Supporting Information

Modulation of Majority Charge Carrier from Hole to Electron by Incorporation of Cyano Groups in Diketopyrrolopyrrole-Based Polymers

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Figure S1. TGA thermograms of the polymers.

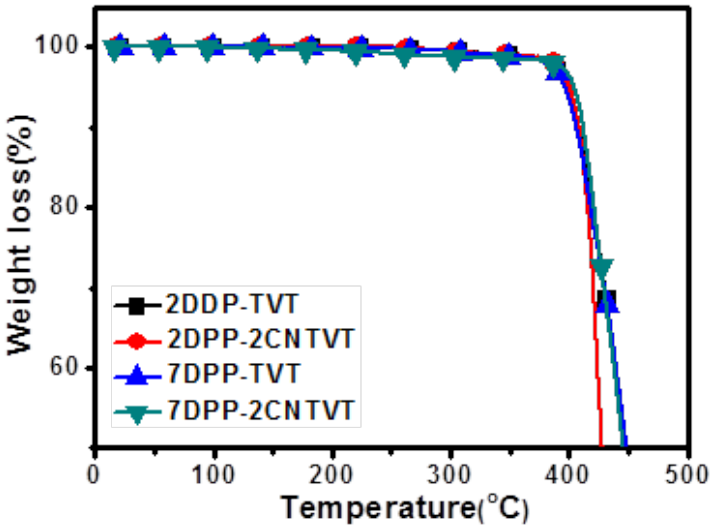


Figure S2. Cyclic voltammograms of the polymers.

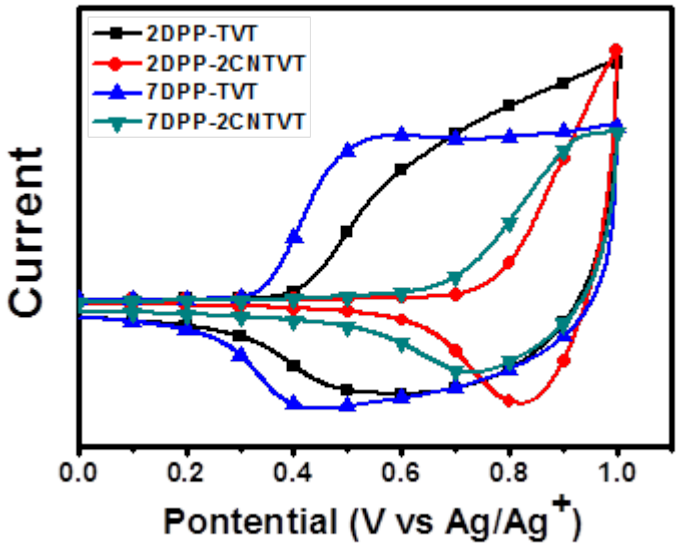


Figure S3. Energy-minimized structures (B3LYP/6-31G(d)) of the HOMO (bottom) and LUMO (top) of the model compounds DPP-TVT and DPP-2CNTVT, respectively.

