Supplementary Information

A planar cyclopentadithiophene-benzothiadiazole based copolymer with sp^2 hybridized bis(alkylsulfanyl)methylene substituents for organic thermoelectric devices

Jiae Lee,[†,⊥] Jaeyun Kim, [‡,⊥] Thanh Luan Nguyen,[†,⊥] Miso Kim,[†] Juhyung Park,[‡] Yeran Lee,[†] Sungu Hwang,[§] Young-Wan Kwon,[&] Jeonghun Kwak,[*,‡] and Han Young Woo[*,†]

[†]*Department of Chemistry, College of Science, Korea University, Seoul 02841, Republic of Korea*
[‡]*School of Electrical and Computer Engineering, University of Seoul, Seoul 02504, Republic of Korea*
[§]*Department of Nanomechatronics Engineering, Pusan National University, Miryang 627-706, Republic of Korea*
[&]*KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, Republic of Korea*

* To whom all correspondence should be addressed: E-mail: hywoo@korea.ac.kr (H. Y. Woo); jkwak82@uos.ac.kr (J. Kwak).

1. Supporting Figures

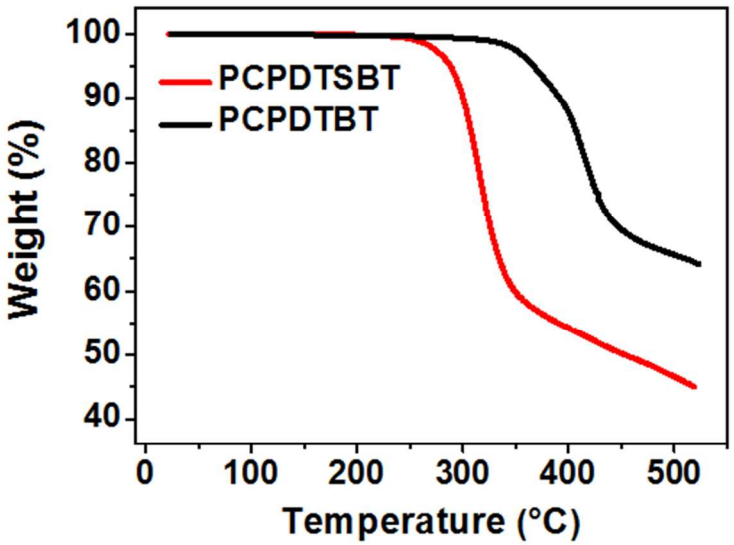

Figure S1. TGA data for PCDTSBT and PCPDTBT.

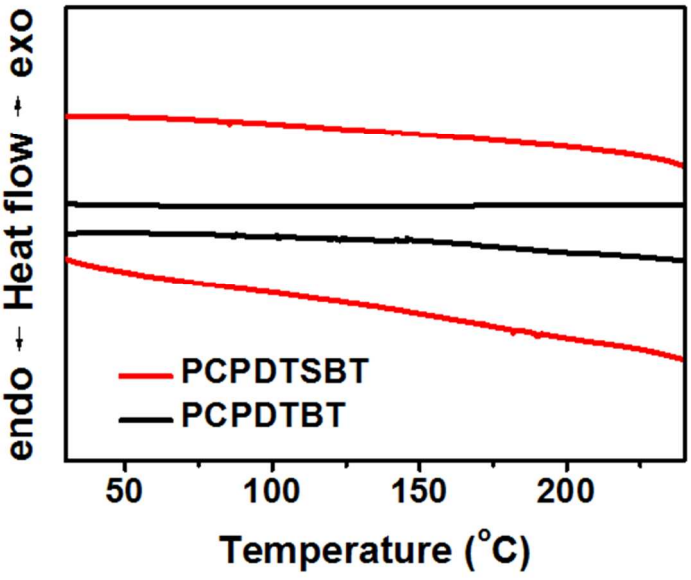

Figure S2. DSC thermograms of PCPDTSBT and PCPDTBT.

