Electronic Supplementary Material (ESI) for Polymer Chemistry.

Side-Chain Engineering Approach to Solvent-Resistant Semiconducting Polymer Thin Films

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Supplementary Information

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1. General information

6,6'-dibromoisoinigo[1] and bis(trimethylstannyl)thiophene[2] were synthesized according to procedure reported in the literature. Vinyl group end-functionalized polyisobutylene was purchased from BASF as Glissopal® 1000 (Mn = 1000g / mol). Other starting materials and reagents were purchased from Aldrich and Alfa-Aesar, and used as received without further purification. Toluene, CH_2Cl_2, DMF and THF were dried through dry Al_2O_3 columns and used without further treatment. Analytical thin-layer chromatography (TLC) was performed on glass that is precoated with silica gel 60-F_{254} (Sorbtech). Flash column chromatography was carried out using Biotage® Isolera™ Prime instrument with various size of SiO_2 Biotage ZIP® cartridge. UV/vis absorption spectra were recorded using Shimadzu UV-2600, while the fluorescent emission spectra were measured on Horiba Fluoromax-4. ^1H and ^{13}C NMR spectra were obtained on a 500 MHz Varian Inova at room temperature and processed by MestReNova 6.1.0. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents ($CDCl_3$: δ 7.26 for ^1H and 77.16 for ^{13}C at room temperature). Size exclusion chromatography (SEC) was performed on TOSOH EcoSEC (HLC-8320GPC) in THF solution at 40^oC temperature and the molecular weights calculated using a calibration curve based on polystyrene standards, equipped with TSKgel SuperHM-M and TSKgel SuperH-RC. Thermal gravimetric analysis (TGA) was recorded under nitrogen atmosphere with heating rate of 10 ^oC min^{-1} from 40 to 500 ^oC using TA Q500. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) at room temperature with a CHI voltammetric analyzer. n-Bu_4PF_6 (0.1 M) was used as the supporting electrolyte. High-resolution Matrix-assisted laser desorption/ionization (HR-MALDI) mass spectra were measured on Applied Biosystems 4800 MALDI-TOF. Atomic force microscopy (AFM) images were recorded with Bruker Dimension

Icon AFM in a tapping mode and processed using NanoScope Analysis. The evaluations of the FETs and inverters were carried out in atmosphere (humidity 50-60%) on a probe stage using a Keithley 4200 SCS as parameter analyzer.

2. TGA Trace of Monomer 1

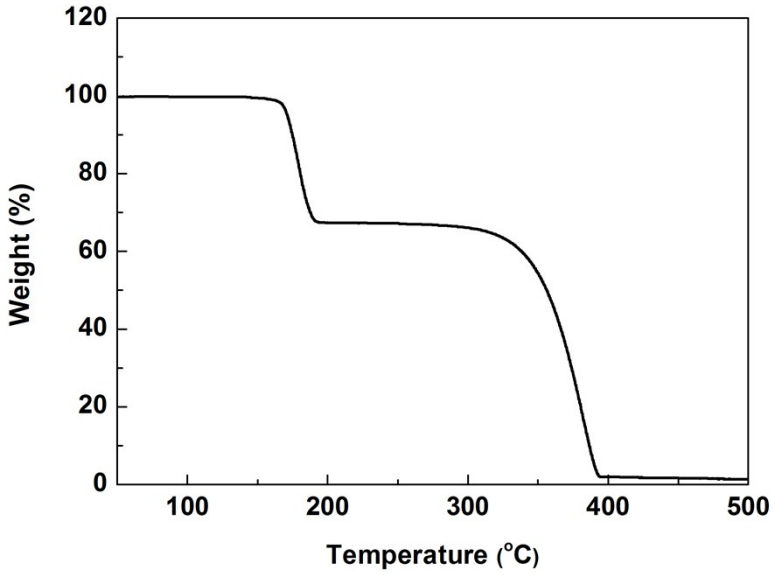

Figure S1. TGA Trace of **Monomer 1**.

3. Solvent Resistant Property of Annealed Thin Film

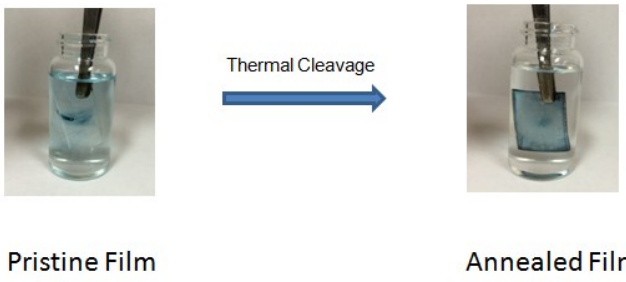

Figure S2. Solvent resistant properties of pristine film and annealed **PIIT-Boc65** thin film in CH_2Cl_2.

3. FT-IR Spectra

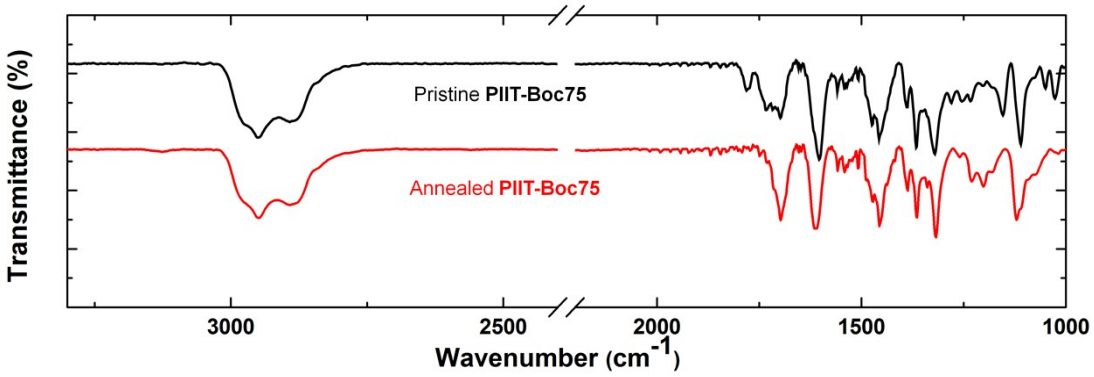

Figure S3. IR spectra comparison of Pristine and Annealed **PIIT-Boc75**.

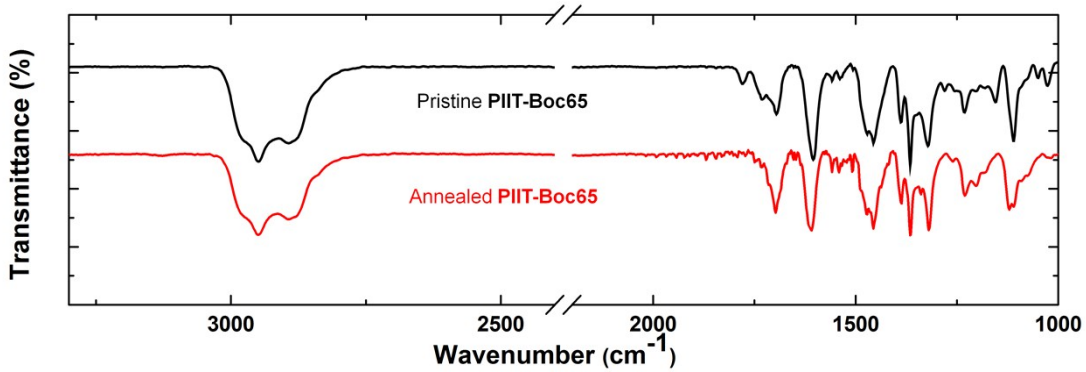

Figure S4. IR spectra comparison of Pristine and Annealed **PIIT-Boc65**.