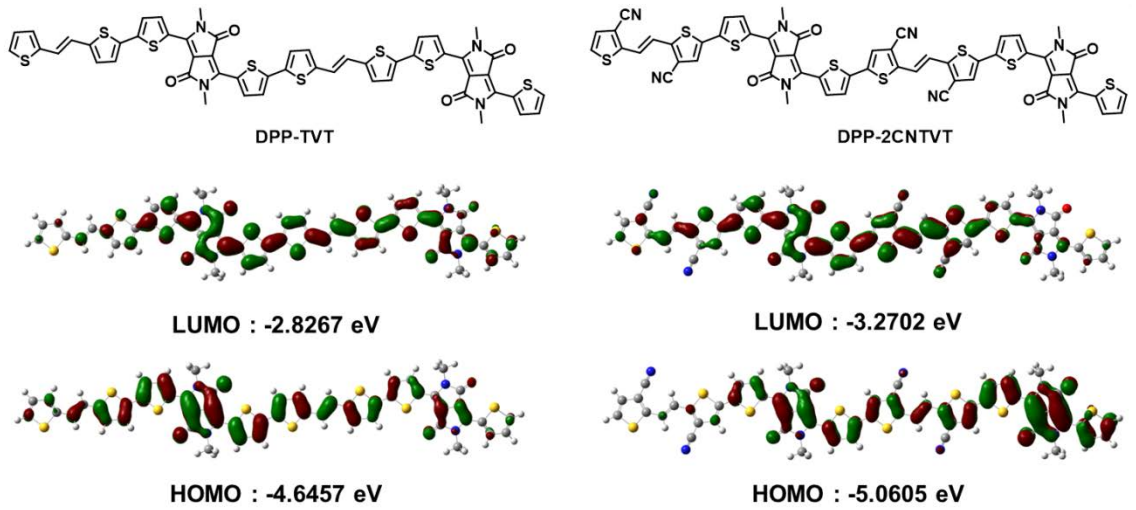


Figure S4. DFT calculated (B3LYP/6-31G(d)) dihedral angles at the minimum energy state of the model compounds and their top and side views.

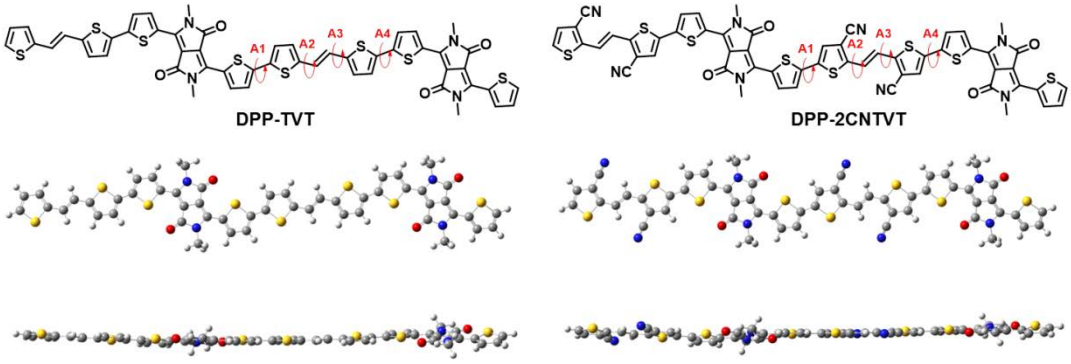


Table S1. DFT calculated dihedral angles of the model compounds.

Dimer	A1	A2	A3	A4
DPP-TVT	1.27	1.68	1.67	2.2
DPP-2CNTVT	0.97	0.69	0.77	3.7

Figure S5. DFT calculated (B3LYP/6-31G(d)) dipole moments of the monomers.

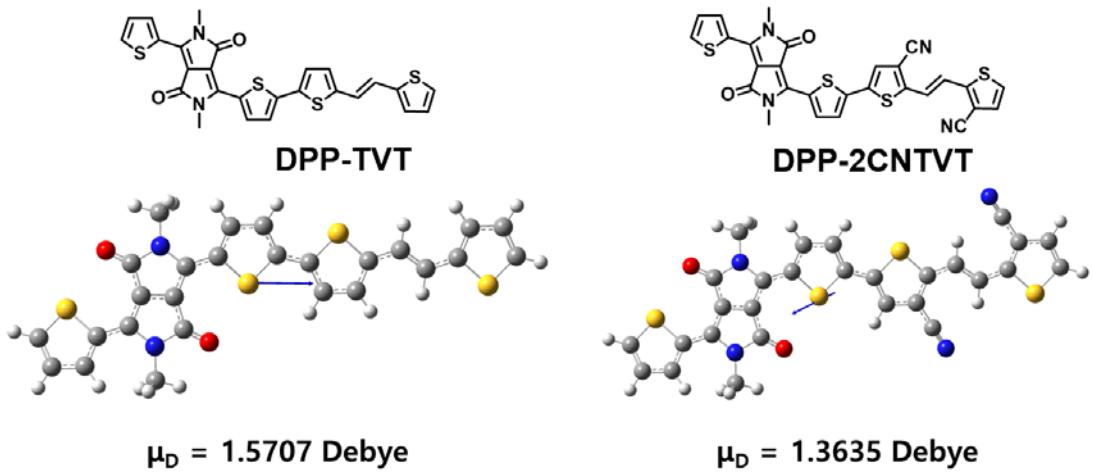


Figure S6. Transfer characteristics of (a) 2DPP-TVT, (b) 7DPP-TVT, (d) 2DPP-2CNTVT, and (e) 7DPP-2CNTVT. Mobility change and threshold voltage shift of the devices with (c) 2DPP-TVT and 7DPP-TVT, and (f) 2DPP-2CNTVT and 7DPP-2CNTVT, under continuous bias stress (1000 cycles, ca. 6 h of biasing), ("c" stands for "cycle").

