	C27	-2.78594	1.24520	0.39200	H51	8.74965	3.59019	0.31695
C04	6.24394	1.65103	-0.20793	C28	-1.40186	1.22341	0.39796	H52	0.83566	-2.09734	0.70074
N05	7.57775	1.98111	-0.36013	C29	-4.99101	0.54301	0.12146	H53	1.01862	1.99531	-0.63728
C06	9.74807	0.78596	-0.56078	C30	-4.93566	2.00664	0.53939	H54	3.46935	1.92949	-0.59623
C07	10.35587	-0.47431	-0.57991	N31	-3.60006	2.33186	0.69639	H55	4.03155	-4.25761	1.27103
C08	9.59218	-1.63204	-0.42651	C32	-6.17246	-0.13523	-0.08375	H56	2.51684	-4.09959	0.33836
C09	8.20871	-1.56500	-0.23604	O33	-5.84371	2.79561	0.76014	H57	2.57253	-3.57772	2.04322
C10	4.99101	-0.54301	0.12147	C34	-3.14568	3.64177	1.11108	H58	-1.01861	-1.99530	-0.63724
O11	5.35246	2.48724	-0.14737	C35	-6.24391	-1.65102	-0.20809	H59	-3.46935	-1.92949	-0.59619
C12	8.04902	3.34300	-0.48912	N36	-7.57773	-1.98112	-0.36015	H60	-0.83567	2.09737	0.70072
C13	4.93565	-2.00661	0.53950	C37	-8.37360	-0.83887	-0.37703	H61	-4.03157	4.25762	1.27100
N14	3.60006	-2.33184	0.69645	C38	-7.56911	0.31740	-0.19702	H62	-2.51682	4.09961	0.33839
C15	2.78593	-1.24518	0.39204	C39	-9.74808	-0.78599	-0.56071	H63	-2.57259	3.57770	2.04325
C16	3.58457	-0.12098	0.05265	C40	-10.35589	0.47427	-0.57981	H64	-10.33145	-1.69187	-0.69097
C17	1.40186	-1.22338	0.39798	C41	-9.59221	1.63201	-0.42643	H65	-11.43130	0.54550	-0.71898
C18	0.73920	-0.03206	0.04027	C42	-8.20873	1.56498	-0.23600	H66	-10.07509	2.60454	-0.44849
C19	1.51520	1.08385	-0.31971	O43	-5.35244	-2.48723	-0.14742	H67	-7.63413	2.46782	-0.10225
C20	2.90920	1.05031	-0.31943	C44	-8.04900	-3.34301	-0.48903	H68	-7.17789	-3.99638	-0.42600
C21	-0.73920	0.03207	0.04026	H45	10.33145	1.69183	-0.69106	H69	-8.54973	-3.49373	-1.45281
C22	3.14567	-3.64176	1.11108	H46	11.43127	-0.54555	-0.71913	H70	-8.74954	-3.59019	0.31713
O23	5.84371	-2.79560	0.76019	H47	10.07505	-2.60457	-0.44863				
C24	-1.51519	-1.08384	-0.31970	H48	7.63411	-2.46784	-0.10231				

Excited State 1: Singlet-A 2.1806 eV 568.57 nm f=0.7209
HOMO-4 → LUMO 0.10573
HOMO-1 → LUMO+1 -0.10950
HOMO → LUMO 0.63339

Excited State 2: Singlet-A 2.3815 eV 520.61 nm f=0.0020
HOMO-5 → LUMO 0.12297
HOMO-4 → LUMO+1 -0.10870
HOMO-3 → LUMO -0.10538
HOMO-2 → LUMO+1 0.18444
HOMO-1 → LUMO 0.59332
HOMO → LUMO+1 -0.15332

Excited State 3: Singlet-A 2.4381 eV 508.52 nm f=0.0044
HOMO-3 → LUMO+1 -0.26154
HOMO-2 → LUMO 0.61091