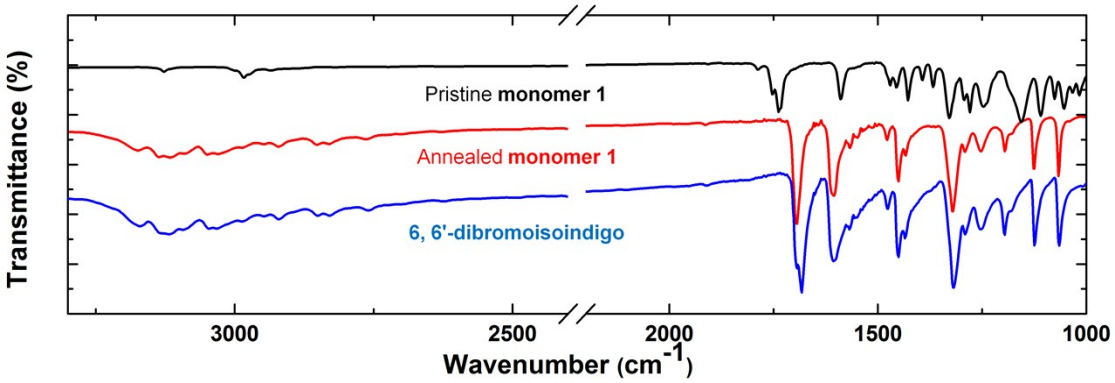

Figure S5. IR spectra comparison of Pristine and Annealed **monomer 1** and **6,6'-dibromoisoindigo**.

4. OFET Profile

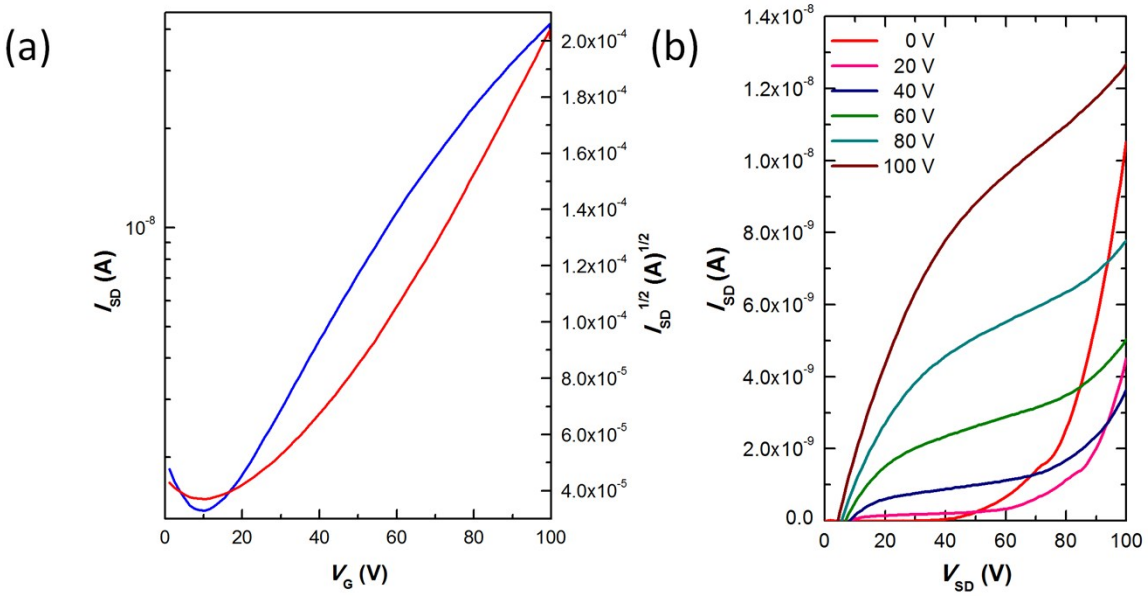

Figure S6. (a) Transfer curve and (b) output curve of **PIIT-Boc75** in immersed annealed film (CH_2Cl_2).

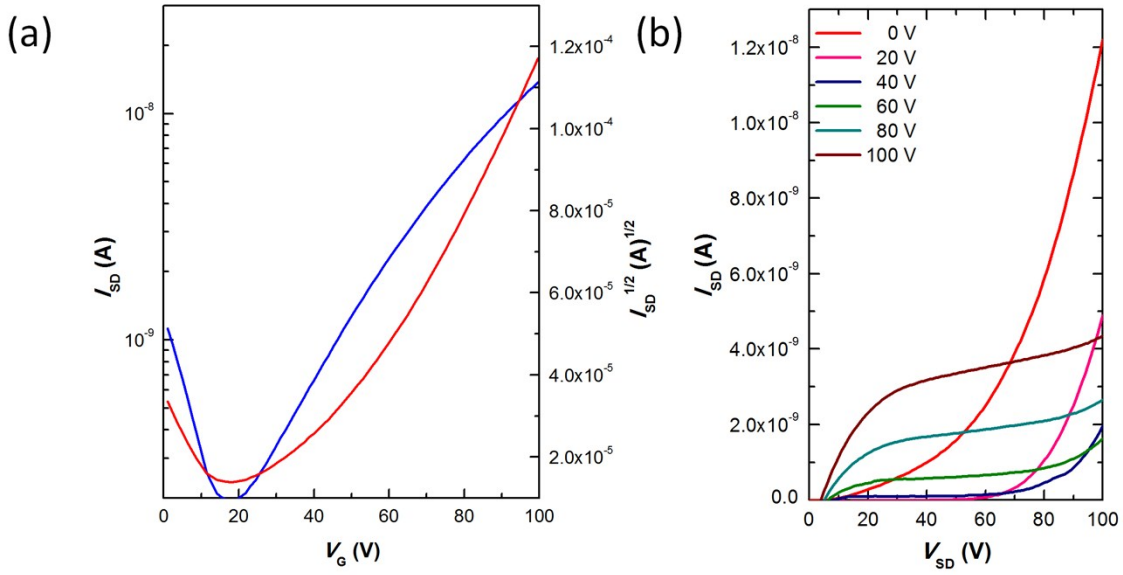

Figure S7. (a) Transfer curve and (b) output curve of **PIIT-Boc75** in immersed annealed film (DMSO).

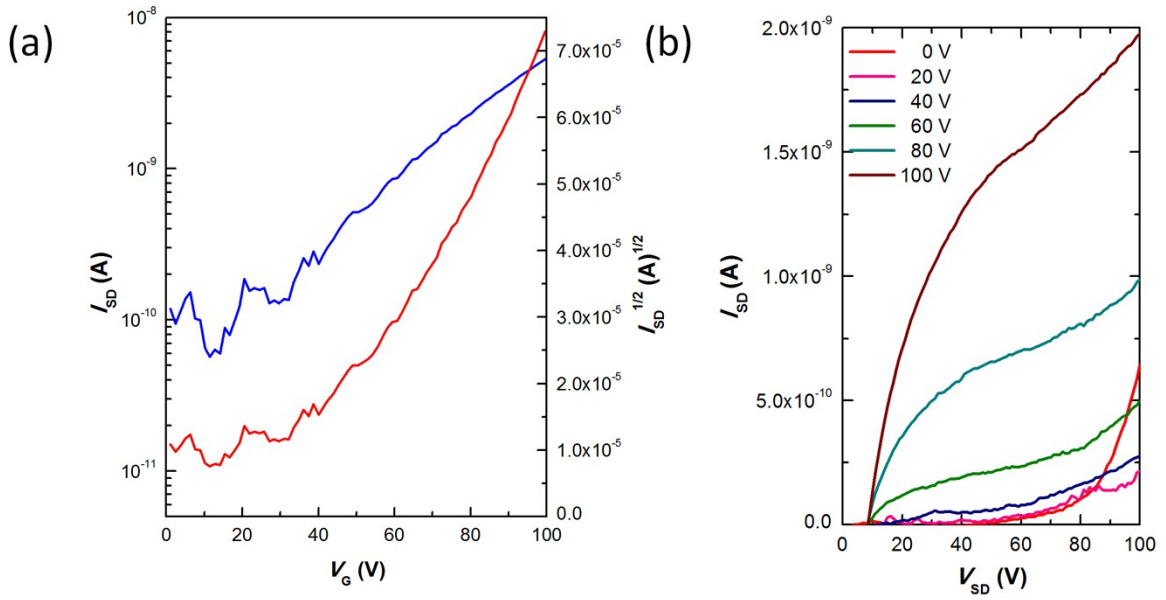

Figure S8. (a) Transfer curve and (b) output curve of **PIIT-Boc75** in immersed annealed film (*p*-xylene).