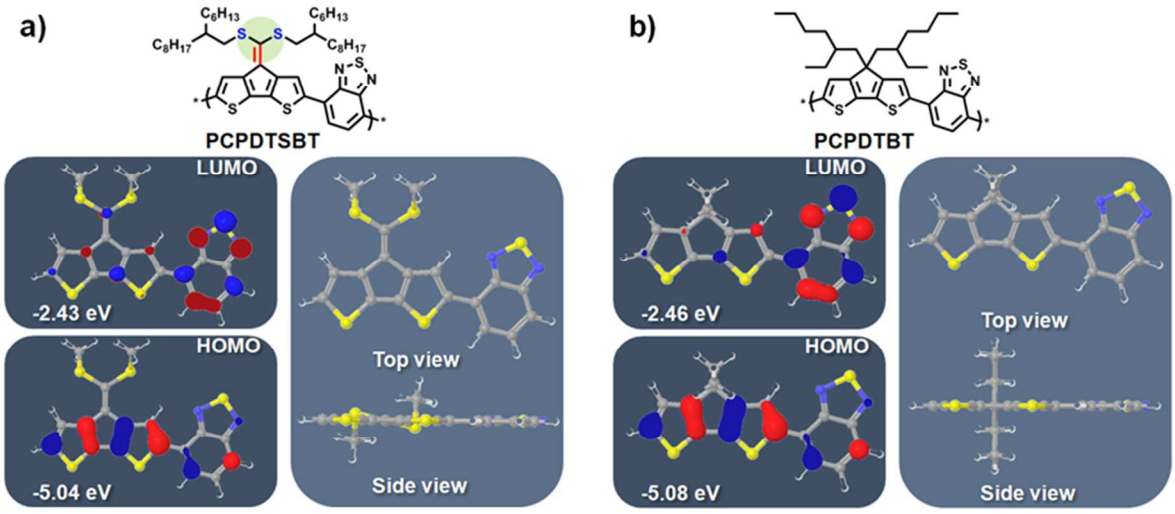

Figure S3. Optimized geometries by DFT calculation and charge density isosurfaces for frontier molecular orbitals of (a) PCPDTSBT and (b) PCPDTBT.

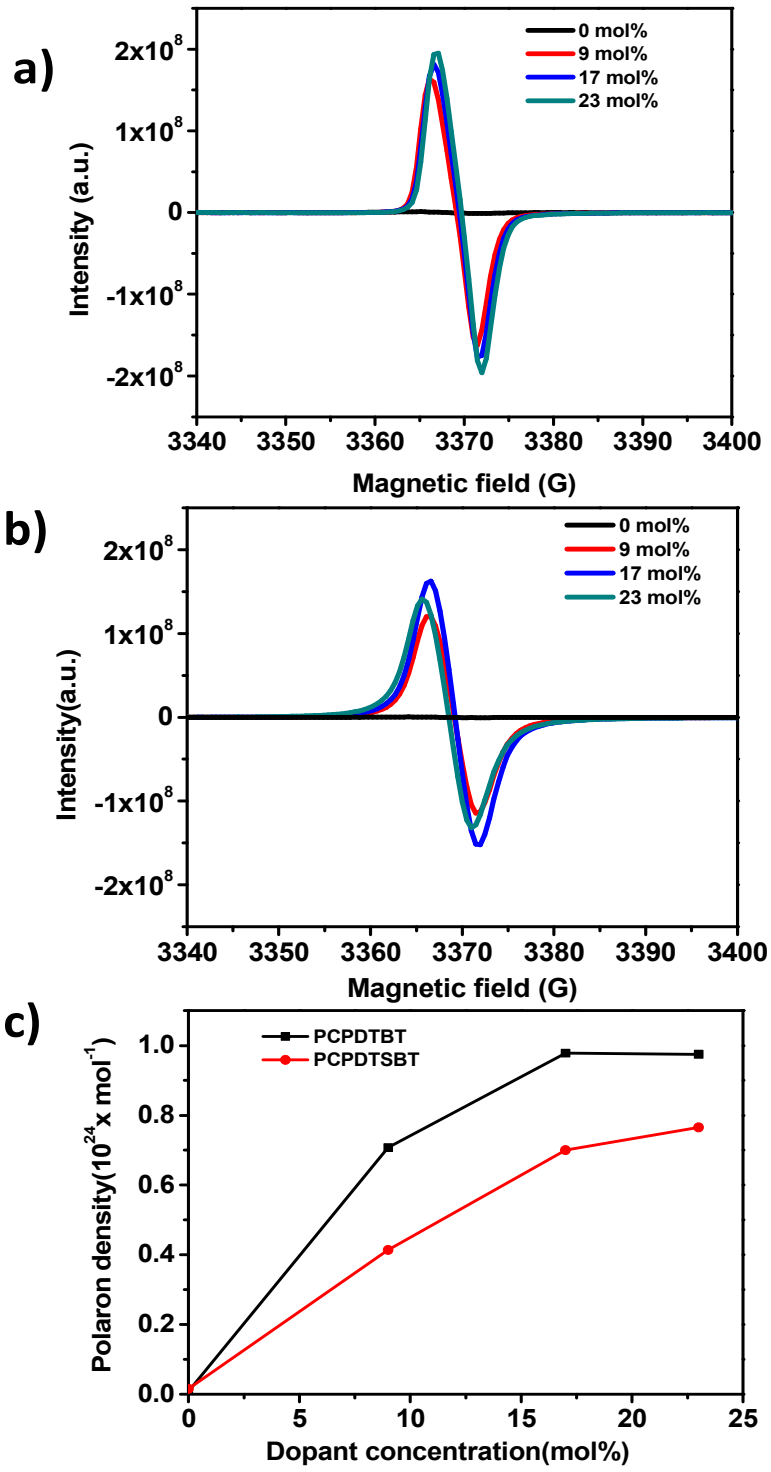

Figure S4. EPR spectra with changing $[B(C_6F_5)_3]$: a) PCPDTSBT, b) PCPDTBT and c) polaron density with different dopant concentration.

