Supporting Information

Improved Performance of Solution-Processed n-Type Organic Field-Effect Transistors by Regulating the Intermolecular Interactions and Crystalline Domains on Macroscopic Scale

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Synthesis of Monomers and Polymers

Synthesis of Br_2-NDIOD: A mixture of NTCDA-Br_2 (0.4 g, 0.93 mmol) (*Precaution: The dibromination of NTCDA by dibromoisocyanuric acid has to be carried out in presence of concentrated H_2SO_4 or Oleum and must be handled with great care*), 2-octyldodecylamine (0.629 g, 2.33 mmol), o-xylene (3 mL), and propionic acid (1 mL) were stirred at 140 °C for 6 h. After cooling to room temperature, most of solvents were removed in vacuo, and the residue was purified by column chromatography on silica gel with a mixture of chloroform : hexane (1:2, v/v) as eluent, affording the slightly yellowish red color solid as product (0.61 g, yield 70%). ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 8.75 (s, 2H), 4.18 (t, 4H), 1.73 (m, 4H), 1.25-1.15 (m, 60H), 0.87 (t, 6H); ^{13}C NMR (150MHz, $CDCl_3$, δ ppm): 163.07, 139.28, 128.87, 128.54, 127.97, 125.60, 124.35, 41.85-14.32 (Aliphatic Carbons). MALDI-TOF: m/z Calcd. 928.41, found. $[M+2H]^+$: 930.11; Elemental Analysis Calcd. C, 64.65; H, 8.25; N, 3.02; found, C, 64.16; H, 8.255; N, 1.46.

Synthesis of NDI-Ph: To a three neck round bottom flask Br_2-NDIOD (0.1 g, 0.107 mmol) and benzene-1,4-diboronic acid (0.0177 g, 0.107 mmol), were added and degassed thrice by freeze thaw cycles. Aqueous solution of K_2CO_3 (0.147 g, 1.07 mmol) in 2 mL deoxygenated water were added under nitrogen. (0.006 g, 0.004 mmol) of $Pd(PPh_3)_4$, two drops of aliquat and 6 mL THF were added under nitrogen atmosphere, degassed thrice by freeze thaw cycles (15 minutes each). The dark red solution was stirred at 80 °C for 36h. Phenyl boronic acid was added under nitrogen and the reaction was continued for other 12h. The brown sticky mixture was cooled to room temperature. The mixture was extracted with $CHCl_3$, washed with 100 mL water thrice and dried over anh. $MgSO_4$. The solution was concentrated to 5 mL and dropped in 50 mL methanol. The brown color precipitate was filtered and washed with methanol twice (0.076 g, Yield 84 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.5-8.8 (br, m, 2H), 7.4-7.8 (br, m, 4H), 4.0 (br, m, 4H), 1.67 (br, m, 4H), 1.2 (br, m, 60H), 0.87 (br, m, 6H); ^{13}C NMR (150MHz, $CDCl_3$, δ ppm): 163.06, 135.66, 132.00, 131.10, 128.76, 125.07, 124.68, 124.19, 41.14-14.32 (Aliphatic Carbons); GPC: Mn: 6811; Mw: 13579; PDI: 1.99.

Synthesis of NDI-BT: To a three neck round bottom flask, Br_2-NDIOD (0.1 g, 0.107 mmol) and 2,1,3-benzothiadiazole bisboronic ester (0.0415 g, 0.107 mmol), were added and degassed thrice by freeze thaw cycles. Aqueous solution of K_2CO_3 (0.147 g, 1.07 mmol) in 2 mL deoxygenated water was added under nitrogen flow. (0.006 g, 0.004 mmol) of $Pd(PPh_3)_4$, two drops of aliquat and 6 mL THF were added under nitrogen atmosphere, degassed twice by freeze thaw cycles. The dark red solution was stirred at 80 °C for 36h. Phenyl boronic acid was added under nitrogen and the reaction was continued for other 12h. The brown sticky mixture was cooled to room temperature. The mixture was extracted with $CHCl_3$, washed with 100 mL water thrice and dried over anh. $MgSO_4$. The solution was concentrated to 5 mL and dropped in 50 mL methanol. The brown color precipitate was filtered and washed with methanol twice (0.082 g, Yield 85%) ^{1}HNMR (400 MHz, $CDCl_3$, δ ppm): 8.85 (br, m, 2H), 7.6 (br, m, 2H), 4.15 (br, m, 4H), 1.7 (br, m, 4H), 1.2 (br, m, 60H), 0.85 (br, m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 163.07, 135.42, 132.18, 131.10, 129.98, 129.06, 124.68, 124.19, 41.14-14.33 (Aliphatic Carbons); GPC: Mn: 5171; Mw: 6627; PDI: 1.74.

Synthesis of Br_2-PDIOD: A mixture of PTCDA-Br_2 (0.4 g, 0.72 mmol) (*Precaution: The dibromination of PTCDA by bromine in concentrated H_2SO_4 and must be handled with great care*), octadecylamine (0.58 g, 2.18 mmol), o-xylene (3 mL), and propionic acid (1 mL) were stirred at 140 °C for 6h. After cooling to room temperature the solvents were removed in vacuo and the product was purified by column chromatography on silica gel, using a mixture of chloroform: hexane (1:2, v/v) as eluent, yielding red color solid as product (0.49 g, yield 65%). ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 9.47 (d, J = 8.0 Hz, 2H), 8.90 (s, 2H), 8.69 (d, J = 8.0 Hz, 2H), 4.184 (t, 4H), 1.729 (m, 4H), 1.25-1.42 (m, 60H), 0.853 (t, 6H); ^{13}C NMR (150MHz, $CDCl_3$, δ ppm): 163.08, 162.57, 138.20, 133.18, 133.02, 130.21, 129.47, 128.71, 127.16, 123.43, 123.00, 120.99, 41.05-14.32 (Aliphatic Carbons); MALDI-TOF: m/z calcd. 1053.44, found, $[M+2H]^+$: 1055.47; Elemental Analysis Calcd. C, 68.43; H, 7.66; N, 2.66; found, C, 68.33; H, 7.19; N, 1.84.

Synthesis of PDI-Ph: To a three neck round bottom flask Br_2-PDIOD (0.1 g, 0.095 mmol) and benzene-1, 4-diboronic acid (15.7mg, 0.0949mmol) were added and degassed thrice by freeze thaw cycles. Aqueous solution of K_2CO_3 (0.131 g, 0.949 mmol) in 2 mL deoxygenated water were added under nitrogen. (0.0054 mg, 0.004 mmol) of $Pd(PPh_3)_4$, two drops of aliquat and 6 mL THF were added under nitrogen atmosphere, degassed thrice by freeze thaw cycles. The dark red solution was stirred at 80 °C for 36h. Phenyl boronic acid was added under nitrogen and the reaction was continued for other 12h. The brown sticky mixture was cooled to room temperature. The mixture was extracted with $CHCl_3$, washed with 100 mL water thrice and dried over anh. $MgSO_4$. The solution was concentrated to 5 mL and dropped in 50 mL methanol. The precipitate was filtered and washed with methanol twice to get black color solid. (0.076 g, Yield 83%) ^{1}H NMR (600MHz, $CDCl_3$, δ ppm): 8.57 (br, m, 2H), 8.30 (br, m, 4H), 7.69 (br, m, 2H), 4.1-4.4 (br, m, 4H), 1.67 (br, m, 4H), 1.2 (br, m, 60H), 0.86 (br, m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 163.49, 163.18, 136.50, 135.50, 134.61, 133.88, 132.30, 131.45, 129.14, 128.70, 126.45, 124.50, 123.46, 123.22, 40.97-14.16 (Aliphatic Carbons); GPC: Mn: 16082; Mw: 24657; PDI: 1.53.

Synthesis of PDI-BT: To a three neck round bottom flask Br_2-PDIOD (0.1 g, 0.095 mmol), 2,1,3-benzothiadiazole bisboronic ester (0.037 g, 0.0949 mmol), were added and degassed thrice by freeze thaw cycles. Aqueous solution of K_2CO_3 (0.131 g, 0.949 mmol) in 2 mL deoxygenated water were added under nitrogen. (0.0054 g, 0.004 mmol) of $Pd(PPh_3)_4$, two drops of aliquat and 6 mL THF were added under nitrogen atmosphere, degassed thrice by freeze thaw cycles. The

dark red solution was stirred at 80 °C for 36h. Phenyl boronic acid was added under nitrogen and the reaction was continued for other 12h. The brown sticky mixture was cooled to room temperature. The mixture was extracted with $CHCl_3$, washed with 100 mL water thrice and dried over anh. $MgSO_4$. The solution was concentrated to 5 mL and dropped in 50 mL methanol .The precipitate was filtered and washed with methanol twice to get black color solid. (0.084 g, Yield 86%). ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 8.76 (br, m, 2H), 8.10 (br, m, 4H), 7.83 (br, m, 2H), 4.1-4.4 (br, m, 4H), 1.67 (br, m, 4H), 1.2 (br, m, 60H), 0.86 (br, m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, δ ppm): 163.46, 163.23, 136.19, 134.54, 133.04, 132.31, 132.00, 131.80, 131.43, 129.07, 128.52, 127.79, 124.19, 123.24, 40.99-14.31 (Aliphatic Carbons); GPC: Mn: 30619 Da; Mw: 35739 Da; PDI: 1.16.