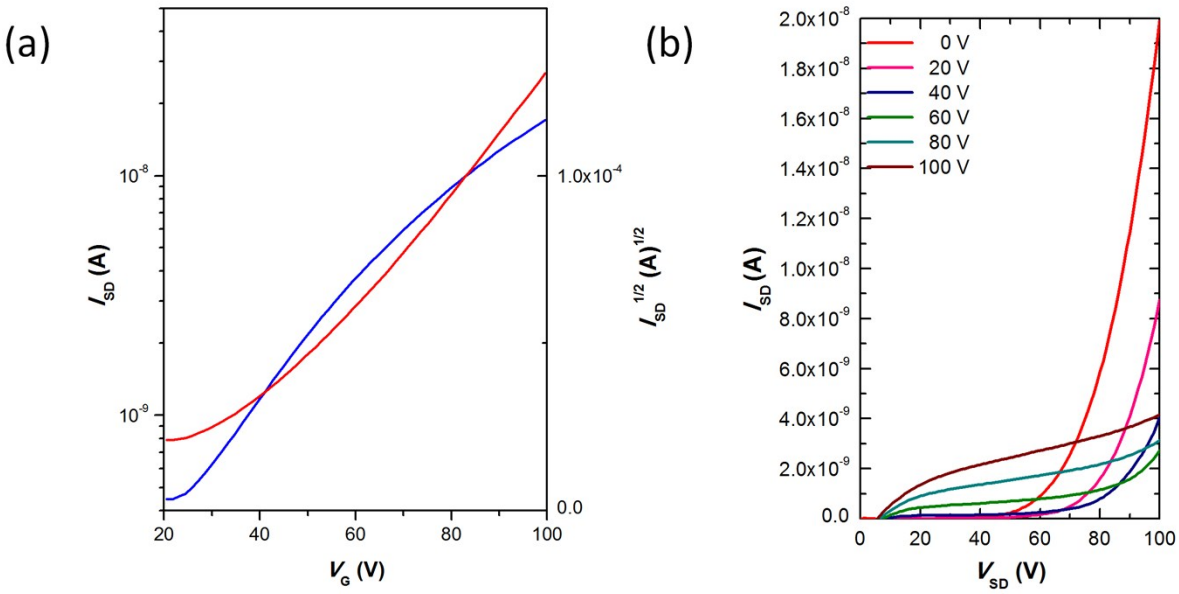

Figure S9. (a) Transfer curve and (b) output curve of **PIIT-Boc70** in pristine film.

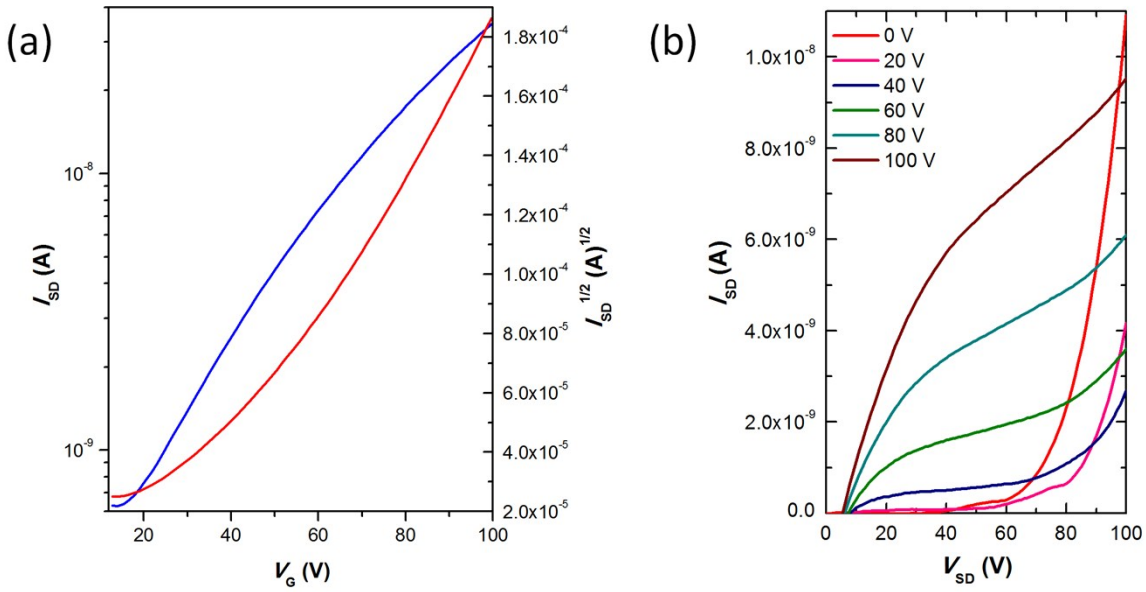

Figure S10. (a) Transfer curve and (b) output curve of **PIIT-Boc70** in annealed film.

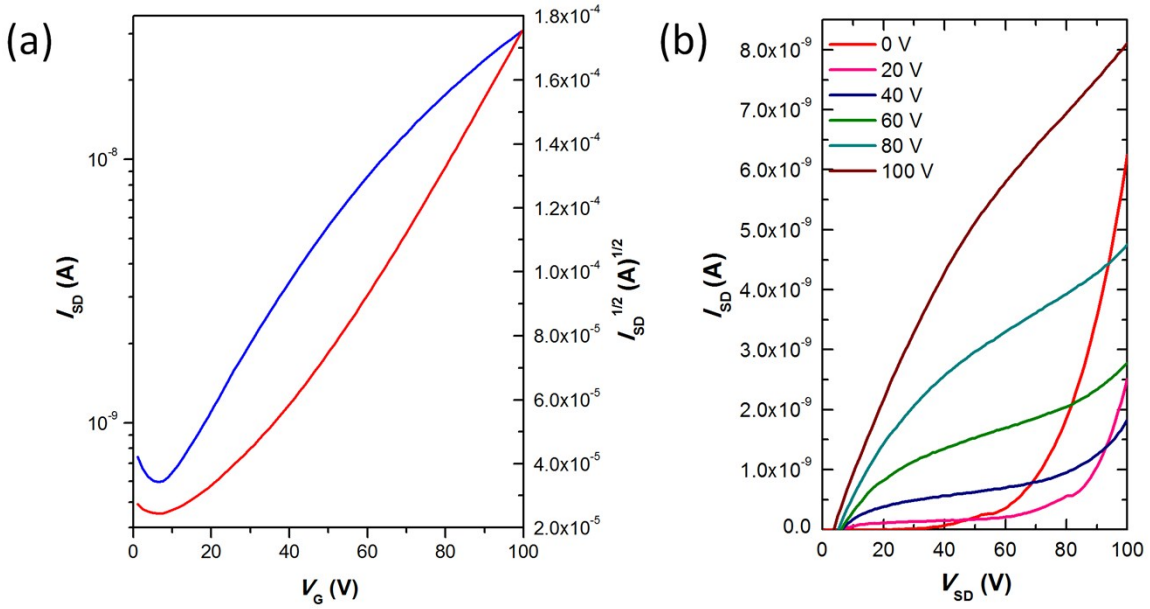

Figure S11. (a) Transfer curve and (b) output curve of **PIIT-Boc75** in immersed annealed film (CH_3Cl).