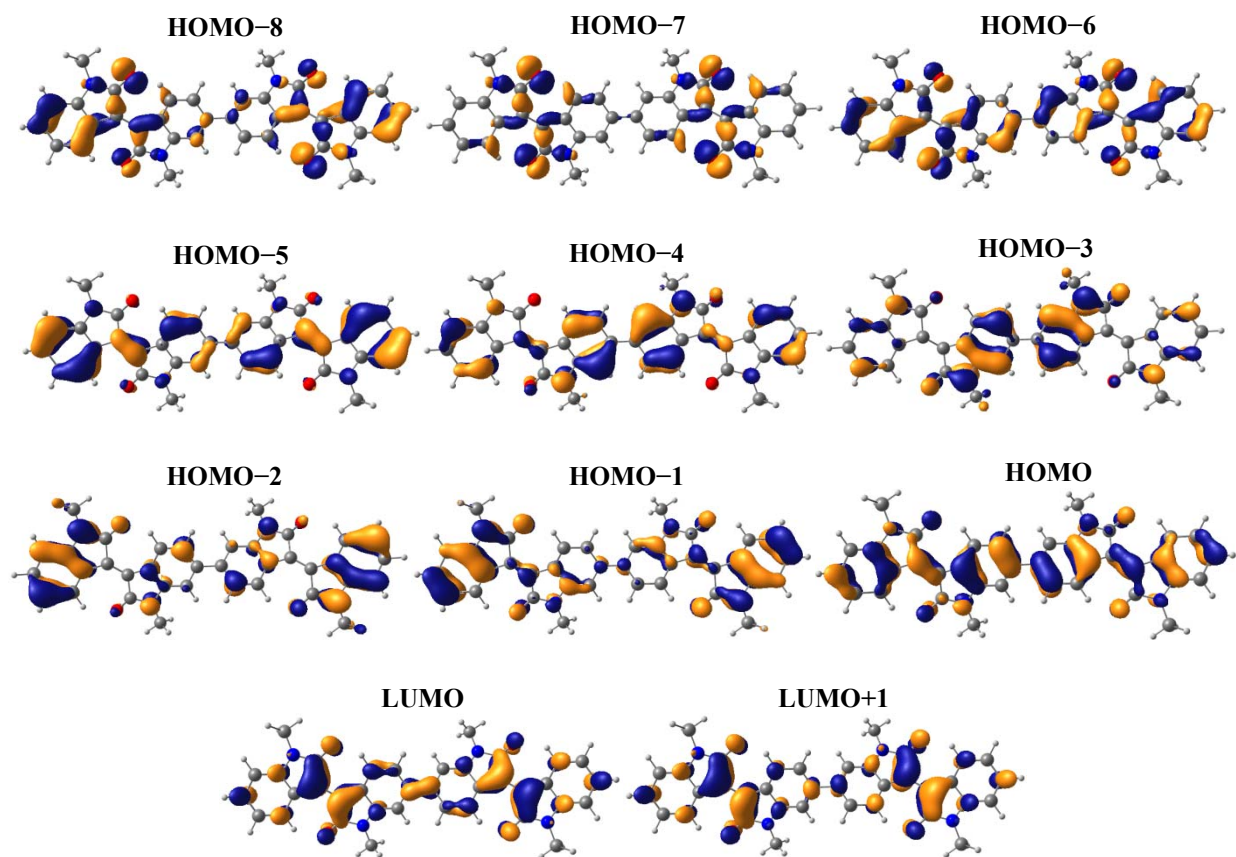
HOMO-1 → LUMO+1 0.16061

Excited State 4: Singlet-A 2.4467 eV 506.74 nm f=0.0022
HOMO-4 → LUMO+1 -0.10163
HOMO-3 → LUMO 0.49218
HOMO-2 → LUMO+1 -0.23685
HOMO → LUMO+1 -0.38129

Excited State 5: Singlet-A 2.5527 eV 485.70 nm f=0.0000
HOMO-3 → LUMO 0.37840
HOMO-1 → LUMO 0.27143
HOMO → LUMO+1 0.51127

Excited State 6: Singlet-A 2.7689 eV 447.77 nm f=0.2106
HOMO-5 → LUMO+1 0.10498
HOMO-4 → LUMO -0.28067