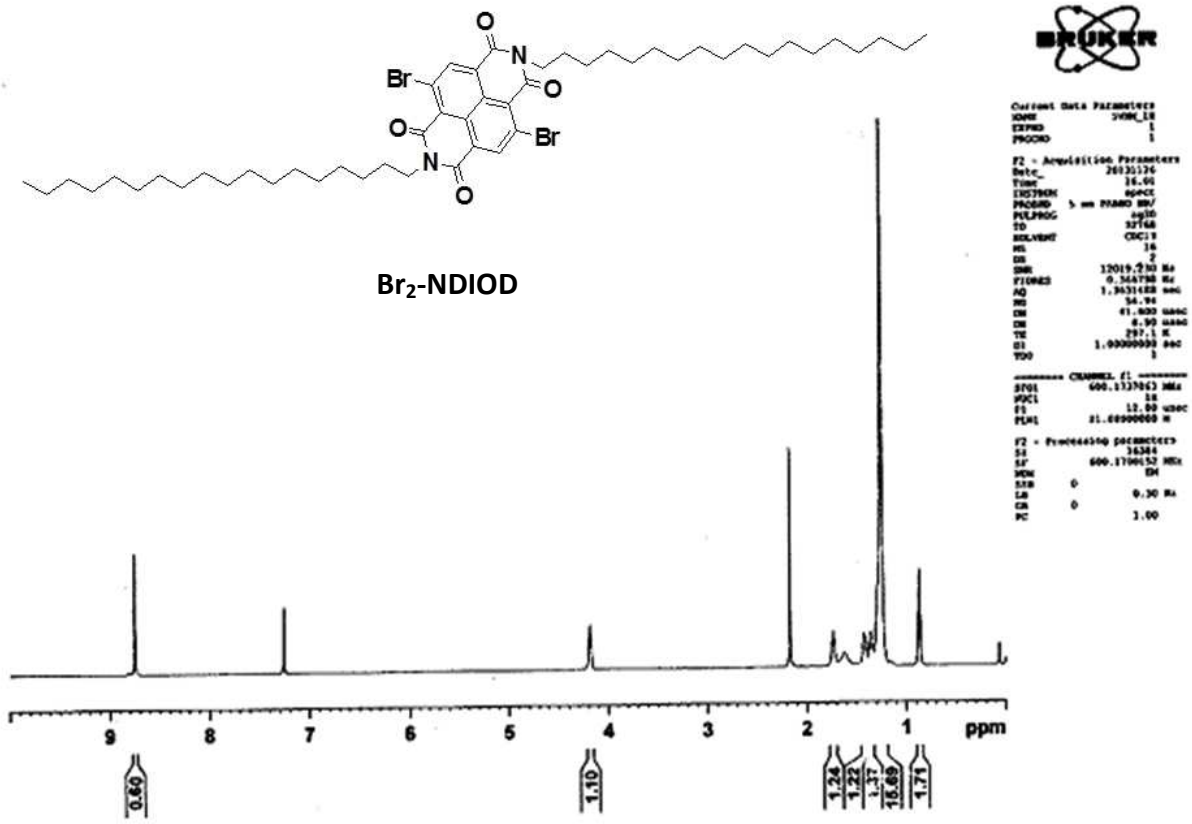


Figure S1: ^{1}H NMR Spectra of Br_2-NDIOD ($CDCl_3$, 600MHz)

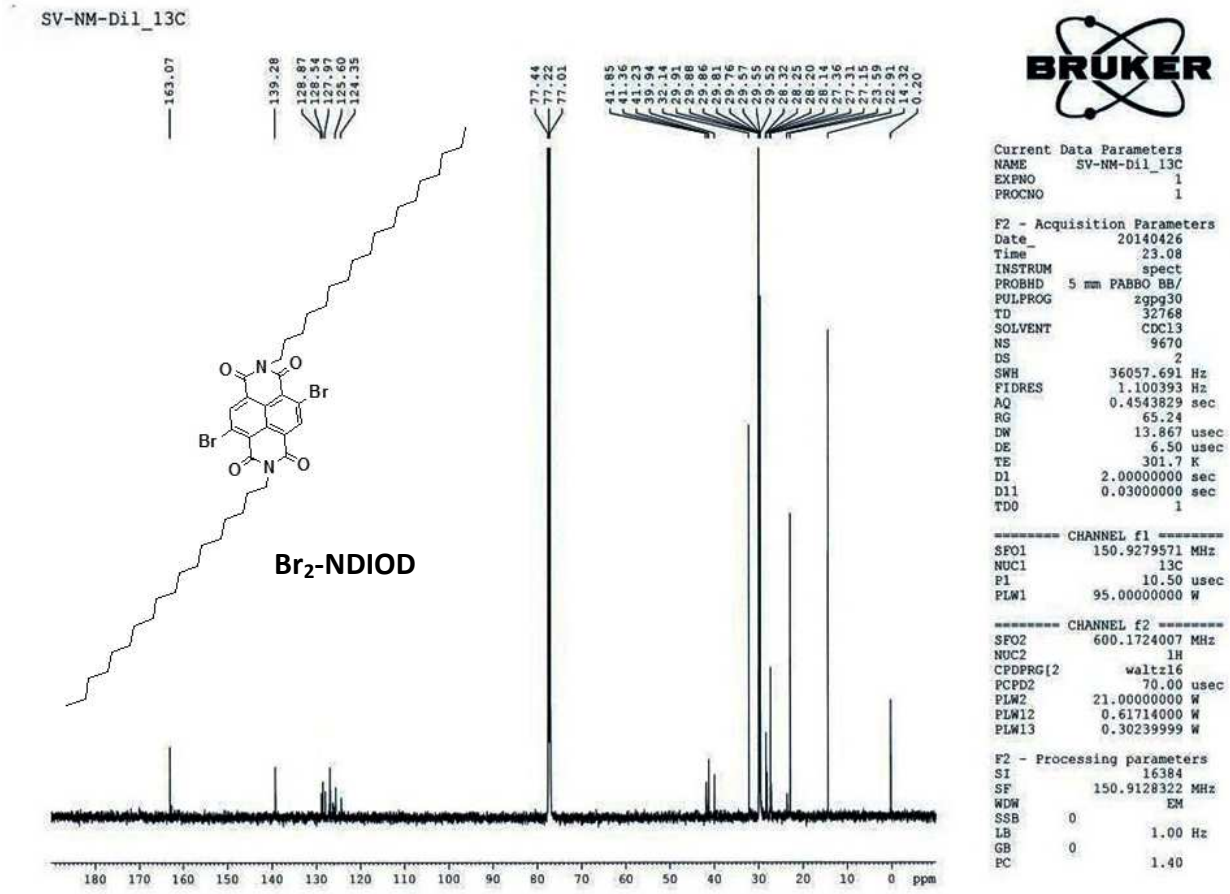


Figure S2: ^{13}C NMR Spectra of Br_2-NDIOD ($CDCl_3$, 150 MHz)