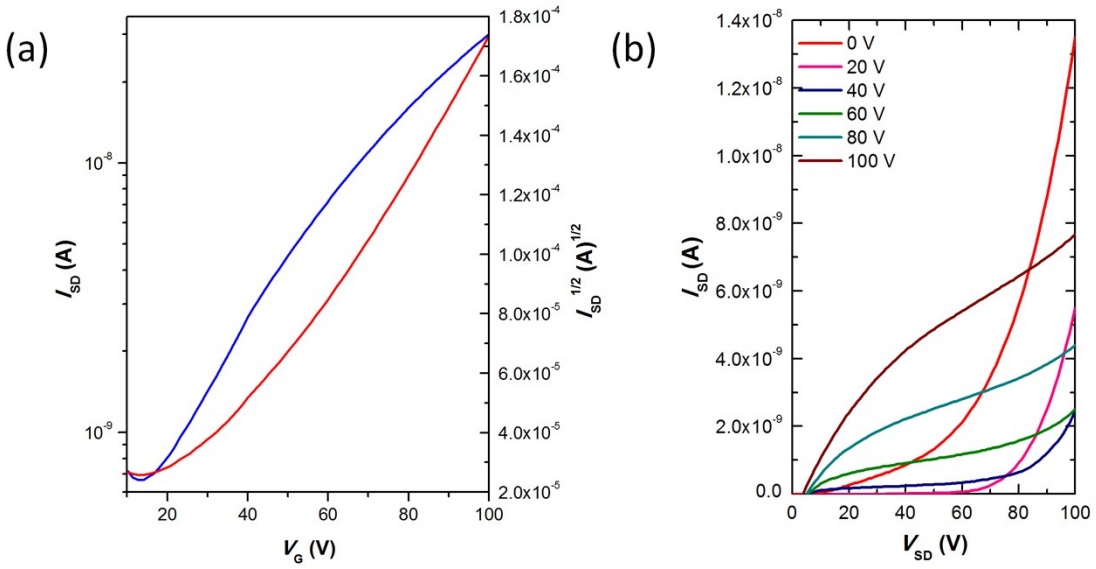

Figure S12. (a) Transfer curve and (b) output curve of **PIIT-Boc75** in immersed annealed film (CH_2Cl_2).

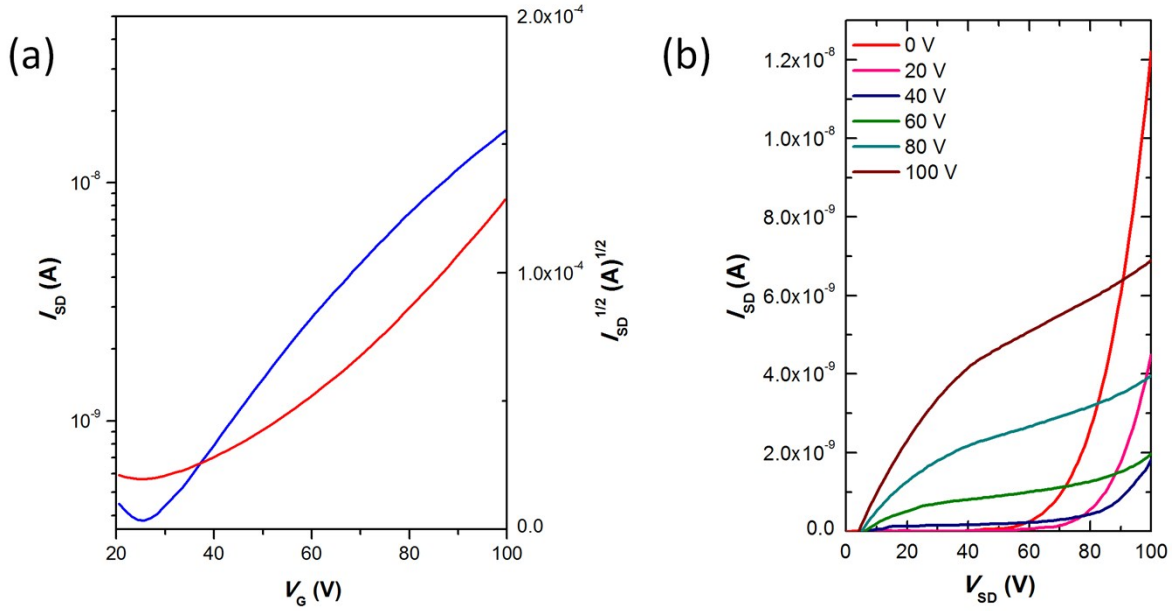

Figure S13. (a) Transfer curve and (b) output curve of **PIIT-Boc75** in immersed annealed film (DMSO).

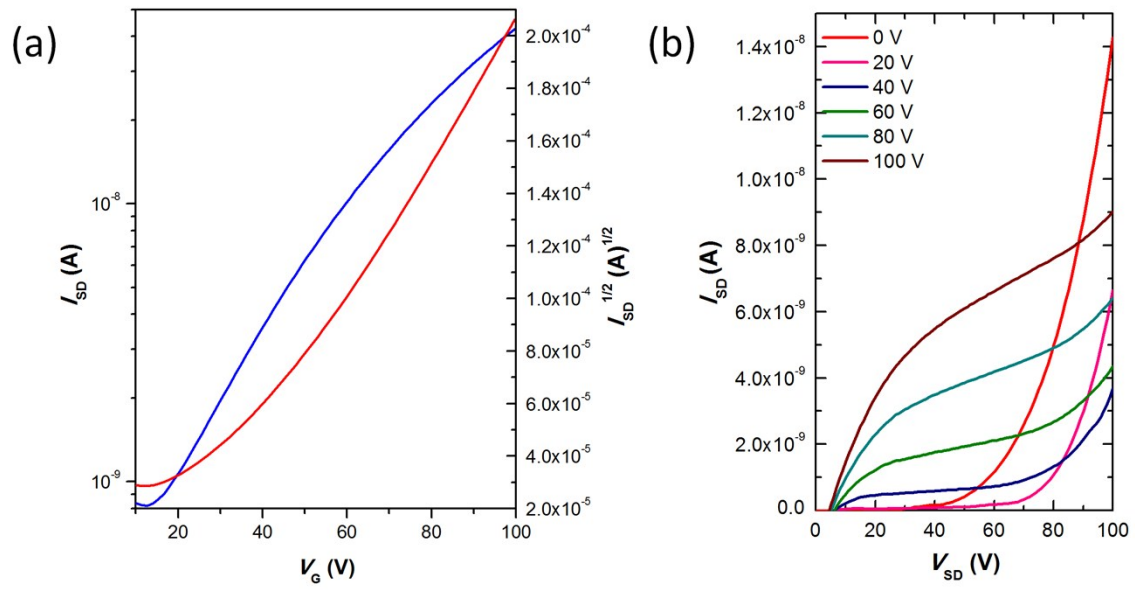

Figure S14. (a) Transfer curve and (b) output curve of **PIIT-Boc75** in immersed annealed film (*p*-xylene).