HOMO-3 → LUMO+1	0.21095	HOMO-1 → LUMO	-0.14914
HOMO-1 → LUMO+1	0.55412		
HOMO → LUMO	0.16938		
Excited State 7: Singlet-A	2.9569 eV	419.30 nm	f=0.4220
HOMO-8 → LUMO	-0.10519		
HOMO-4 → LUMO	0.49288		
HOMO-3 → LUMO+1	-0.20841		
HOMO-2 → LUMO	-0.20491		
HOMO-1 → LUMO+1	0.33425		
Excited State 8: Singlet-A	2.9762 eV	416.59 nm	f=0.0000
HOMO-3 → LUMO	0.28748		
HOMO-2 → LUMO+1	0.61417		
Excited State 9: Singlet-A	2.9856 eV	415.27 nm	f=0.0372
HOMO-4 → LUMO	0.31520		
HOMO-3 → LUMO+1	0.56864		
HOMO-2 → LUMO	0.24235		
Excited State 10: Singlet-A	3.1214 eV	397.20 nm	f=0.0014
HOMO-8 → LUMO+1	0.16764		
HOMO-7 → LUMO	0.36745		
HOMO-6 → LUMO+1	-0.20734		
HOMO-5 → LUMO	0.45450		
HOMO-4 → LUMO+1	-0.19086		



B. ii-BTD

C01	4.75040	0.03808	-0.18241	C12	0.00083	1.51124	-0.16580	C23	-4.44321	-0.44463	-0.10798
C02	6.16192	0.39067	-0.13419	C13	-0.51582	0.24744	0.15294	C24	-6.74952	0.39085	-0.38846
C03	6.57538	1.67854	0.30798	C14	0.42261	-0.77858	0.43718	C25	-7.19137	-0.93334	-0.48637
C04	5.59794	2.56409	0.67849	C15	1.79285	-0.58216	0.45244	C26	-6.28404	-1.99088	-0.41303
C05	4.21289	2.22465	0.62924	C16	-1.85520	-0.35765	0.19178	C27	-4.91803	-1.75892	-0.22585
C06	3.74294	0.99459	0.20720	C17	-1.60801	-1.82426	0.52258	C28	-5.38895	3.13563	-0.16257
N07	4.53578	-1.20580	-0.62889	N18	-0.24240	-1.97880	0.67281	C29	0.38347	-3.24096	1.00496
S08	6.01253	-1.85407	-0.94982	C19	-3.11465	0.17503	0.02881	O30	-2.40568	-2.73720	0.68621
N09	6.97794	-0.58989	-0.53993	C20	-3.37983	1.67427	0.00054	O31	-2.60067	2.61179	0.10776
C10	2.29283	0.70212	0.16017	N21	-4.74694	1.83973	-0.12232	H32	7.63138	1.92277	0.34281
C11	1.37843	1.72294	-0.15898	C22	-5.39083	0.60815	-0.20871	H33	5.87144	3.55513	1.02961

H34	3.49587	2.96747	0.96448	H39	-8.25063	-1.13293	-0.62454	H44	-5.92336	3.27767	-1.10941
H35	1.75270	2.70310	-0.43680	H40	-6.63882	-3.01394	-0.49643	H45	-0.41054	-3.98222	1.10347
H36	-0.66755	2.32226	-0.40813	H41	-4.22997	-2.58651	-0.15564	H46	0.93188	-3.16599	1.95115
H37	2.46883	-1.39704	0.67536	H42	-4.60600	3.88944	-0.07038	H47	1.07881	-3.54929	0.21577
H38	-7.44609	1.22035	-0.45684	H43	-6.09919	3.24432	0.66542				

Excited State 1: Singlet-A 2.3058 eV 537.71 nm $f=0.2476$
HOMO-2 → LUMO 0.18663
HOMO → LUMO 0.62204

Excited State 2: Singlet-A 2.4385 eV 508.45 nm $f=0.0005$
HOMO-1 → LUMO 0.66878
HOMO-1 → LUMO+1 0.14342

Excited State 3: Singlet-A 2.7323 eV 453.77 nm $f=0.0334$
HOMO-1 → LUMO+1 0.12423
HOMO → LUMO+1 0.66026