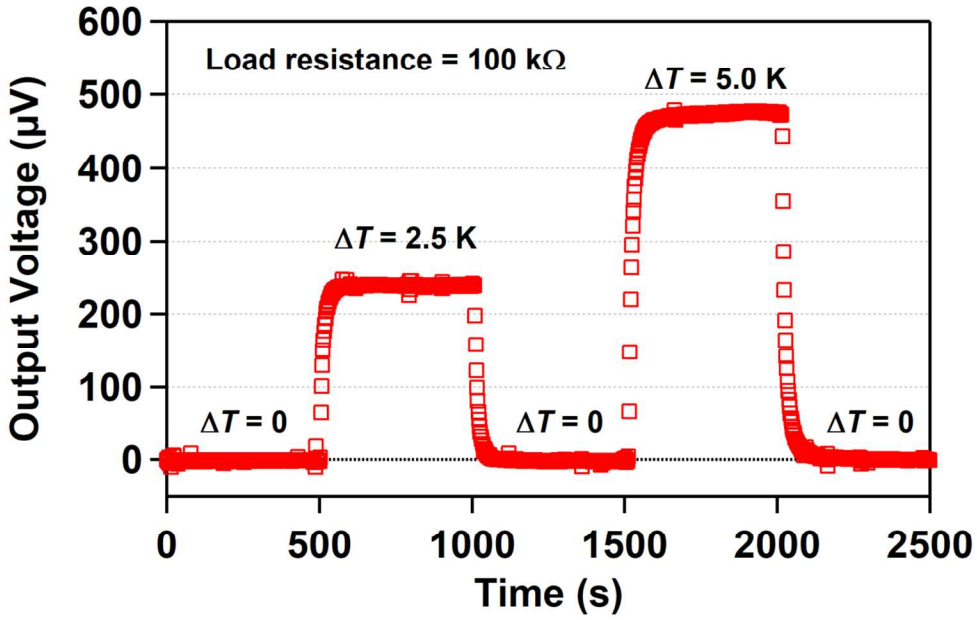

Figure S5. Output voltage measured at a load resistor (100 kΩ) with changing the temperature difference with time.

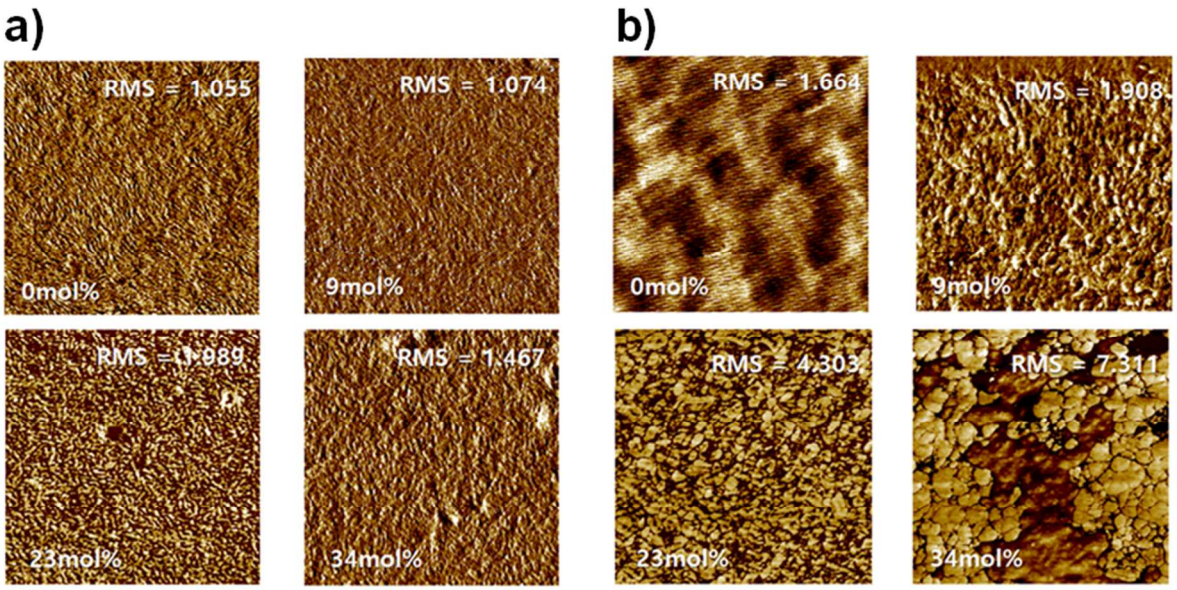

Figure S6. AFM images of (a) PCPDTSBT and (b) PCPDTBT films with changing $B(C_6F_5)_3$ mol%. Scan size : $2 \times 2\ \mu m^2$.