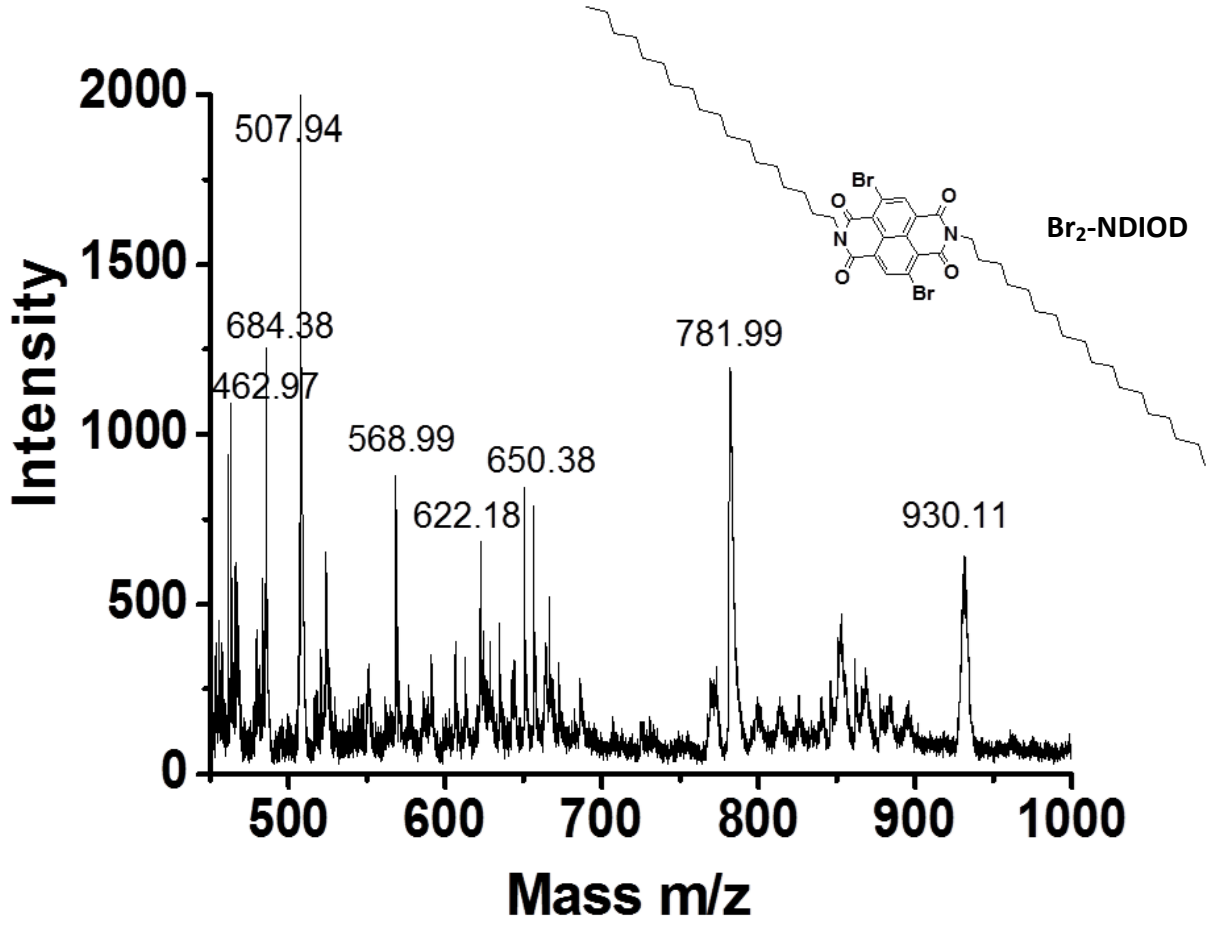


Figure S3: MALDI-TOF Spectra of Br_2-NDIOD

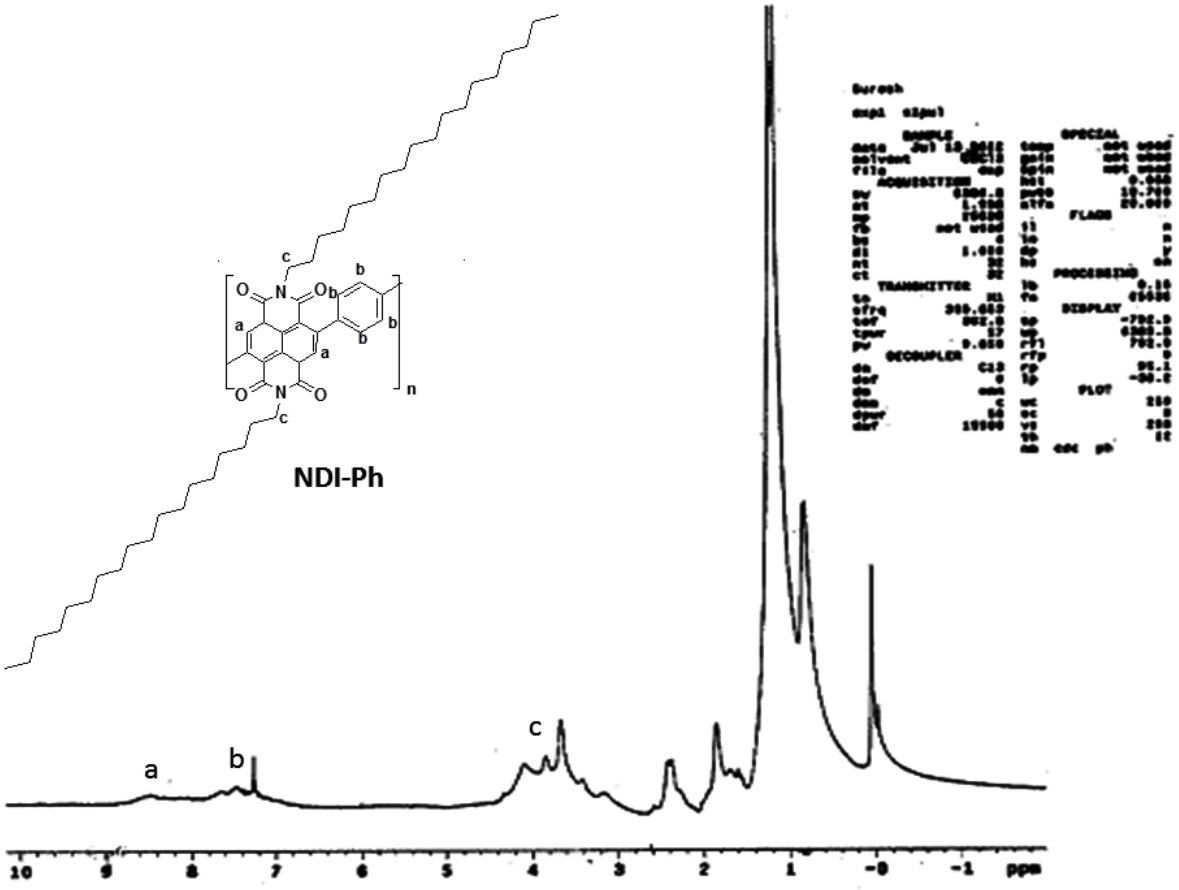


Figure S4: ^{1}H NMR Spectra of NDI-Ph ($CDCl_3$, 400MHz)

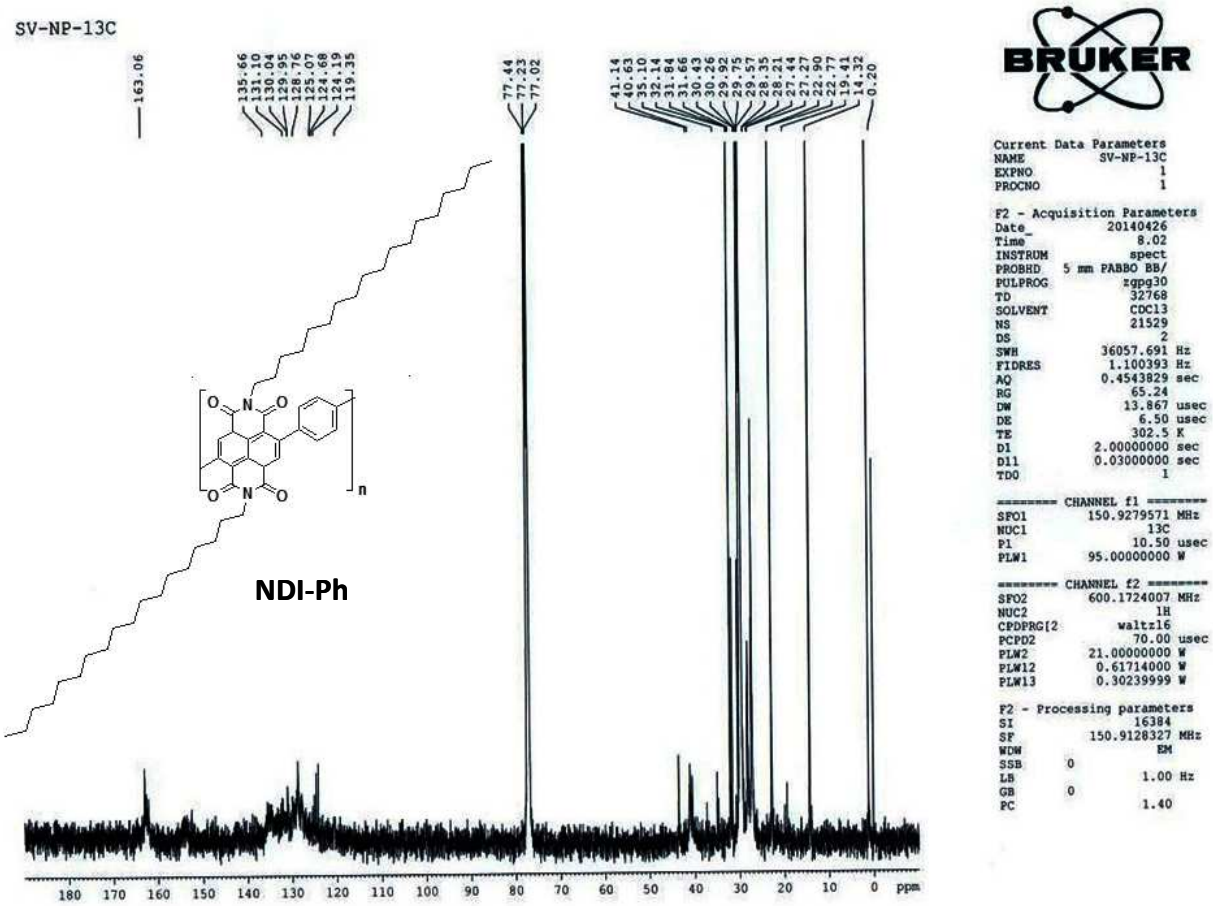


Figure S5: ^{13}C NMR Spectra of NDI-Ph ($CDCl_3$, 150 MHz)