Excited State 4: Singlet-A 2.9347 eV 422.48 nm $f=0.4432$
HOMO-4 → LUMO -0.15617
HOMO-2 → LUMO 0.62214
HOMO → LUMO -0.12409

Excited State 5: Singlet-A 3.1211 eV 397.25 nm $f=0.0084$
HOMO-2 → LUMO+1 0.22654
HOMO-1 → LUMO -0.14151
HOMO-1 → LUMO+1 0.62587
HOMO → LUMO+1 -0.14138

Excited State 6: Singlet-A 3.2472 eV 381.82 nm $f=0.0814$
HOMO-4 → LUMO 0.54055
HOMO-4 → LUMO+1 0.17429

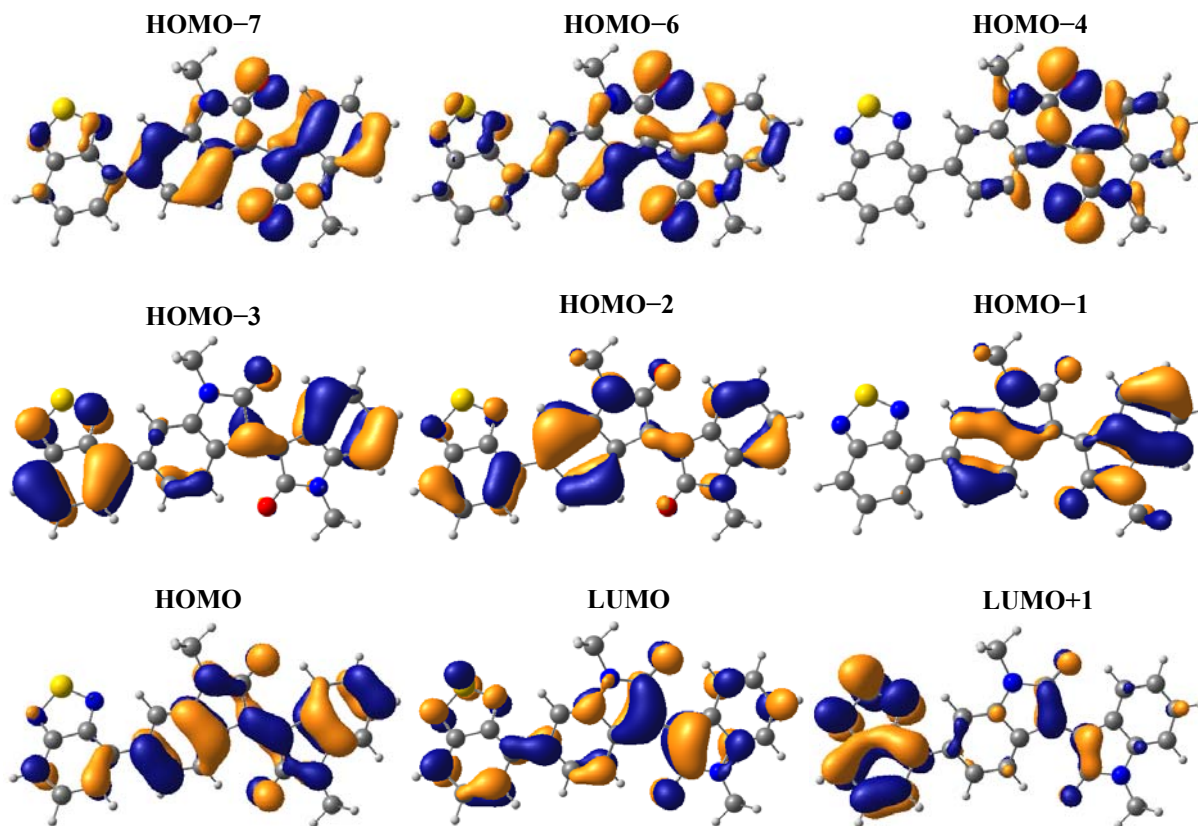
HOMO-3 → LUMO -0.32201
HOMO-2 → LUMO 0.14807

Excited State 7: Singlet-A 3.3740 eV 367.47 nm $f=0.0041$
HOMO-3 → LUMO -0.20194
HOMO-2 → LUMO+1 0.62264
HOMO-1 → LUMO+1 -0.20850