2. Supporting Tables

Table S1. Polaron density of PCPDTSBT and PCPDTBT with changing [$B(C_6F_5)_3$].

$(C_6F_5)_3$ (mol%)	PCPDTSBT		PCPDTBT	
	Polaron density ($\times 10^{24}$ /mol)	Polaron density/RU*	Polaron density ($\times 10^{24}$ /mol)	Polaron density/RU
0	0.16	0.03	0.08	0.013
9	4.14	0.69	7.08	1.17
17	7.00	1.16	9.78	1.62
23	7.65	1.27	9.75	1.62

*RU: repeating unit

Table S2. Summary of thermoelectric properties of PCPDTSBT and PCPDTBT films doped with $B(C_6F_5)_3$. The data show average values of 10 separate measurements.

Polymer / mol% of $(C_6F_5)_3$	**Seebeck coefficient ($\mu V\ K^{-1}$)**	**Electrical conductivity ($S\ cm^{-1}$)**	**Power factor ($\mu W\ m^{-1}\ K^{-2}$)**
PCPDTSBT	-	$4.97\times10^{-5} \pm 8.50\times10^{-7}$	-
3 mol%	426.75 ± 7.99	$3.53\times10^{-3} \pm 1.17\times10^{-4}$	0.06
9 mol%	190.53 ± 2.42	2.13 ± 0.01	7.73
17 mol%	108.86 ± 1.67	3.20 ± 0.04	3.79
23 mol%	64.02 ± 0.92	6.98 ± 0.06	2.86
29 mol%	58.31 ± 0.40	7.47 ± 0.09	2.54
34 mol%	60.19 ± 0.42	6.19 ± 0.08	2.24
PCPDTBT	-	$1.30\times10^{-5} \pm 2.16\times10^{-6}$	-
3 mol%	522.31 ± 11.42	0.023 ± 0.001	0.63
9 mol%	460.93 ± 5.72	0.10 ± 0.01	2.28
17 mol%	427.03 ± 13.22	0.24 ± 0.01	4.41
23 mol%	219.48 ± 4.38	0.65 ± 0.01	3.12
29 mol%	169.47 ± 5.08	0.57 ± 0.01	1.64
34 mol%	134.14 ± 6.50	0.28 ± 0.04	0.50

Table S3. GIWAXS packing parameters of PCPDTSBT and PCPDTBT thin films with changing dopant concentration (0–34 mol%).

Polymer / mol% of $(C_6F_5)_3$	Lamellar spacing		π-π stack			
	q_{xy} (Å^{-1})	d-spacing (Å)	q_z (Å^{-1})	d-spacing (Å)	FWHM (Å^{-1})[a]	CCL (Å)[b]
PCPDTSBT	0.25	25.1	1.66	3.78	0.22	26.0
9 mol%	0.23	27.3	1.70	3.69	0.21	27.2
23 mol%	0.23	27.3	1.71	3.67	0.19	30.1
34 mol%	0.23	27.3	1.71	3.67	0.20	28.6
PCPDTBT	-	-	1.58	3.97	0.33	17.3
9 mol%	0.55	22.8	1.58	3.97	0.39	14.6
23 mol%	-	-	1.58	3.97	0.34	16.8
34 mol%	0.55	22.8	1.58	3.97	0.42	13.6

[a]Full width at half maximum. [b]Crystal coherence length.