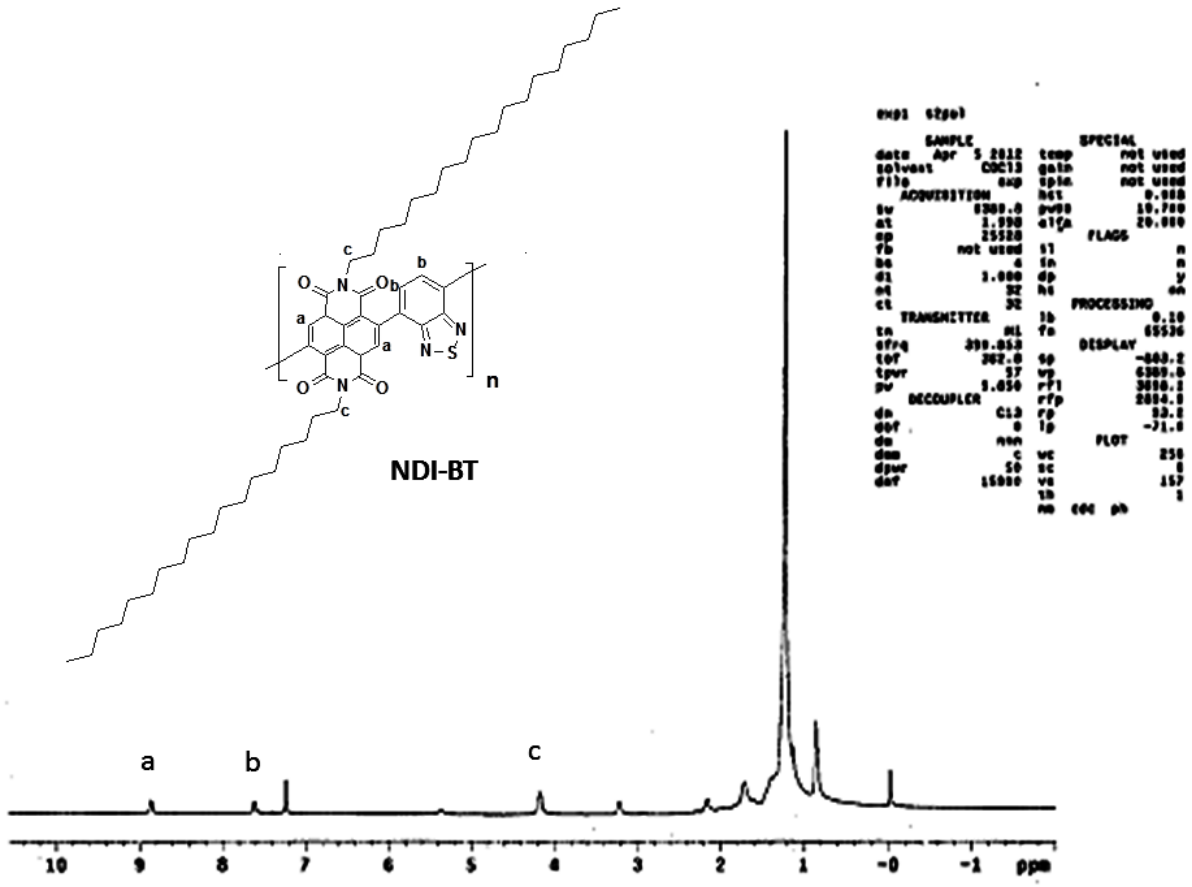


Figure S6: ^{1}H NMR Spectra of NDI-BT ($CDCl_3$, 400 MHz)

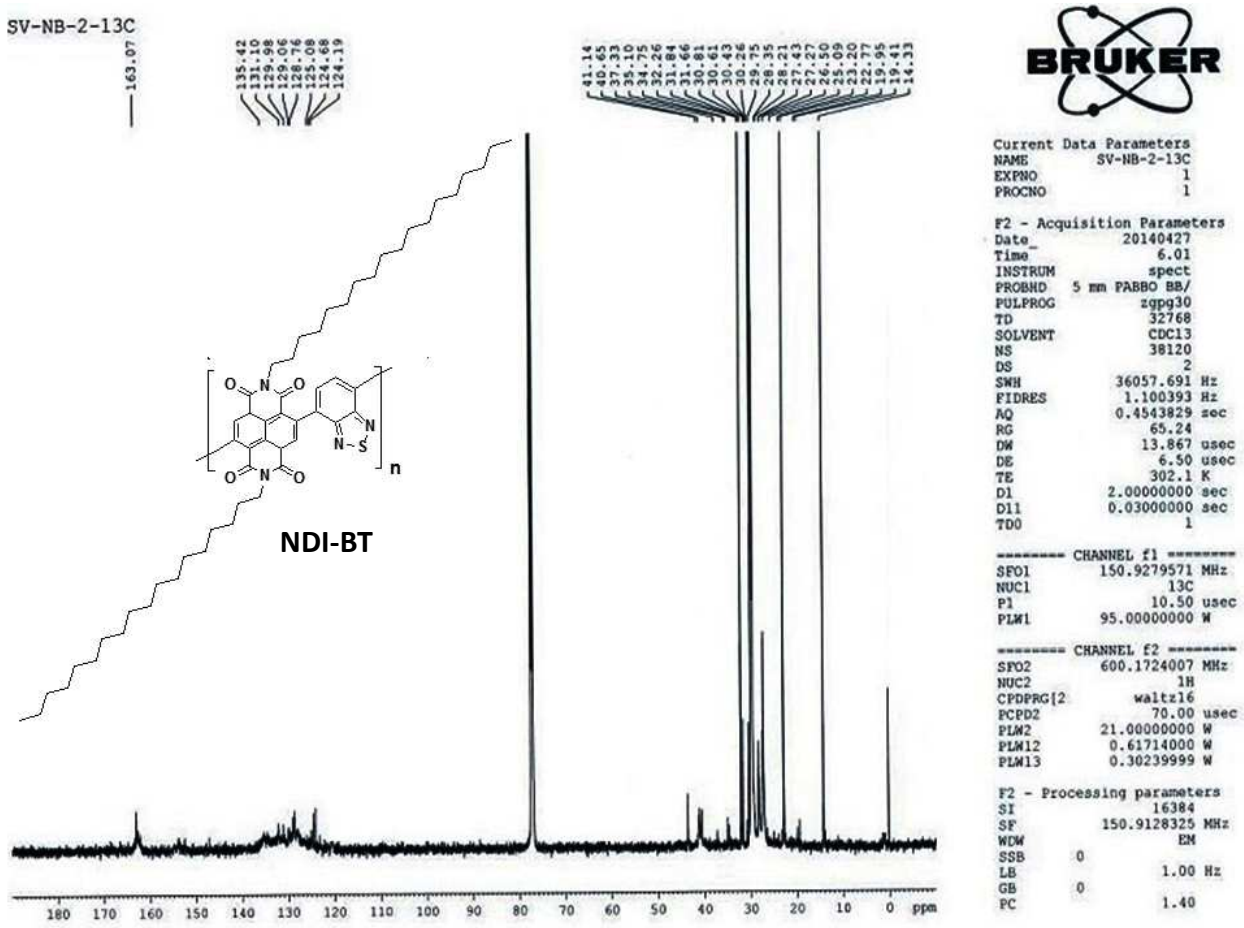


Figure S7: ^{13}C NMR Spectra of NDI-BT ($CDCl_3$, 150 MHz)

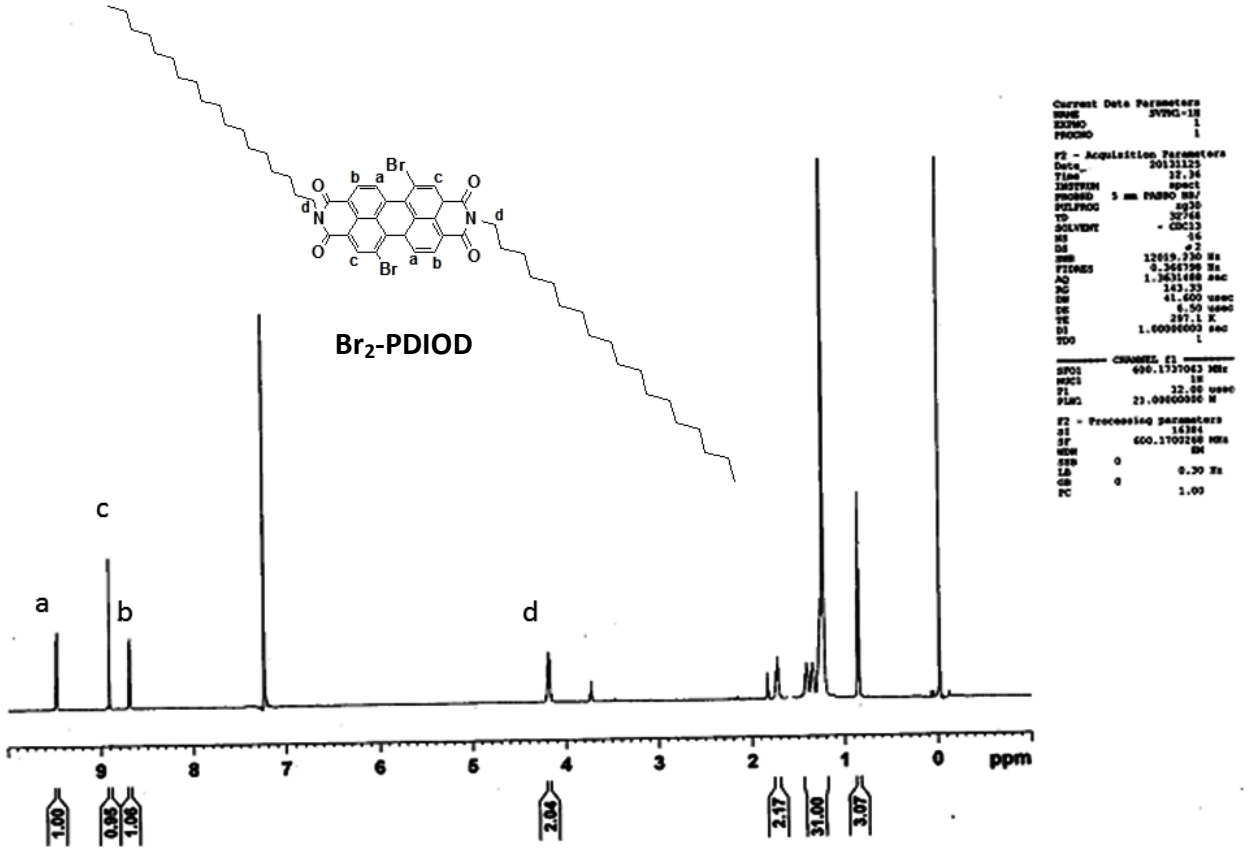


Figure S8: ^{1}H NMR Spectra of Br_2-PDIOD ($CDCl_3$, 600 MHz)