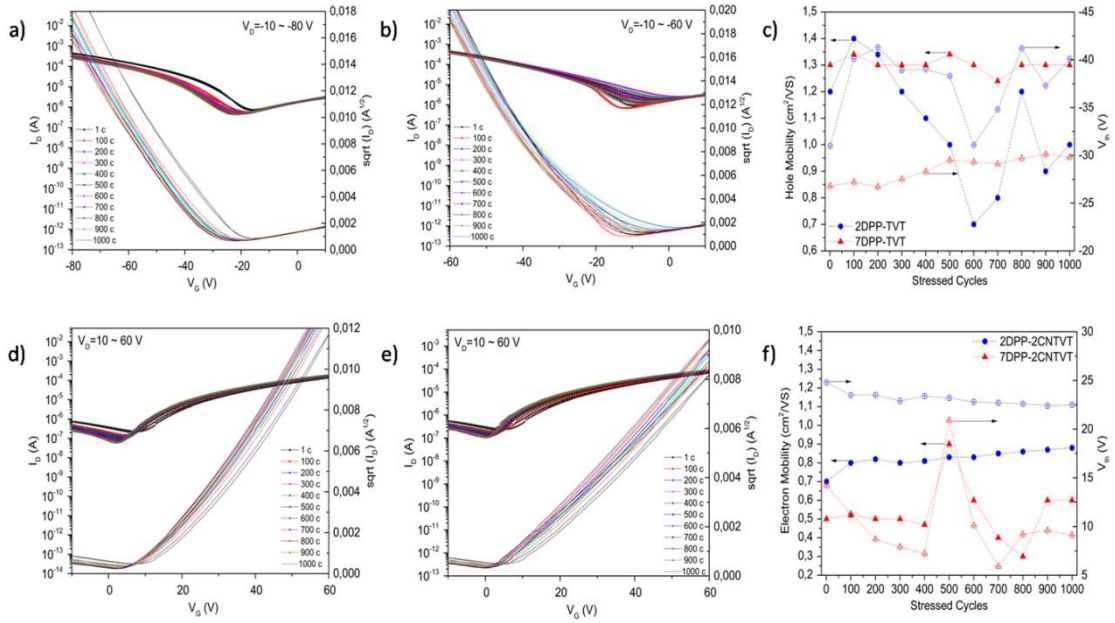


Figure S7. Transfer characteristics of (a) 2DPP-TVT, (b) 7DPP-TVT, d) 2DPP-2CNTVT, e) 7DPP-2CNTVT and mobility change and threshold voltage shift of the devices with (c) 2DPP-TVT, 7DPP-TVT and (f) 2DPP-2CNTVT, 7DPP-2CNTVT, respectively, under ambient conditions.