3. NMR Spectra

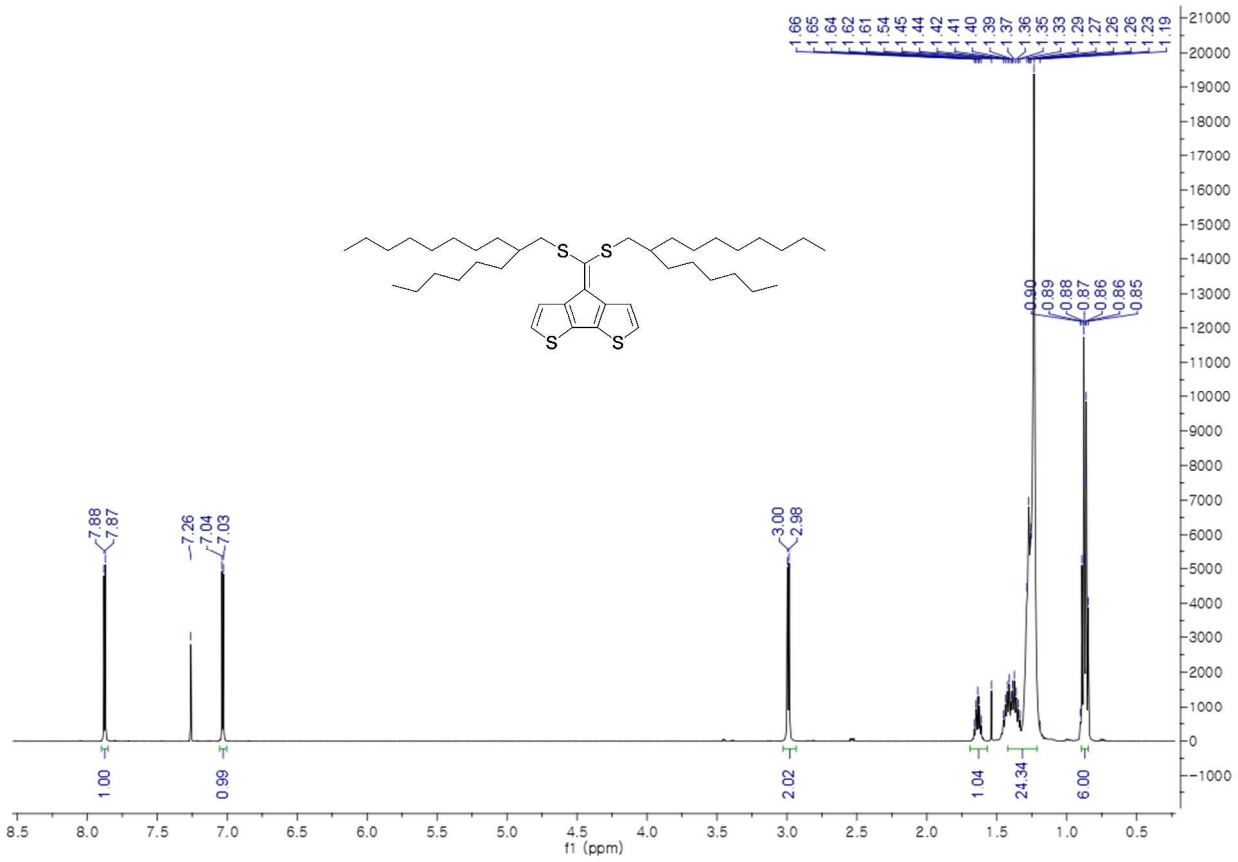

Figure S7. ^{1}H NMR spectrum of compound 1.