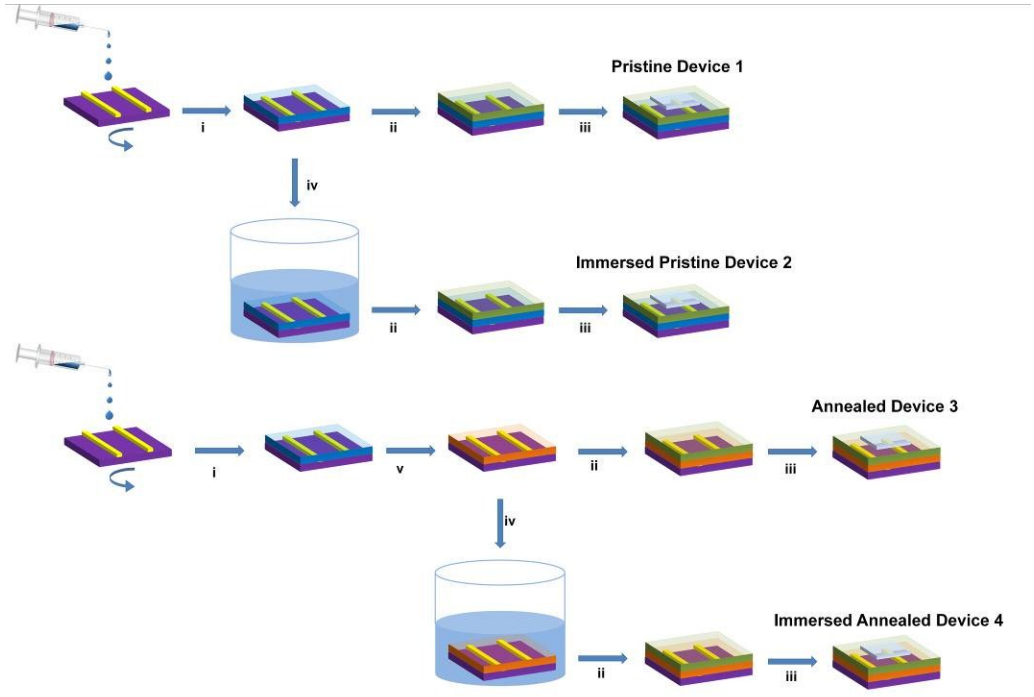

Figure S15. Device fabrication of TG/BC OFET structure. (i) spin casting active layer; (ii) spin casting CYTOP dielectric layer; (iii) vacuum depositing gate electrode; (iv) immersing into solvent for 5 min at room temperature; (v) annealing for 10 min at 180°C.

Table S1. OFET property of **PIID-Boc75** in pristine film, annealed film and immersed annealed film.

PIIT-Boc75		μ ($cm^2V^{-1}s^{-1}$)	V_{th} (V)
Pristine[a]		1.61E-04	1.98
Annealed[b]		2.15E-04	6.15
CH_2Cl_2	P.[c]	7.22E-05	7.40
	A.[d]	3.15E-04	25.96
CF	P.	1.09E-05	13.22
	A.	1.38E-04	23.69
p-Xylene	P.	6.26E-05	37.25
	A.	4.90E-05	43.77
DMSO	P.	N. A[e]	N. A
	A.	1.22E-04	42.73

a. Pristine film (Device 1); b Annealed film (Device 3); c. Immersed pristine film (Device 2); d. Immersed annealed film (Device 4); e. Not available.

Table S2. OFET property of **PIID-Boc70** in pristine film, annealed film and immersed annealed film.

PIIT-Boc70		μ ($cm^2V^{-1}s^{-1}$)	V_{th} (V)
pristine[a]		9.67E-05	29.31
annealed[b]		2.02E-04	30.15
CH_2Cl_2	P.[c]	N. A.[e]	N. A.
	A.[d]	1.62E-04	27.30
CF	P.	N. A.	N. A.

	A.	1.38E-04	20.09
p-Xylene	P.	N. A.	N. A.
	A.	1.99E-04	22.21
DMSO	P.	8.95E-05	29.66
	A.	1.20E-04	37.58

a. Pristine film (Device 1); b Annealed film (Device 3); c. Immersed pristine film (Device 2); d. Immersed annealed film (Device 4); e. Not available.

5. GIXRD pattern

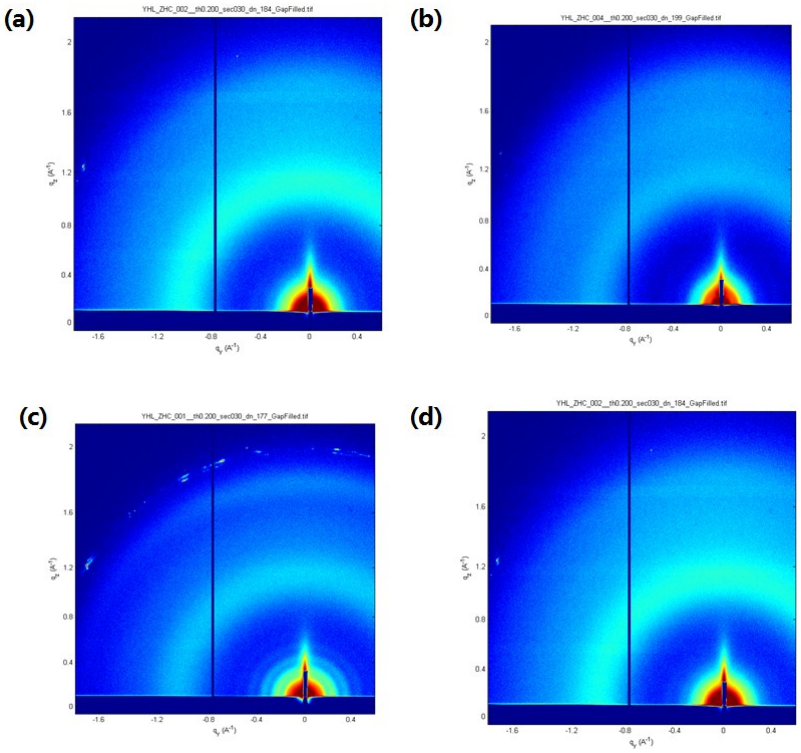

Figure 16. GIXRD pattern of (a) pristine and (b) annealed **PIIT-Boc75** films; and (c) pristine and (d) annealed **PIIT-boc70** films.