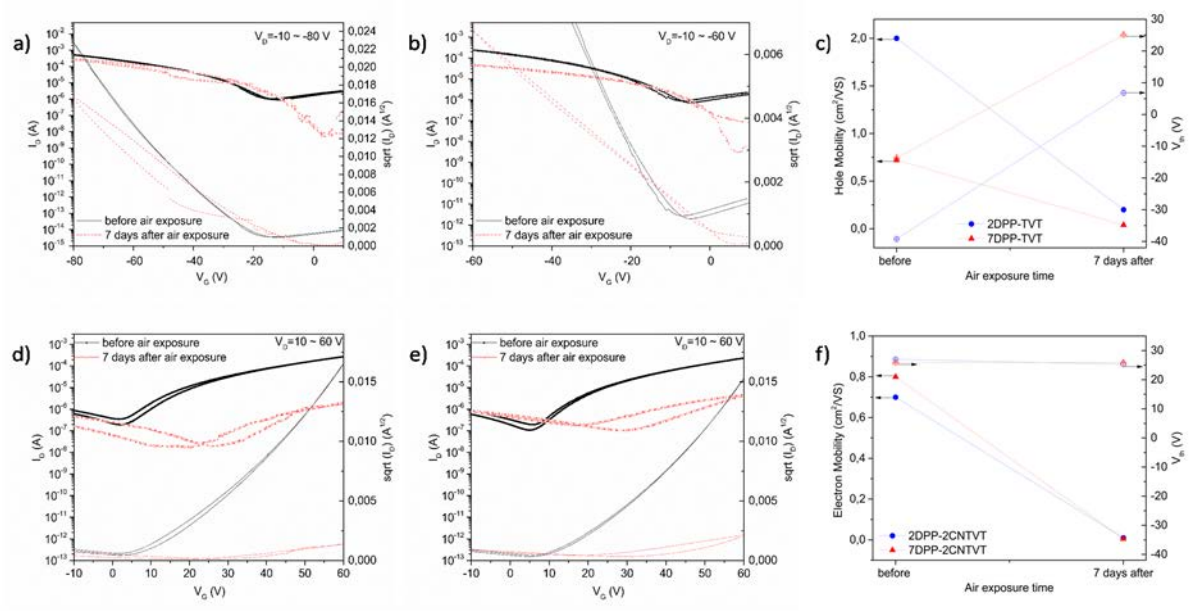


Figure S8. Azimuthal angle scans extracted from the lamellar diffraction (at q(100)) of the polymer films (a) 2DPP-TVT, (b) 2DPP-2CNTVT, (c) 7DPP-TVT, and (d) 7DPP-2CNTVT.

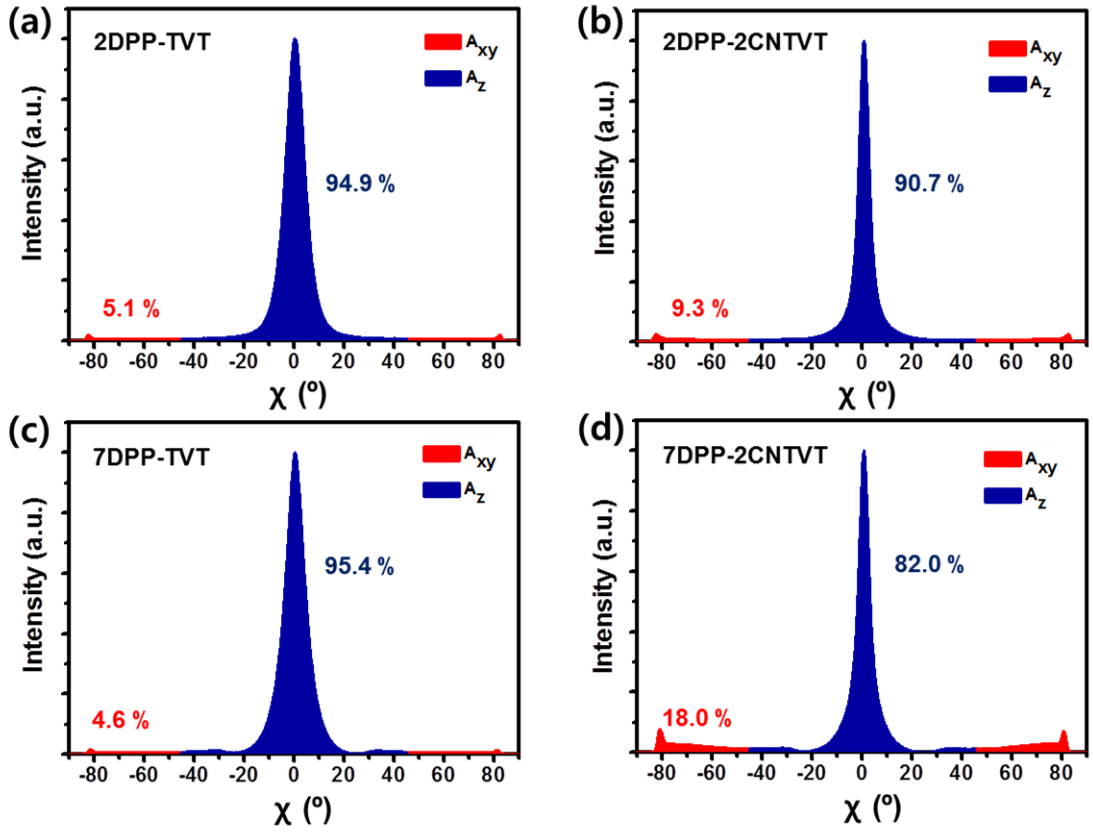


Table S2. Solid state packing parameters of the polymers thin films.