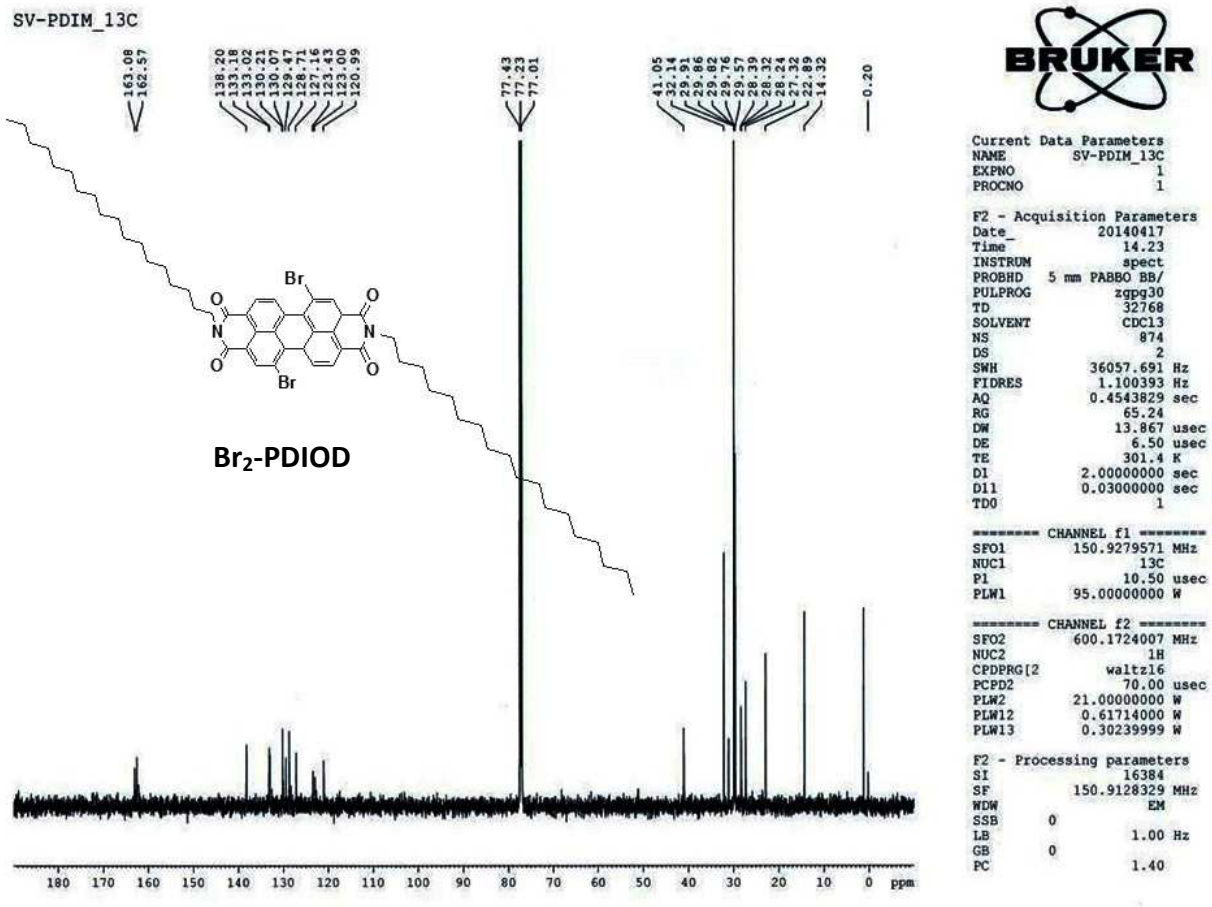


Figure S9: ^{13}C NMR Spectra of Br_2-PDIOD ($CDCl_3$, 150 MHz)