Excited State 8: Singlet-A 3.5225 eV 351.97 nm $f=0.0478$
HOMO-7 → LUMO -0.18994
HOMO-6 → LUMO -0.35718
HOMO-6 → LUMO+1 -0.11371
HOMO-4 → LUMO 0.26705
HOMO-3 → LUMO 0.41073
HOMO-2 → LUMO+1 0.12731

Excited State 9: Singlet-A 3.5976 eV 344.63 nm $f=0.0144$
HOMO-7 → LUMO 0.30332
HOMO-7 → LUMO+1 0.10772
HOMO-6 → LUMO 0.41336
HOMO-6 → LUMO+1 0.12445
HOMO-4 → LUMO 0.18061
HOMO-3 → LUMO 0.35388

Excited State 10: Singlet-A 3.8915 eV 318.61 nm $f=0.0342$
HOMO-3 → LUMO+1 0.66554



C. il_4

C01	19.31000	-0.76357	1.79832	C47	-5.00925	-0.31984	-0.83244	H93	17.90595	-3.67127	2.78700
C02	18.61140	0.27105	1.12183	C48	-5.01976	-1.78098	-1.25946	H94	19.18411	-2.86792	3.74087
C03	17.21241	-0.16461	0.98267	N49	-3.70028	-2.16681	-1.41405	H95	19.57561	-3.59497	2.15973
C04	17.16566	-1.53866	1.63678	C50	-1.45494	-1.15911	-1.11087	H96	12.17936	1.73408	-1.28472
N05	18.44756	-1.82253	2.07014	C51	-0.73977	0.00099	-0.75125	H97	11.91510	-1.58700	1.44945
C06	20.65267	-0.67539	2.13764	C52	-1.46523	1.15019	-0.39006	H98	14.35183	-1.58675	1.73075
C07	21.33426	0.50024	1.80362	C53	-2.85914	1.17885	-0.38927	H99	15.56551	3.46936	-2.14737
C08	20.67185	1.54560	1.15882	C54	-6.16102	0.40720	-0.61716	H100	13.94300	3.70006	-1.43814
C09	19.32042	1.44177	0.81632	O55	-5.96301	-2.52608	-1.48692	H101	14.16472	2.58476	-2.81253
C10	16.11499	0.41870	0.38868	C56	-3.30474	-3.49420	-1.83355	H102	10.17199	2.16113	-0.28355
O11	16.23238	-2.32169	1.75358	C57	-6.16837	1.92244	-0.46934	H103	7.74609	2.12882	-0.64094
C12	18.80711	-3.05944	2.72920	N58	-7.48698	2.30639	-0.30401	H104	10.23930	-2.13893	-0.00203
C13	16.21361	1.62971	-0.52958	C59	-8.32880	1.19842	-0.30118	H105	7.00071	-4.30074	-0.19794
N14	14.93320	1.90095	-0.97873	C60	-7.57220	0.01407	-0.50814	H106	8.39208	-3.83650	0.82071
C15	14.01431	1.01701	-0.42127	C61	-9.70098	1.20497	-0.11997	H107	8.58906	-3.97822	-0.94644
C16	14.68542	0.07917	0.40758	C62	-10.39392	-0.02243	-0.13019	H108	0.92821	2.05699	-1.41526
C17	12.64323	1.02096	-0.61203	C63	-9.65713	-1.20596	-0.31404	H109	0.92830	-2.03807	-0.07168
C18	11.86170	0.05551	0.05423	C64	-8.27503	-1.19978	-0.49772	H110	3.37953	-2.08132	-0.11038
C19	12.50871	-0.86534	0.89725	C65	-11.86172	-0.05545	0.05404	H111	4.21696	4.07135	-1.99040
C20	13.89106	-0.86061	1.07971	C66	-7.89926	3.68467	-0.14674	H112	2.69279	3.98024	-1.06422