polymer	Annealing Temperature (^{o}C)	lamellar stacking		π-π stacking		orientation	A_{xy}/A_z
		q (Å^{-1})	d (Å)	q (Å)	d (Å)		
2DPP-TVT	250	0.270	23.2	1.676	3.748	edge-on	0.054
2DPP-2CNTVT	200	0.252	24.9	1.732	3.627	bimodal	0.102
7DPP-TVT	200	0.206	30.5	1.743	3.605	edge-on	0.048
7DPP-2CNTVT	250	0.206	30.5	1.750	3.590	bimodal	0.219

Figure S9. AFM height (top) and phase (bottom) images of (a) 2DPP-TVT, (b) 2DPP-2CNTVT, (c) 7DPP-TVT, and (d) 7DPP-2CNTVT films deposited at an optimal annealing temperature. The scale bar is 500 nm.

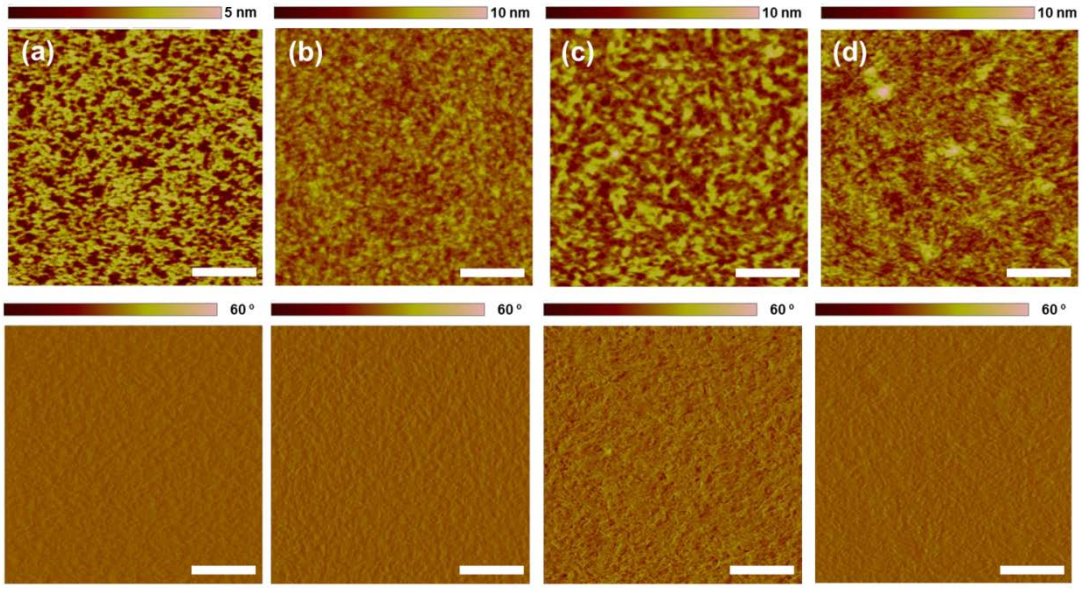
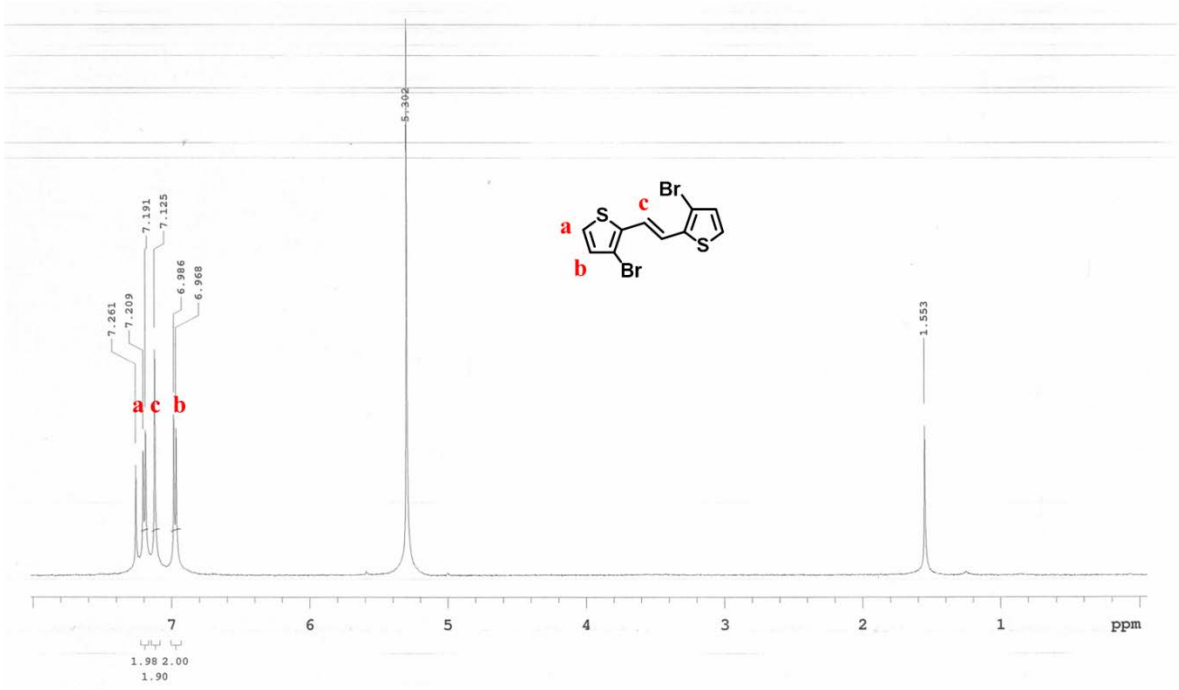