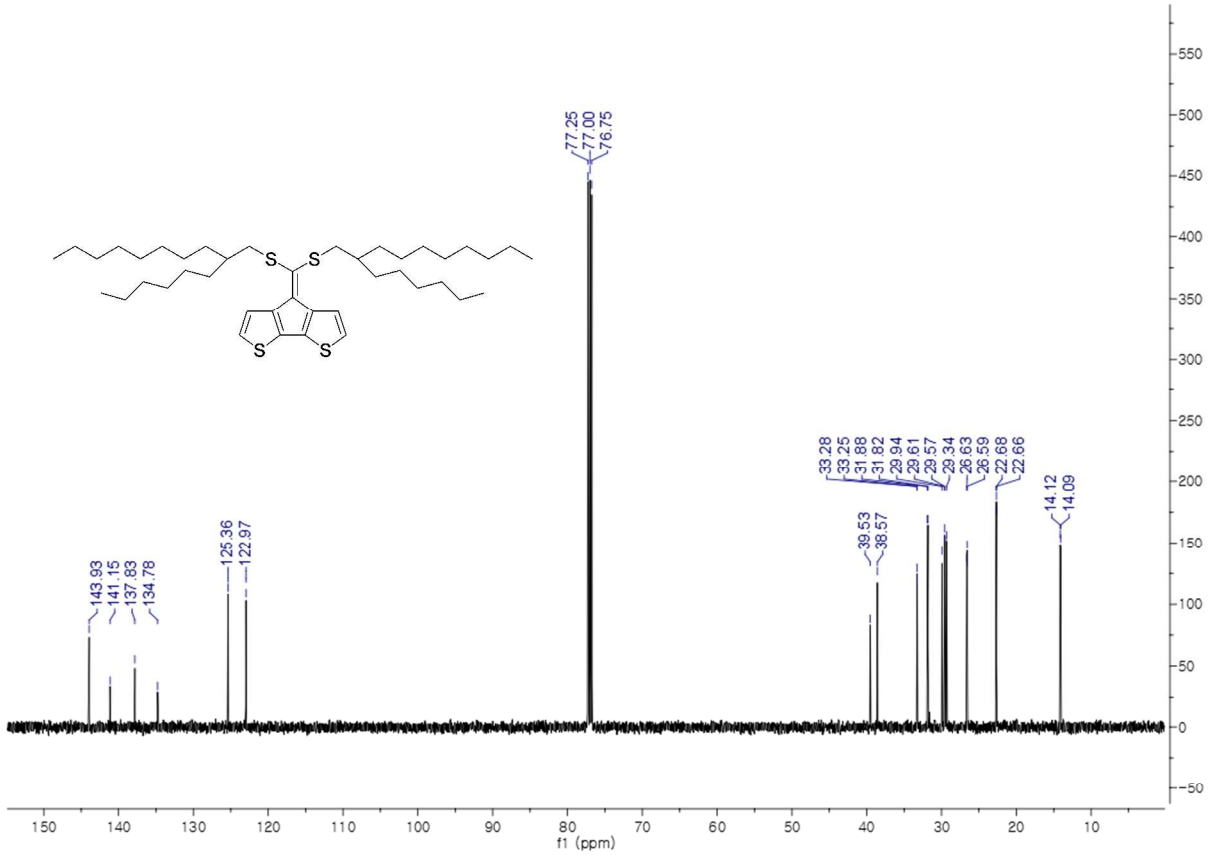

Figure S8. ^{13}C NMR spectrum of compound 1.

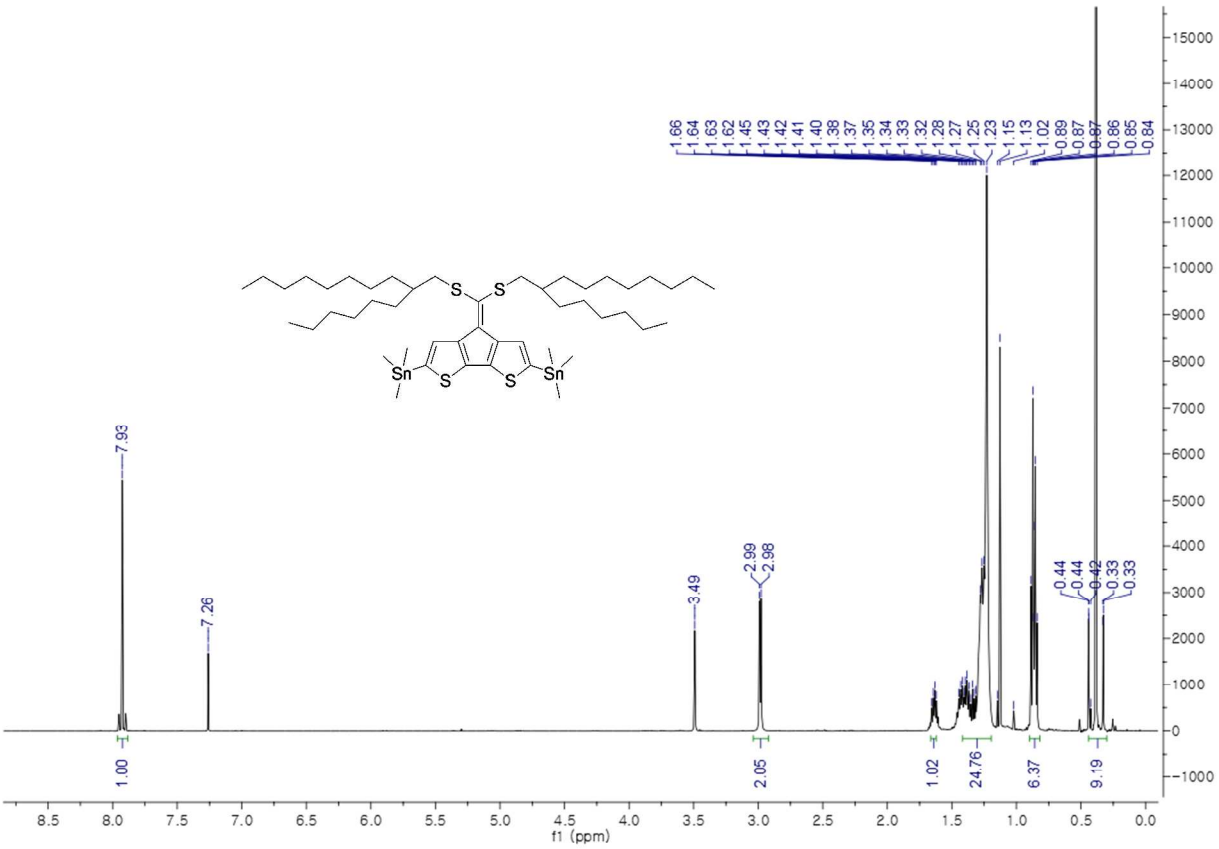

Figure S9. ^{1}H NMR spectrum of compound 2.