6. ^{1}H and ^{13}C NMR Spectra

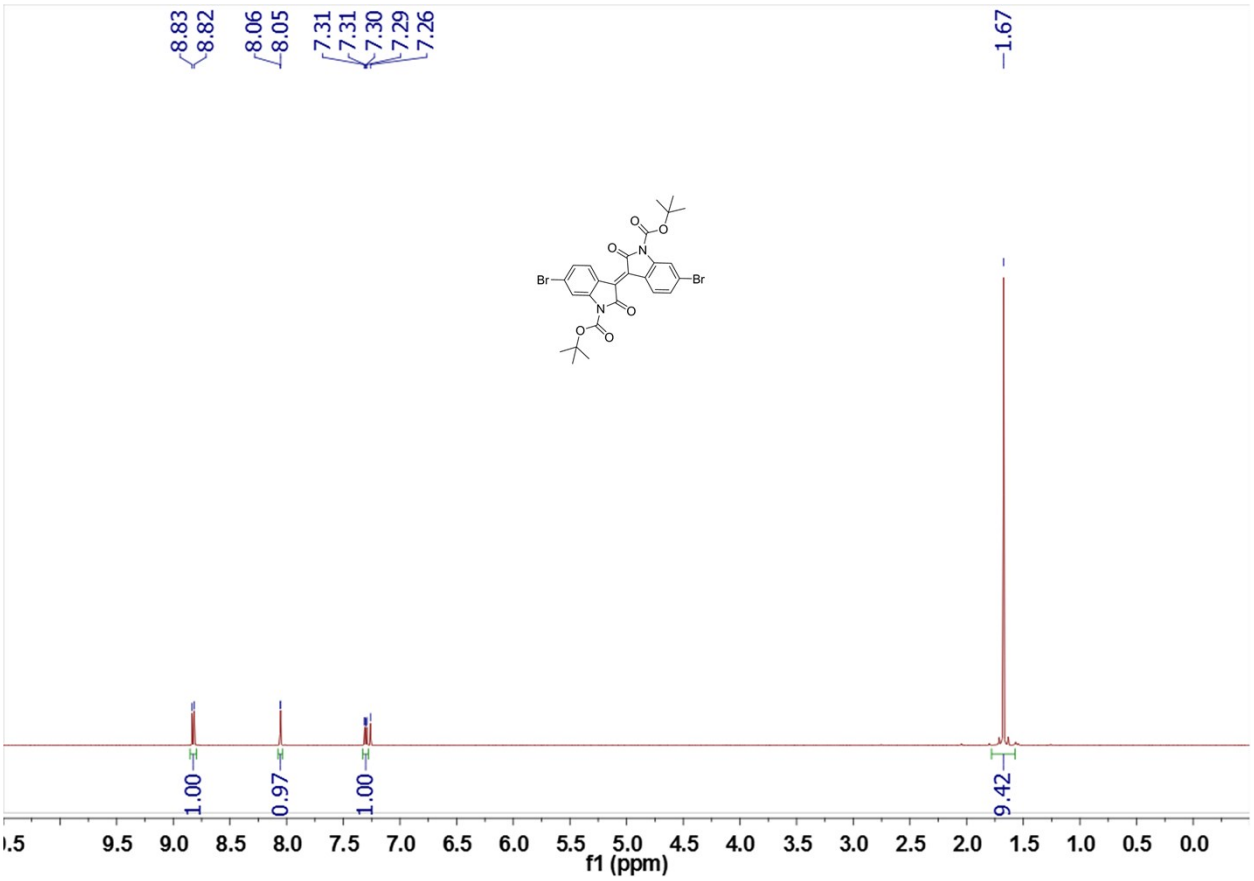

Figure S17. ^{1}H NMR of **Monomer1** (500 MHz, $CDCl_3$, RT).

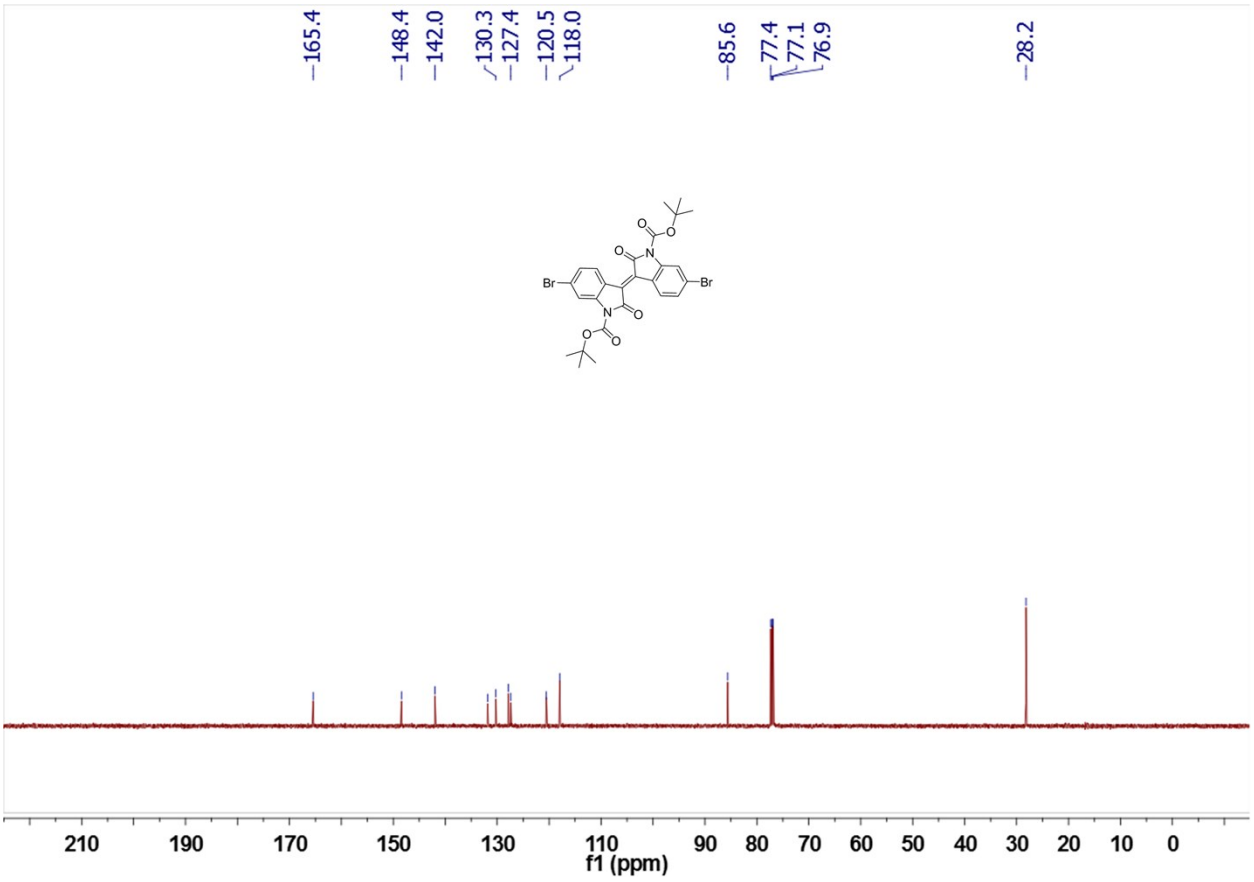

Figure S18. ^{13}C NMR of **Monomer 1** (500 MHz, $CDCl_3$, RT).