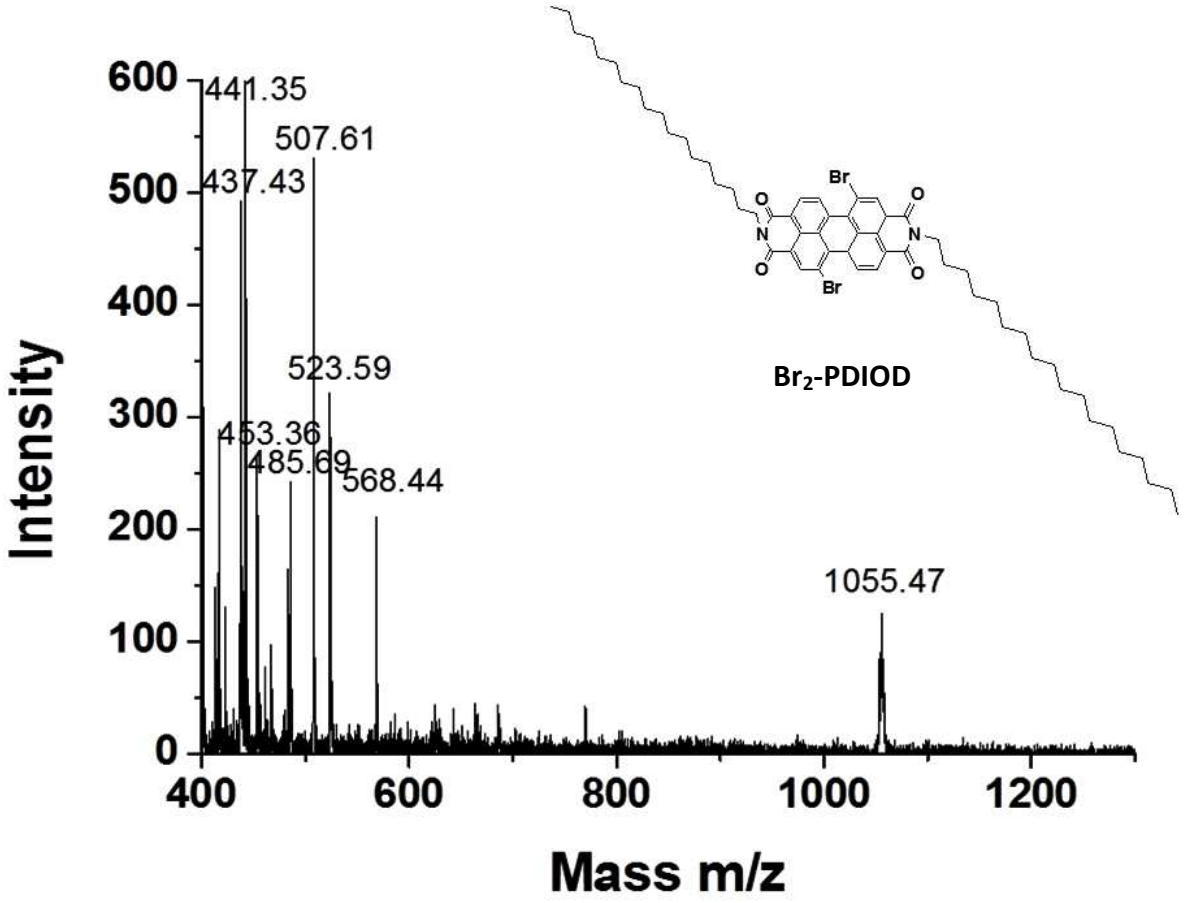


Figure S10: MALDI-TOF Spectra of Br_2-PDIOD

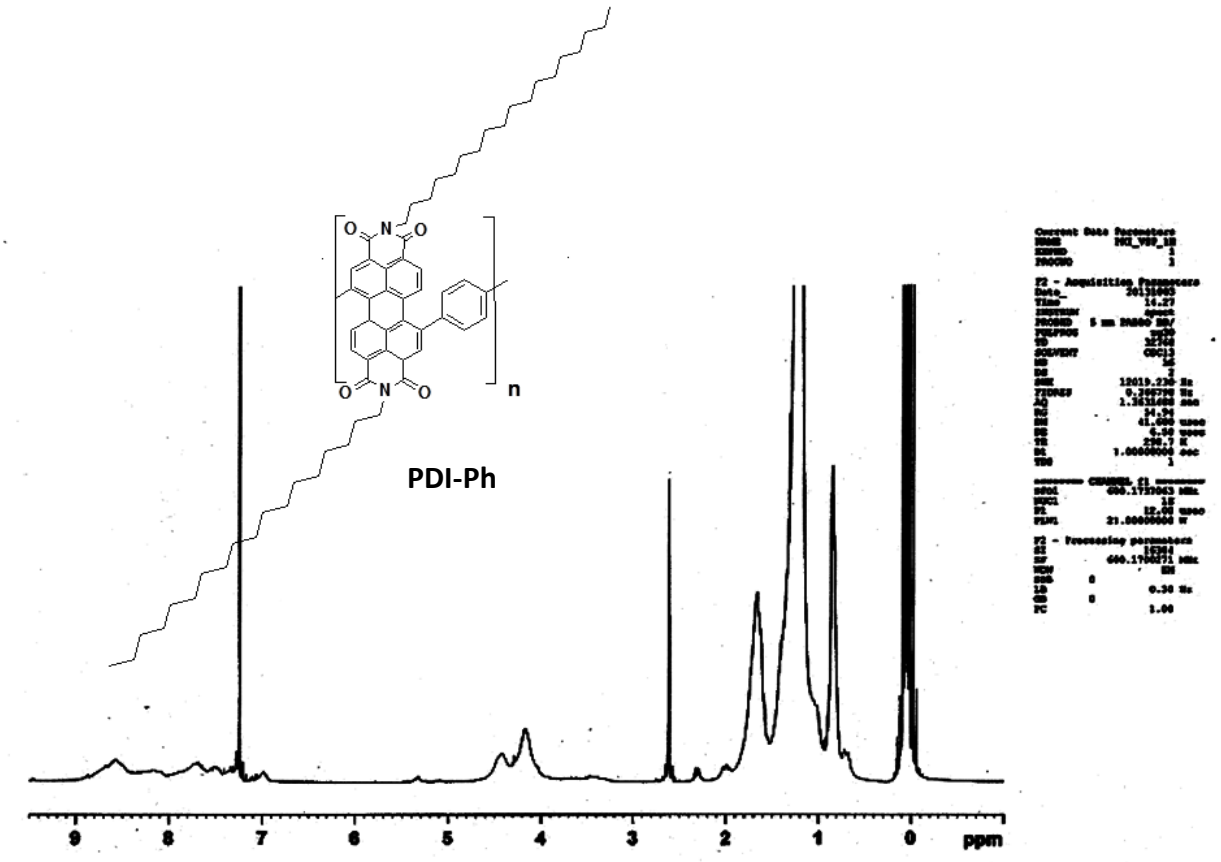


Figure S11: ^{1}H NMR Spectra of PDI-Ph polymer ($CDCl_3$, 600 MHz)

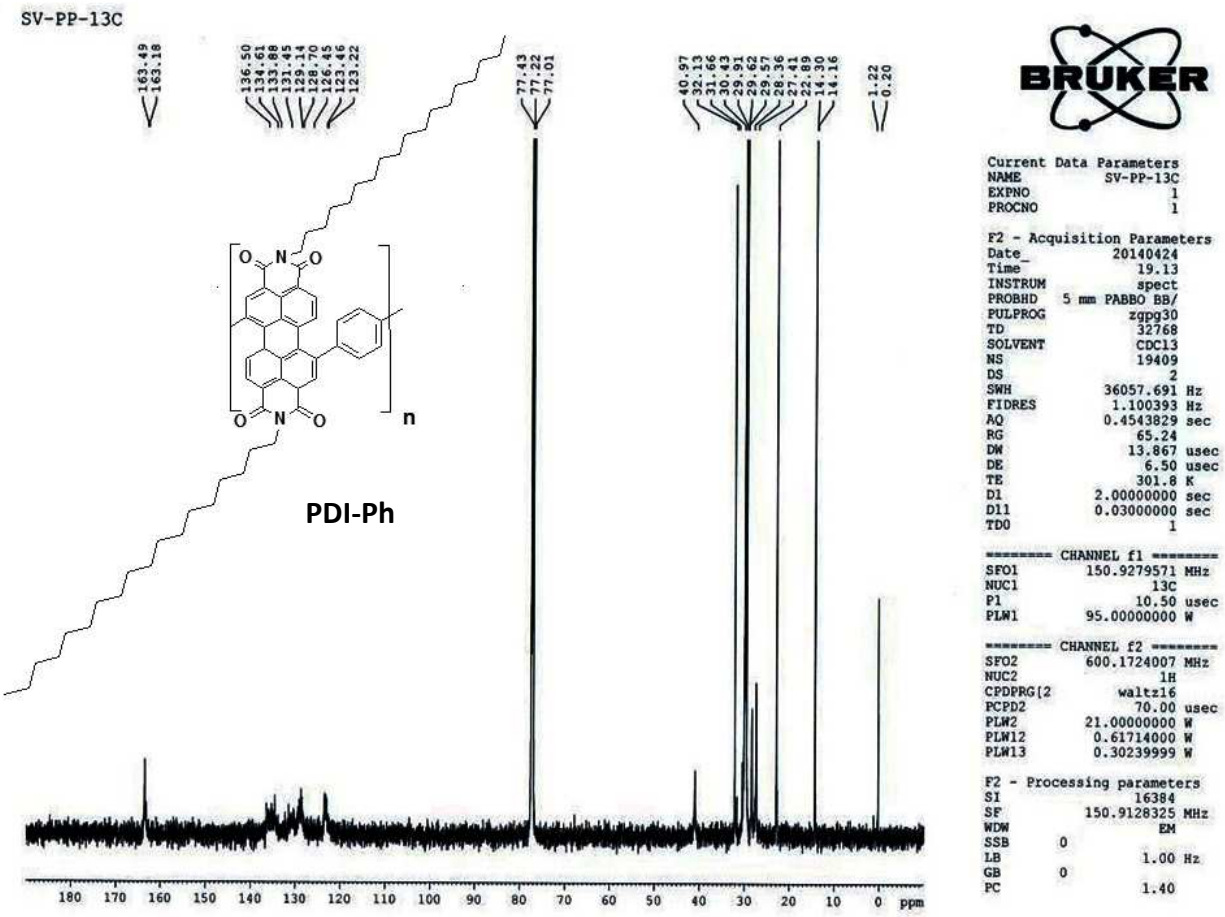


Figure S12: ^{13}C NMR Spectra of PDI-Ph ($CDCl_3$, 150 MHz)

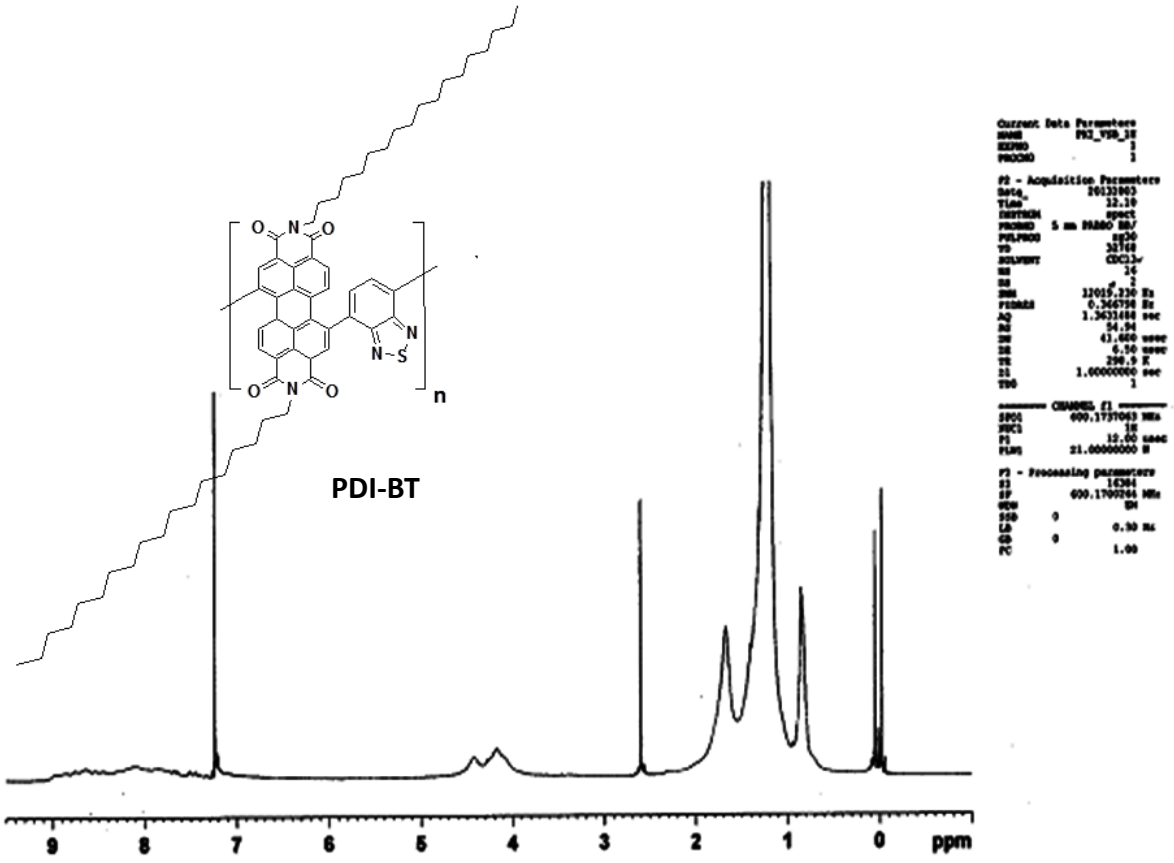


Figure S13: ^{1}H NMR Spectra of PDI-BT polymer ($CDCl_{3,}$ 600 MHz)