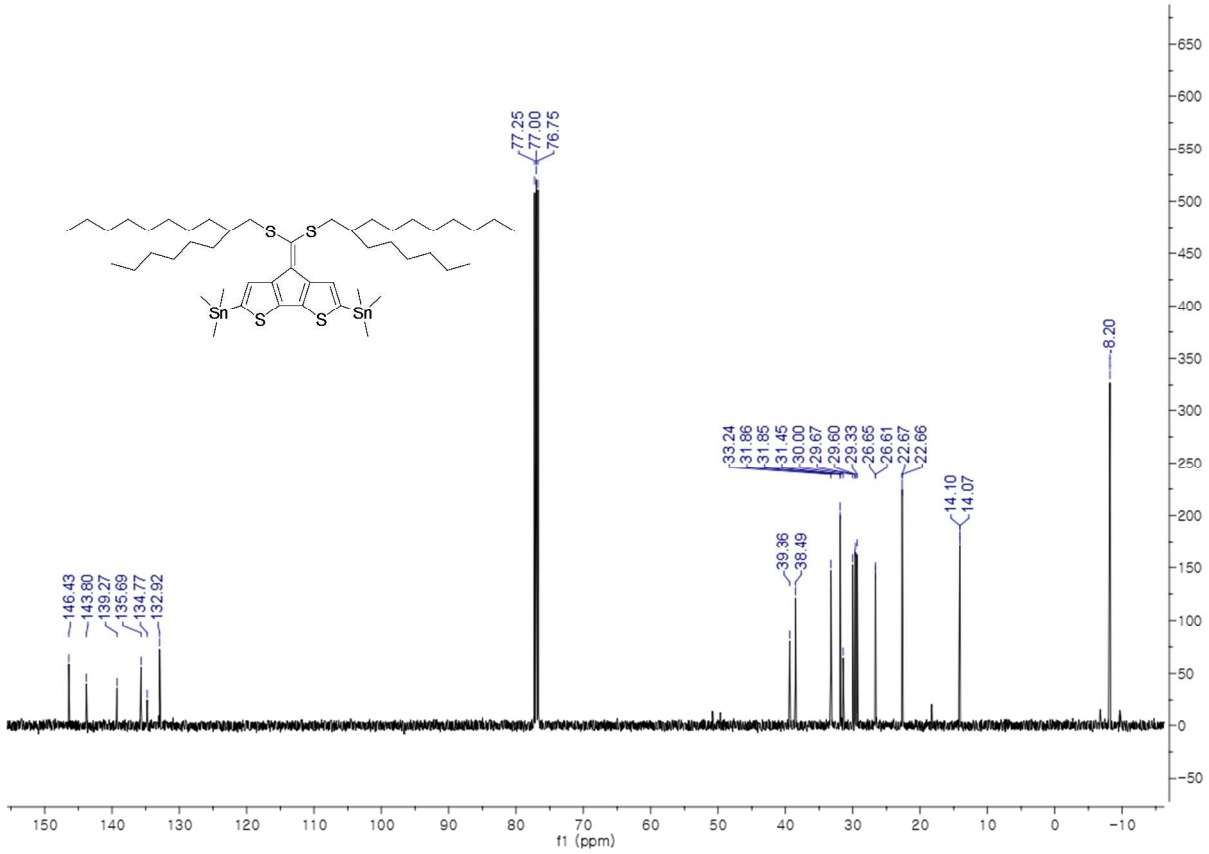

Figure S10. ^{13}C NMR spectrum of compound 2.