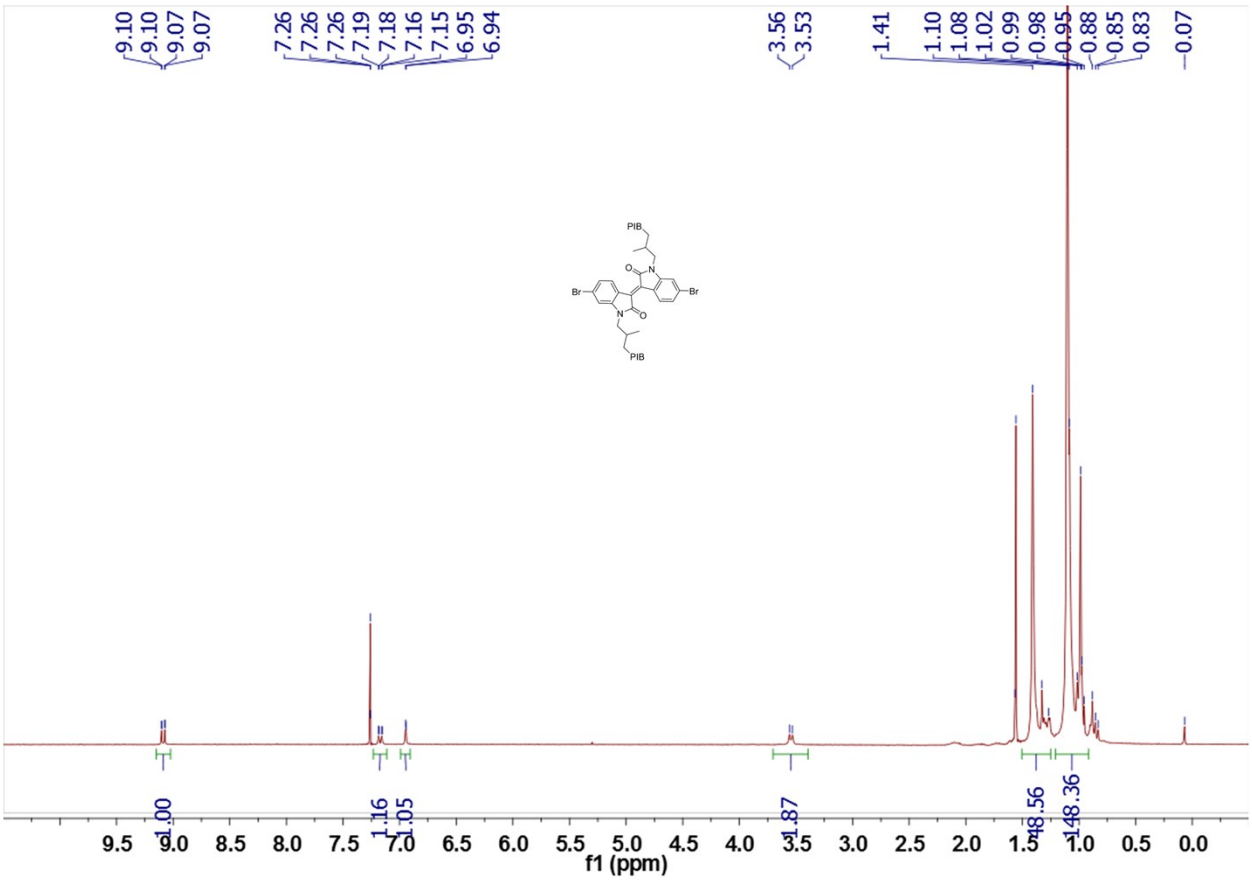

Figure S19. ^{1}H NMR of **Monomer 2** (500 MHz, $CDCl_3$, RT).

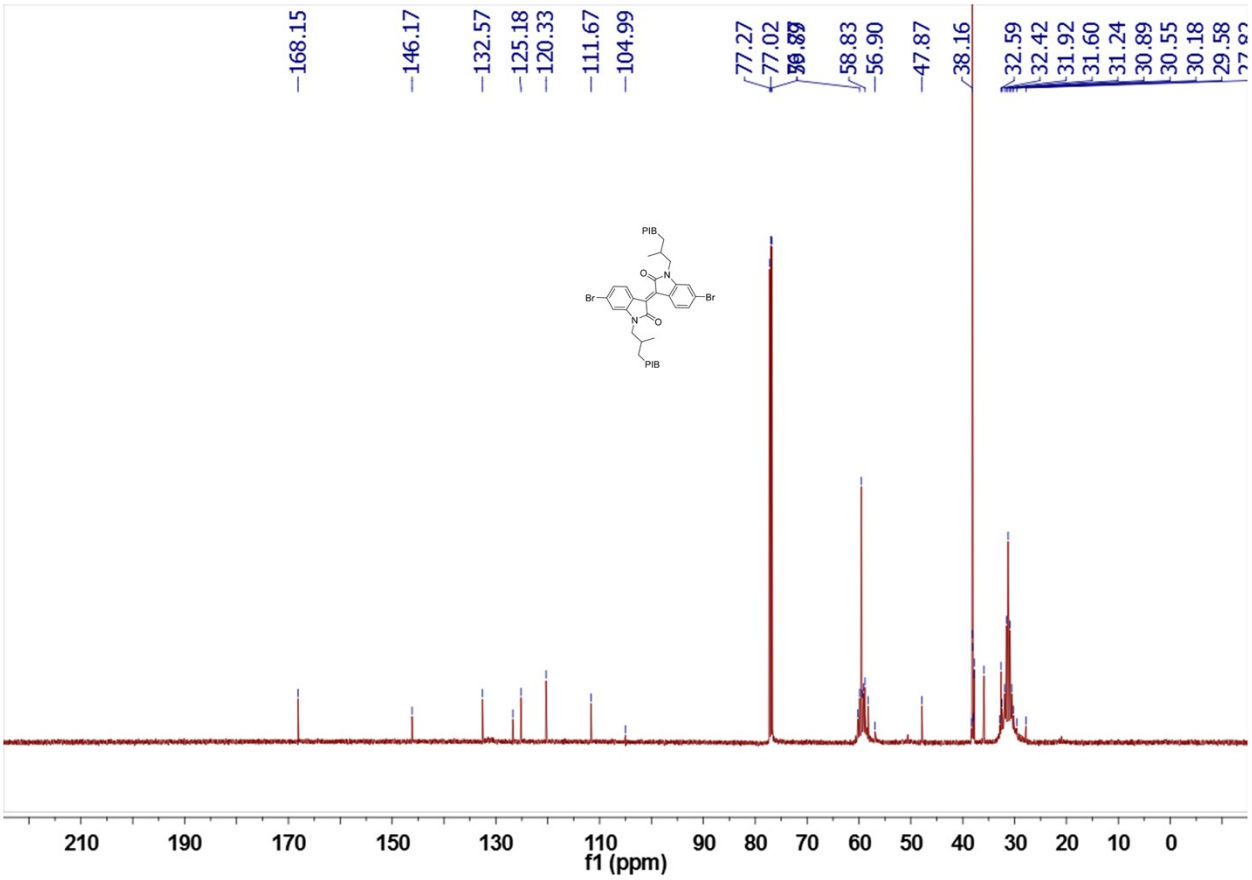

Figure S20. ^{13}C NMR of **Monomer 2** (500 MHz, $CDCl_3$, RT).

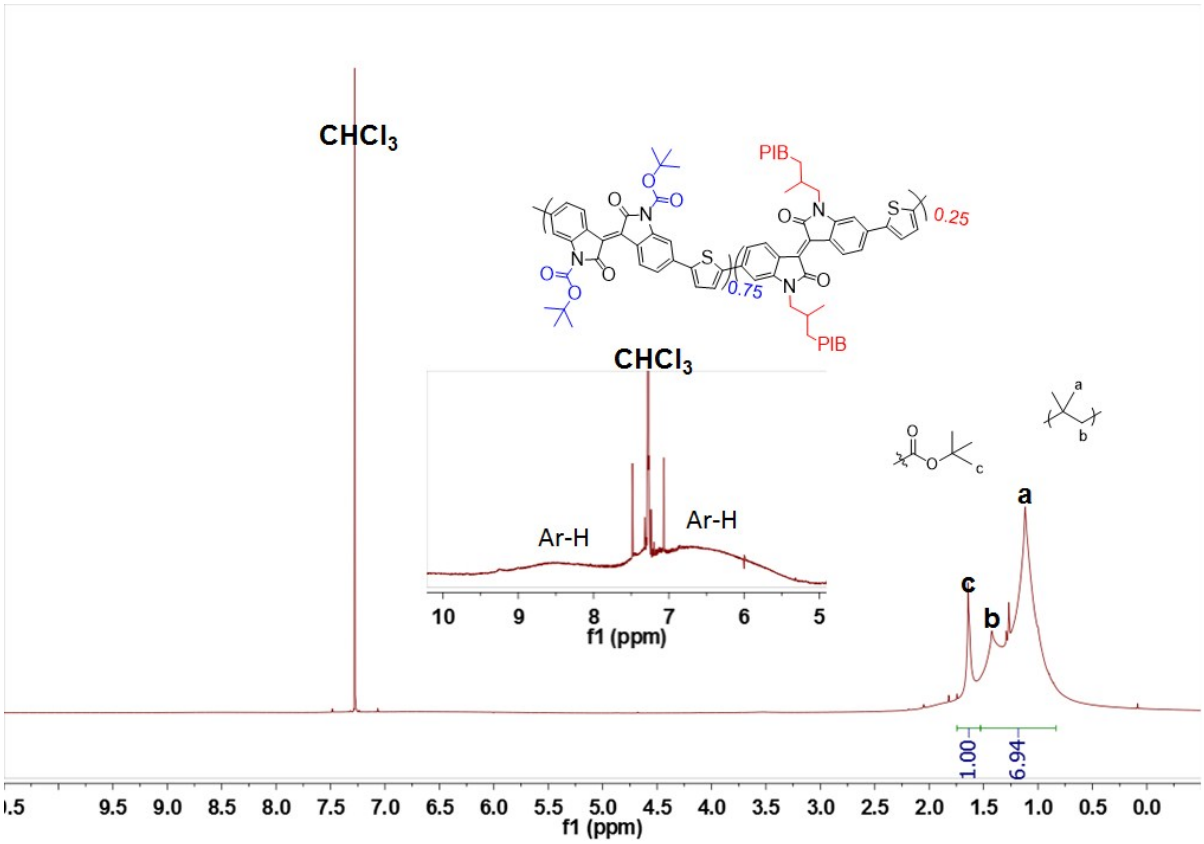

Figure S21. H NMR of **PIIT-Boc75** (500 MHz, $CDCl_3$, RT).