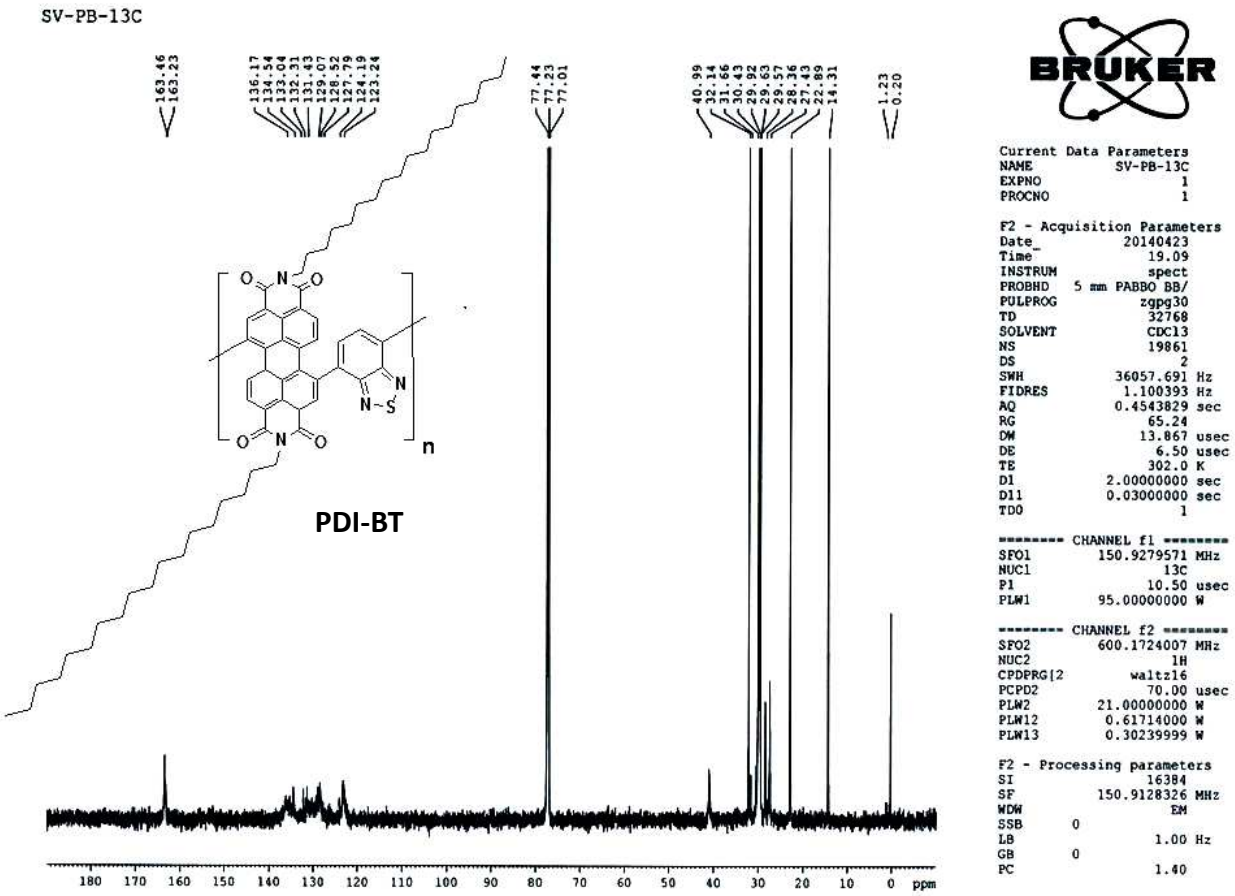
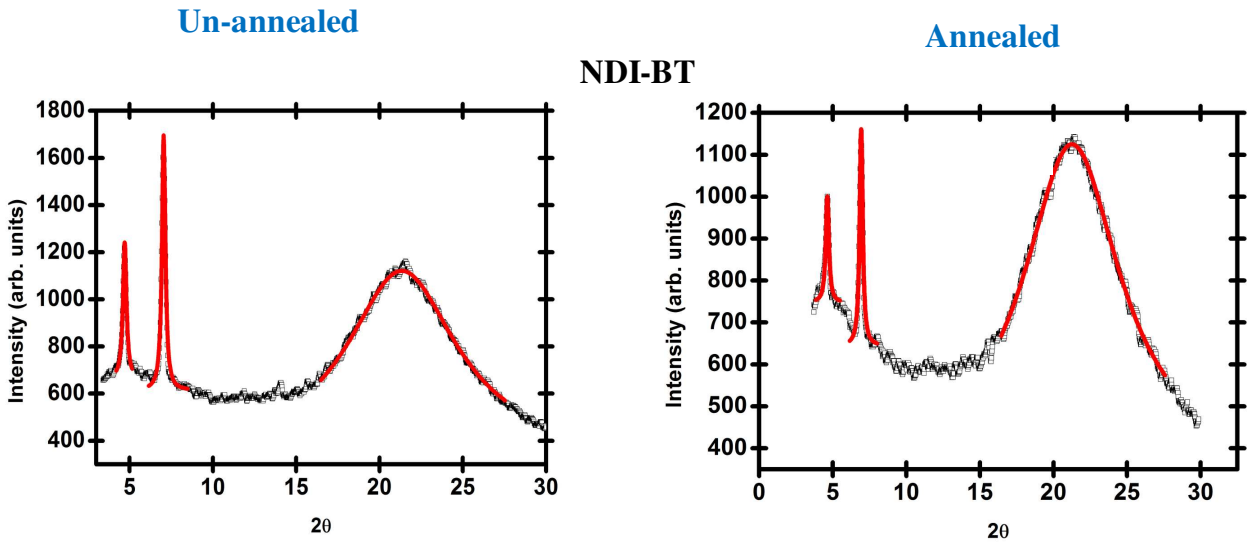


Figure S14: ^{13}C NMR Spectra of PDI-BT ($CDCl_3$, 150 MHz)



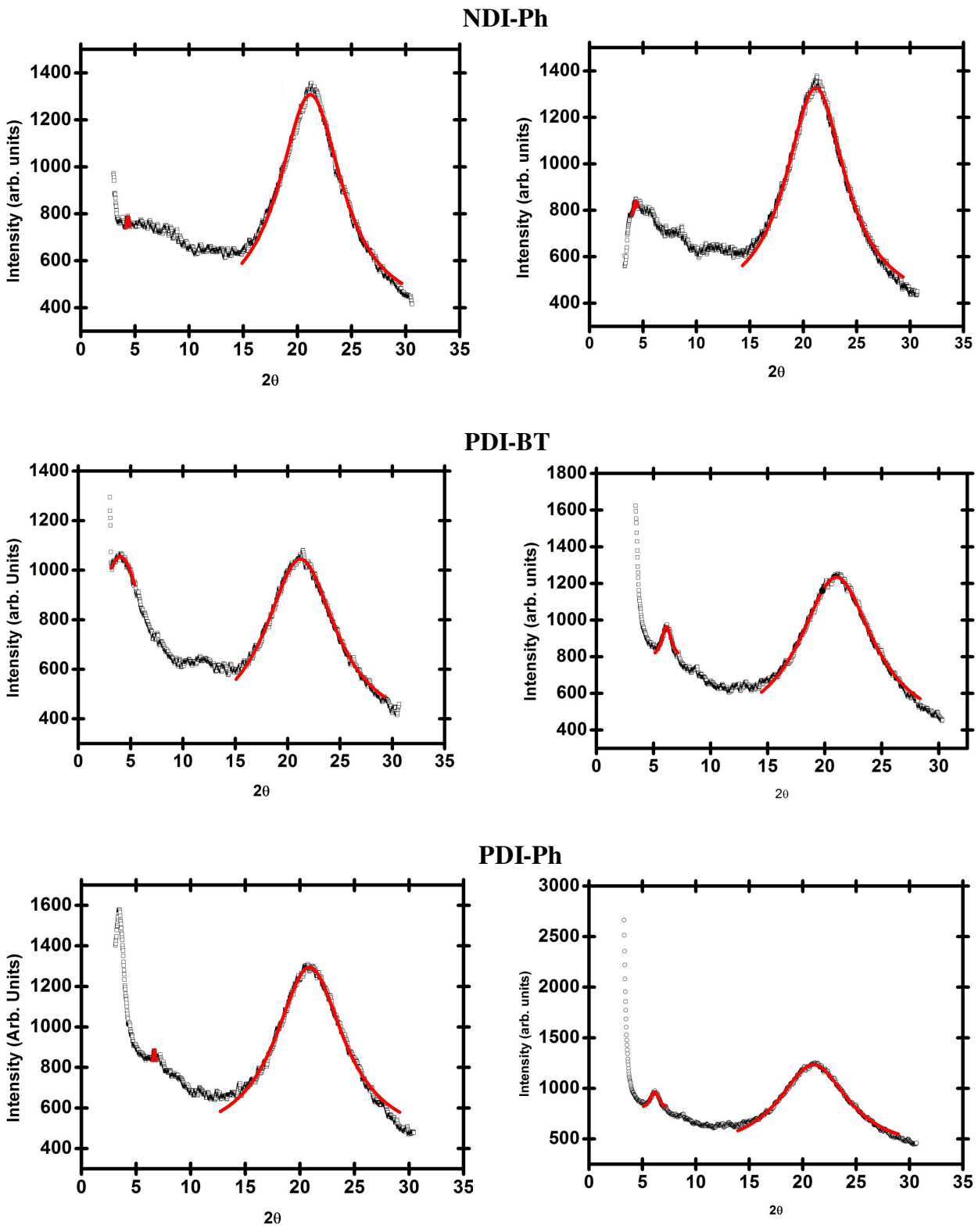
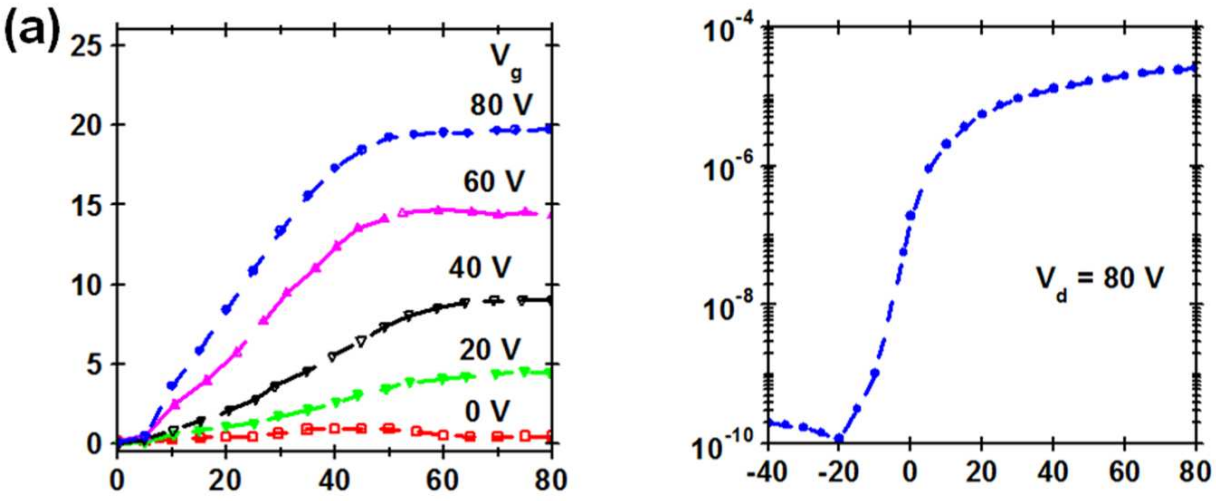