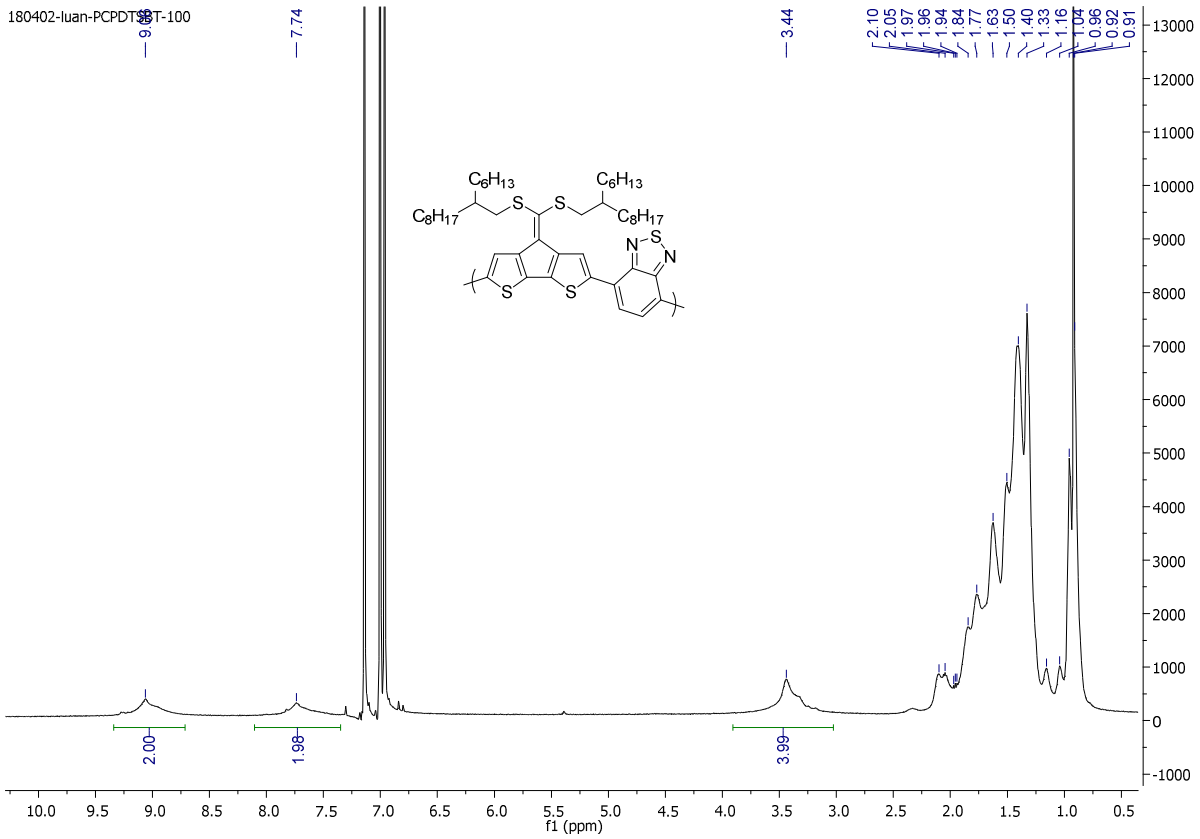

Figure S11. ^{1}H NMR spectrum of PCPDTSBT.

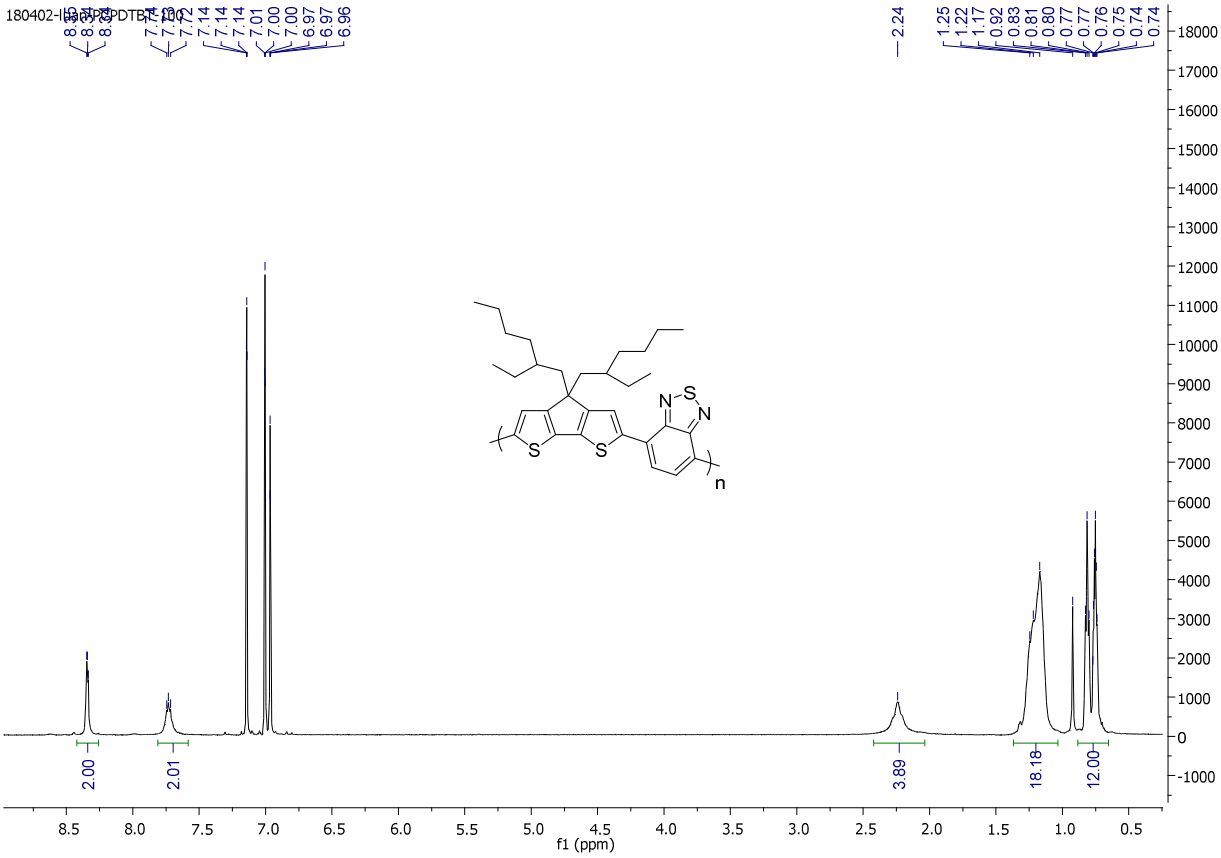

Figure S12. ^{1}H NMR spectrum of PCPDTBT.