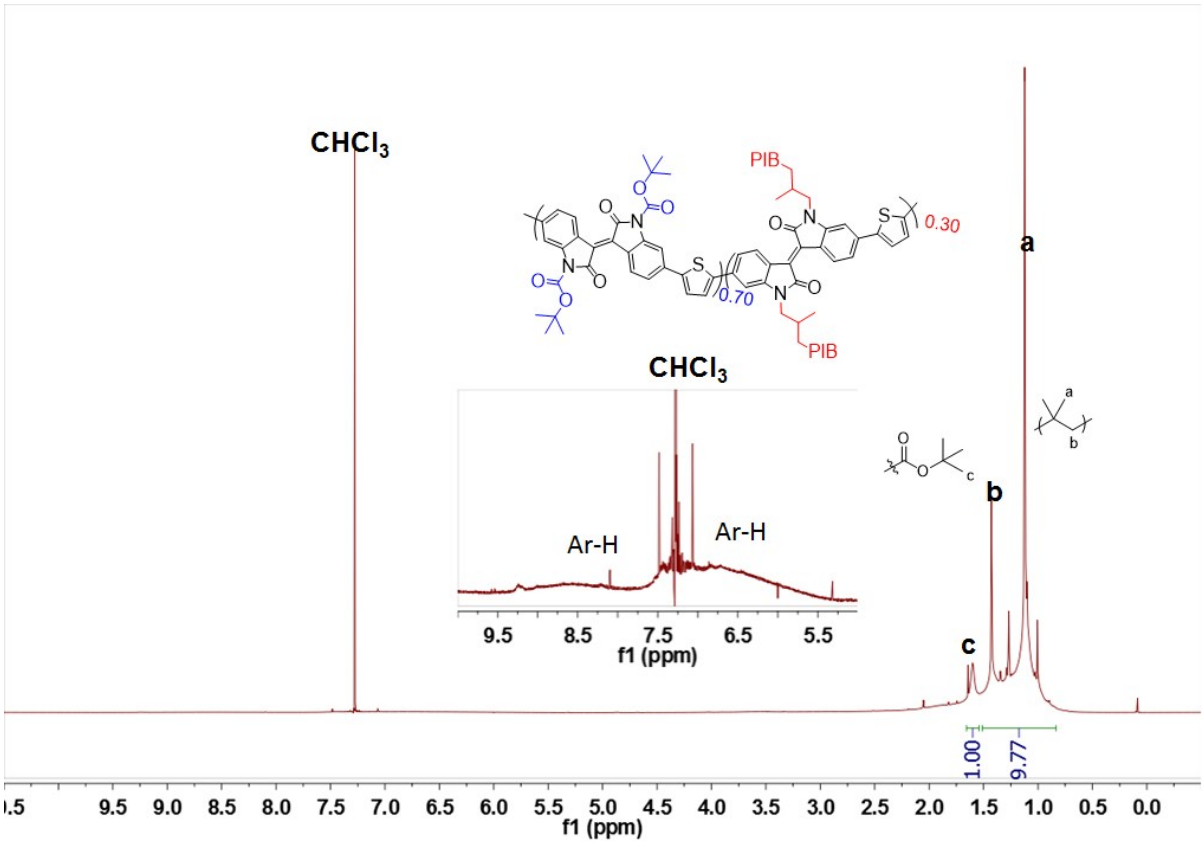

Figure S22. H NMR of **PIIT-Boc70** (500 MHz, $CDCl_3$, RT).

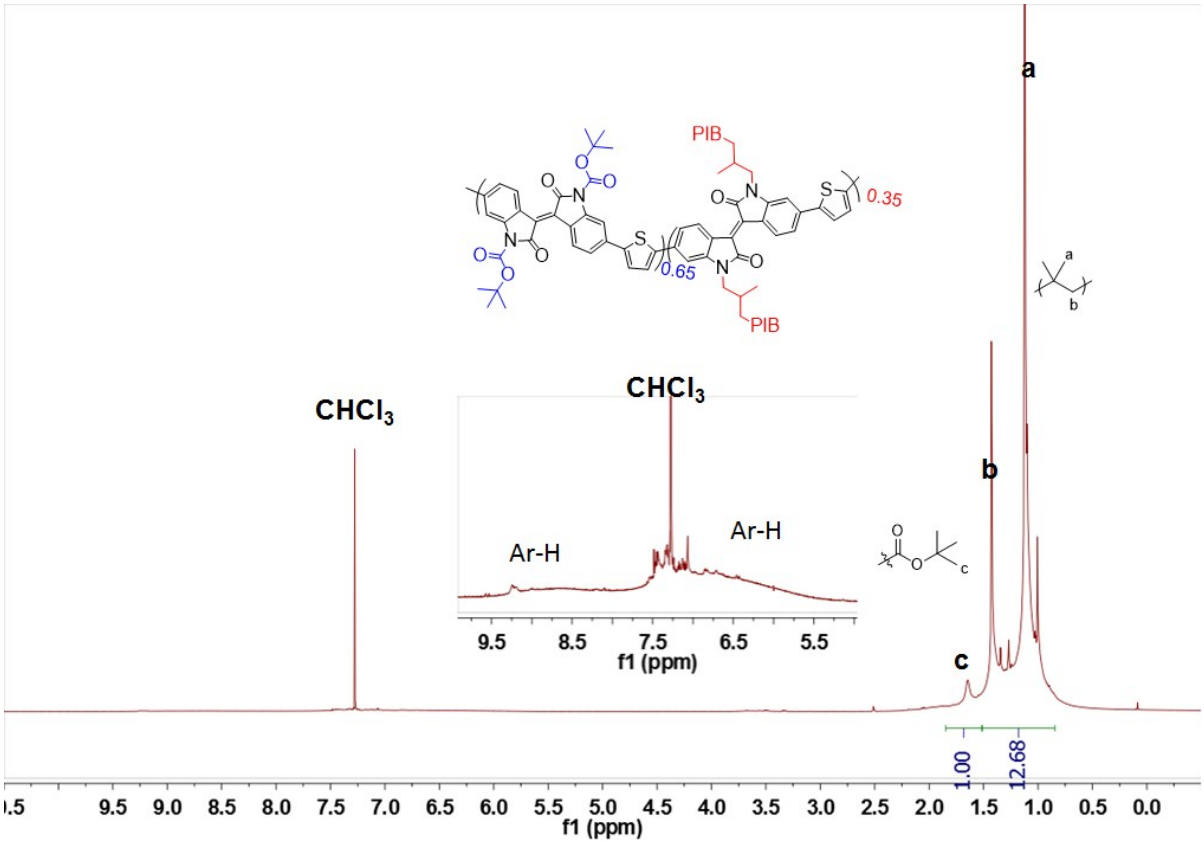

Figure S23. H NMR of **PIIT-Boc65** (500 MHz, $CDCl_3$, RT).

7. Reference

1. J. Mei, K. R. Graham, R. Stalder and J. R. Reynolds, *Org. Lett.*, 2010, **12**, 660–663.

2. G. Zhang, Y. Fu, Z. Xie and Q. Zhang, *Macromolecules*, 2011, **44**, 1414–1420.