Figure S15: XRD spectra of the annealed (right side) and as spun (left side) polymer films fitted with Lorentzian to correctly estimate the peaks.

		As cast films	Annealed Films
Polymers	**(00n)**	**FWHM**	**FWHM**
NDI-Ph	(001) π-π	0.3326 7.1387	0.5331 6.8727
NDI-BT	(001) (002) π-π	0.2542 - 8.0554	0.2526 - 7.9907
PDI-Ph	(001) (002) π-π	- 1.0112 7.9777	- 0.713 7.6657
PDI-BT	(001) (002) π-π	- 7.1364 8.2268	- 1.0482 7.9777

Table S1: Table showing the variation in the FWHM of the XRD spectra with annealing of the polymer films.



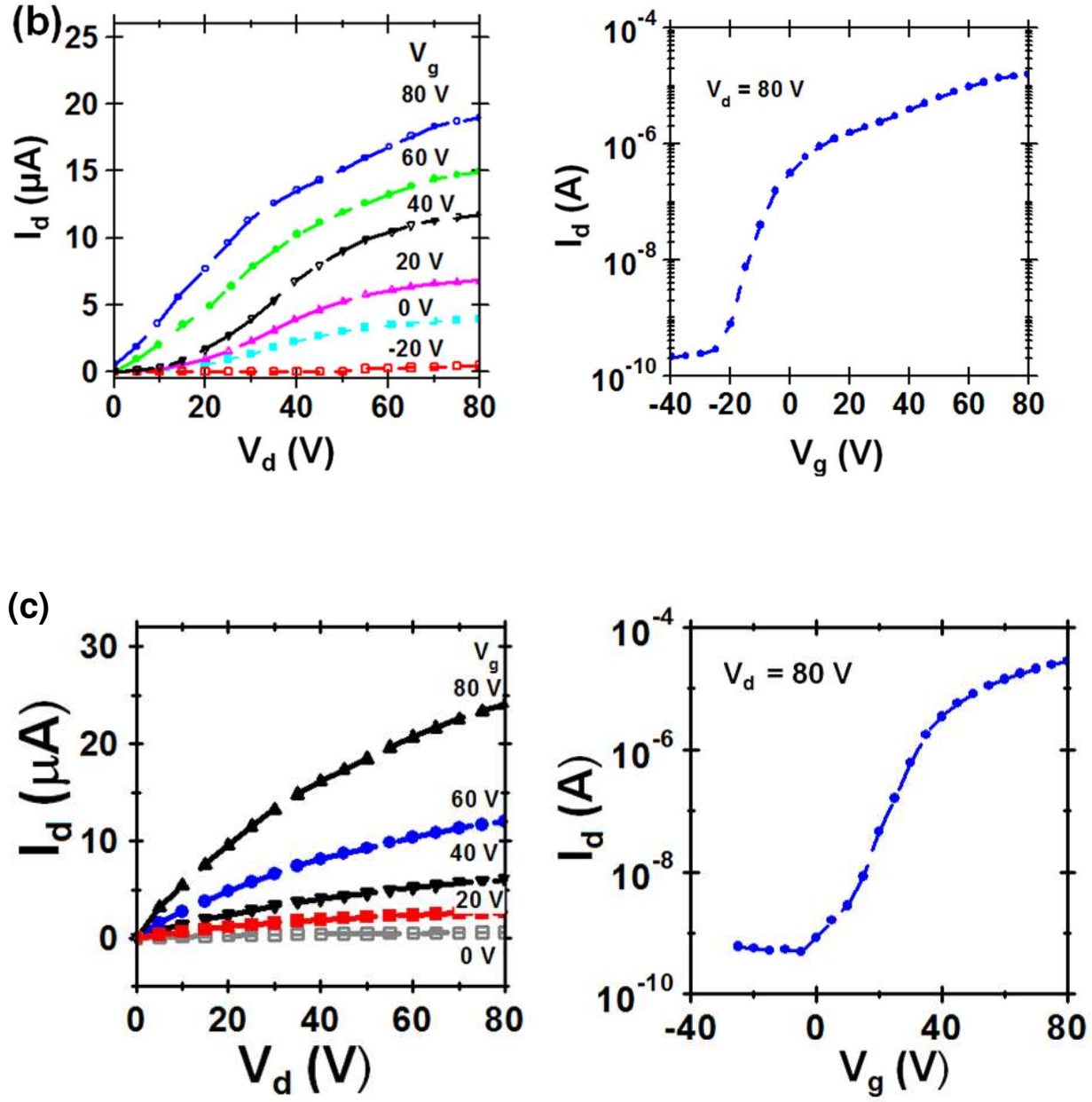


Figure S16: Typical output and transconductance characteristics for FETs fabricated with (a) NDI-BT; (b) PDI-BT and (c) N2200. Typical BCB dielectric capacitance (C_i ~ 2 - 4 nF/cm^2) and device dimensions are W ≈ 1 mm and L ≈ 60-100 μm.

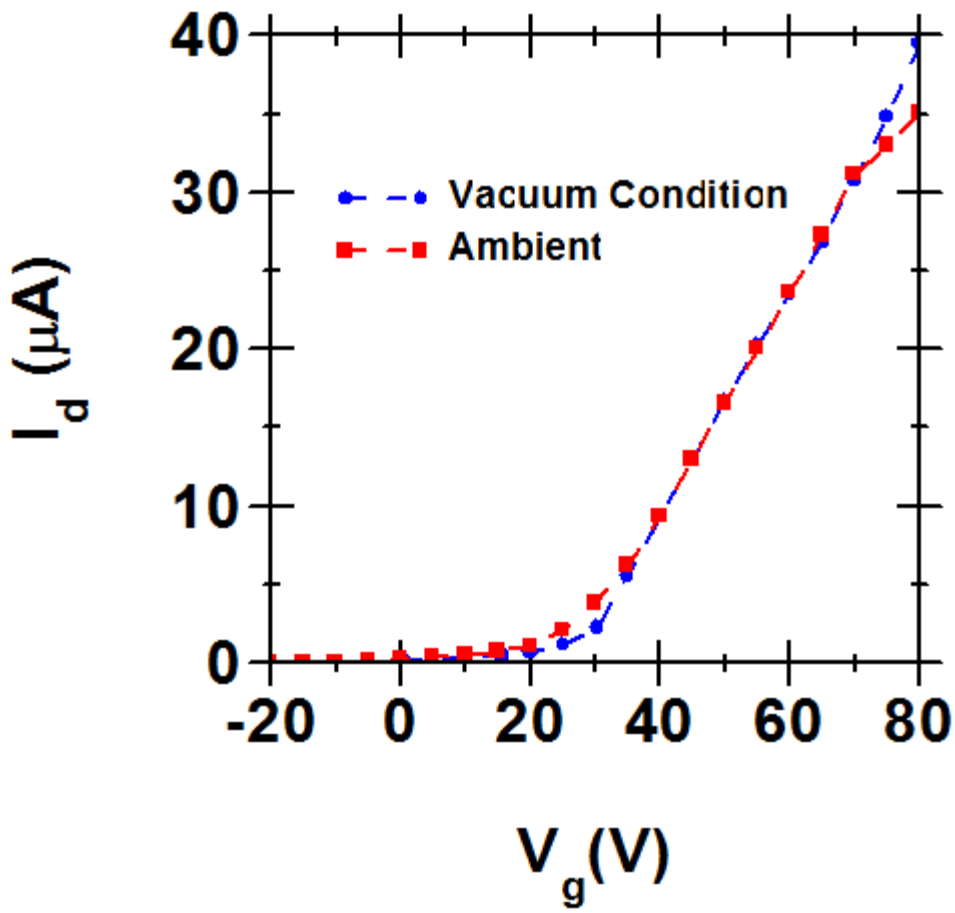


Figure S17: Typical transconductance characteristics for FETs fabricated with NDI-Ph polymer. Typical BCB dielectric capacitance (C_i ~ 2 - 4 nF/cm^2) and device dimensions are W ≈ 1 mm and L ≈ 100 μm.