C21	10.39390	0.02251	-0.12998	O67	-5.24296	2.72108	-0.51965	H113	2.73367	3.45367	-2.76804
C22	14.62552	2.97554	-1.89793	C68	-12.50872	0.86535	0.89713	H114	-0.92820	-2.05681	-1.41539
O23	17.19494	2.26471	-0.88940	C69	-13.89107	0.86058	1.07962	H115	-0.92835	2.03820	-0.07164
C24	9.65711	1.20606	-0.31375	C70	-14.68543	-0.07917	0.40744	H116	-3.37957	2.08144	-0.11043
C25	8.27501	1.19990	-0.49742	C71	-14.01433	-1.01694	-0.42148	H117	-4.21692	-4.07115	-1.99072
C26	7.57217	-0.01395	-0.50790	C72	-12.64325	-1.02088	-0.61225	H118	-2.69278	-3.98007	-1.06449
C27	8.32877	-1.19831	-0.30103	C73	-16.11500	-0.41874	0.38858	H119	-2.73361	-3.45343	-2.76830
C28	9.70095	-1.20488	-0.11984	C74	-16.21363	-1.62963	-0.52984	H120	-10.23933	2.13900	-0.00210
C29	6.16099	-0.40706	-0.61695	N75	-14.93321	-1.90087	-0.97898	H121	-10.17200	-2.16104	-0.28389
C30	6.16833	-1.92231	-0.46917	C76	-17.21239	0.16445	0.98272	H122	-7.74611	-2.12869	-0.64131
N31	7.48694	-2.30628	-0.30392	O77	-17.19494	-2.26471	-0.88956	H123	-7.00075	4.30085	-0.19788
C32	5.00923	0.31999	-0.83225	C78	-14.62553	-2.97545	-1.89818	H124	-8.39209	3.83651	0.82079
O33	5.24293	-2.72094	-0.51960	C79	-17.16565	1.53842	1.63701	H125	-8.58913	3.97839	-0.94633
C34	7.89923	-3.68457	-0.14679	N80	-18.44754	1.82221	2.07045	H126	-11.91512	1.58698	1.44936
C35	5.01976	1.78115	-1.25922	C81	-19.30995	0.76323	1.79861	H127	-14.35184	1.58668	1.73071
N36	3.70029	2.16699	-1.41382	C82	-18.61135	-0.27130	1.12196	H128	-12.17938	-1.73395	-1.28500
C37	2.83846	1.11916	-1.10504	C83	-20.65259	0.67495	2.13801	H129	-15.56552	-3.46926	-2.14765
C38	3.58647	-0.03877	-0.76201	C84	-21.33415	-0.50068	1.80393	H130	-13.94302	-3.69999	-1.43839
C39	1.45494	1.15928	-1.11077	C85	-20.67173	-1.54595	1.15899	H131	-14.16471	-2.58466	-2.81276
C40	0.73975	-0.00083	-0.75122	C86	-19.32033	-1.44202	0.81640	H132	-21.15600	1.48805	2.65119
C41	1.46519	-1.15005	-0.39005	O87	-16.23241	2.32151	1.75374	H133	-22.38712	-0.59594	2.05515
C42	2.85911	-1.17871	-0.38921	C88	-18.80710	3.05904	2.72964	H134	-21.21063	-2.45559	0.91082
O43	5.96302	2.52626	-1.48659	H89	21.15608	-1.48856	2.65071	H135	-18.82521	-2.25130	0.30328
C44	3.30476	3.49440	-1.83328	H90	22.38726	0.59543	2.05476	H136	-17.90596	3.67090	2.78744
C45	-2.83846	-1.11900	-1.10519	H91	21.21077	2.45524	0.91070	H137	-19.18404	2.86742	3.74132
C46	-3.58648	0.03892	-0.76214	H92	18.82530	2.25113	0.30334	H138	-19.57566	3.59460	2.16026

D. il_2 -BTD₂

C01	12.34635	-0.90714	0.89467	C17	4.78721	-0.06017	-0.62822	C33	-3.05024	-0.94081	0.10787
C02	13.79690	-0.88086	1.00877	O18	5.06381	2.97622	-0.30240	C34	-1.63562	-0.86646	0.01971
C03	14.55542	0.15704	0.39834	C19	3.36949	0.31104	-0.52585	N35	-1.34040	2.58880	-1.13134
C04	13.86881	1.12320	-0.28895	C20	2.60495	-0.83808	-0.86063	S36	-2.66593	3.51944	-1.39454
C05	12.44642	1.10322	-0.40078	N21	3.45077	-1.89067	-1.19876	N37	-3.84503	2.45721	-0.97628
C06	11.65051	0.12461	0.16539	C22	4.77678	-1.51626	-1.07237	N38	11.78757	-1.93927	1.53822
C07	10.17732	0.15482	0.02823	C23	2.65996	1.45591	-0.13553	S39	13.01685	-2.79468	2.21450
C08	9.50630	1.39576	0.02174	C24	1.26558	1.44373	-0.10364	N40	14.30051	-1.89240	1.72684
C09	8.13348	1.41227	-0.14963	C25	0.52446	0.29896	-0.44569	C41	-5.36109	-0.01269	-0.08059
C10	7.35725	0.23822	-0.33767	C26	1.22236	-0.86527	-0.83215	C42	-6.17281	1.05090	0.35091
C11	8.03876	-0.98686	-0.30984	O27	5.70901	-2.26331	-1.33416	C43	-7.55168	0.90863	0.50747
C12	9.42103	-1.01990	-0.12509	C28	3.03610	-3.20811	-1.62903	C44	-8.17385	-0.31554	0.22548
N13	7.30648	2.53187	-0.13292	C29	-0.95134	0.27014	-0.37069	C45	-7.34332	-1.36856	-0.24044
C14	5.97936	2.16590	-0.27242	C30	-1.77972	1.40251	-0.69603	C46	-5.97349	-1.24627	-0.38903
C15	5.94994	0.65162	-0.42572	C31	-3.23404	1.32606	-0.60582	C47	-9.56043	-0.80280	0.19474
C16	7.73899	3.90394	0.02025	C32	-3.89269	0.11533	-0.18768	C48	-9.45961	-2.22865	-0.32919

N49	-8.11675	-2.48616	-0.54235	H64	14.41146	1.92904	-0.77524	H79	-1.06735	-1.74311	0.31540
C50	-10.75308	-0.21971	0.56103	H65	11.97226	1.88513	-0.98621	H80	-5.71821	2.00620	0.58010
O51	-10.33498	-3.06403	-0.50804	H66	10.05243	2.31763	0.19077	H81	-8.13780	1.73985	0.86655
C52	-7.62028	-3.75666	-1.02396	H67	7.49581	-1.90806	-0.45086	H82	-5.38512	-2.07056	-0.77740
C53	-10.82850	1.07064	1.36617	H68	9.92228	-1.97937	-0.11032	H83	-8.48081	-4.41474	-1.15131
N54	-12.16879	1.33064	1.58593	H69	8.24530	4.04957	0.98193	H84	-6.92491	-4.20175	-0.30258
C55	-12.96783	0.36237	0.98383	H70	6.84827	4.53222	-0.01998	H85	-7.10673	-3.63721	-1.98539
C56	-12.15471	-0.61865	0.35681	H71	8.42285	4.18891	-0.78786	H86	-14.94532	1.09335	1.44807
C57	-14.35483	0.32840	0.95402	H72	3.19385	2.35527	0.12797	H87	-16.05207	-0.77359	0.22223
C58	-14.96727	-0.72062	0.25917	H73	0.74353	2.34407	0.19432	H88	-14.68535	-2.49516	-0.92665
C59	-14.19753	-1.68943	-0.38602	H74	0.68273	-1.75712	-1.13182	H89	-12.21837	-2.41207	-0.83334
C60	-12.80082	-1.64749	-0.34380	H75	2.43843	-3.70213	-0.85364	H90	-11.76633	3.01876	2.68762
O61	-9.92959	1.77024	1.81233	H76	3.94037	-3.78888	-1.81553	H91	-13.23356	2.14372	3.20612
C62	-12.64308	2.46956	2.34195	H77	2.44433	-3.14933	-2.55005	H92	-13.26090	3.12457	1.71621
H63	15.63614	0.15874	0.48836	H78	-3.48355	-1.87006	0.46529				

S5. References

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