Figure S10. ^{1}H NMR and ^{13}C NMR spectrum of (*E*)-1,2-bis(3-bromothiophen-2-yl)ethene.



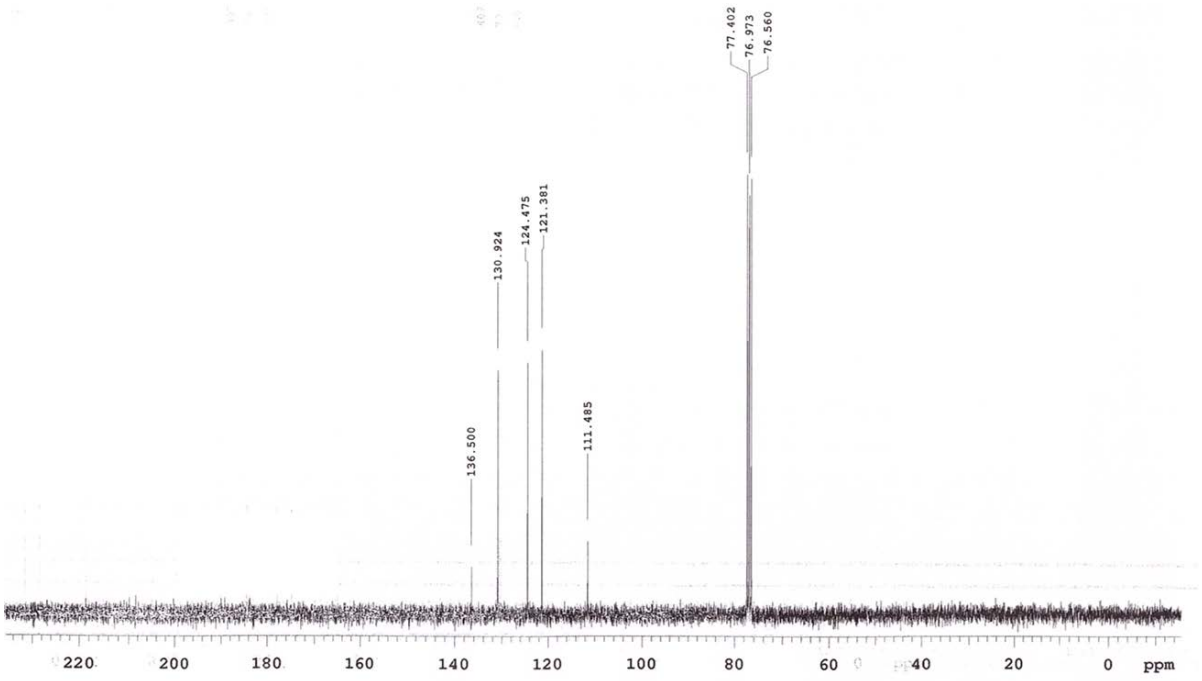


Figure S11. ^{1}H NMR and ^{13}C NMR spectrum of (*E*)-1,2-bis(3-cyanothiophene-2-yl)ethene.

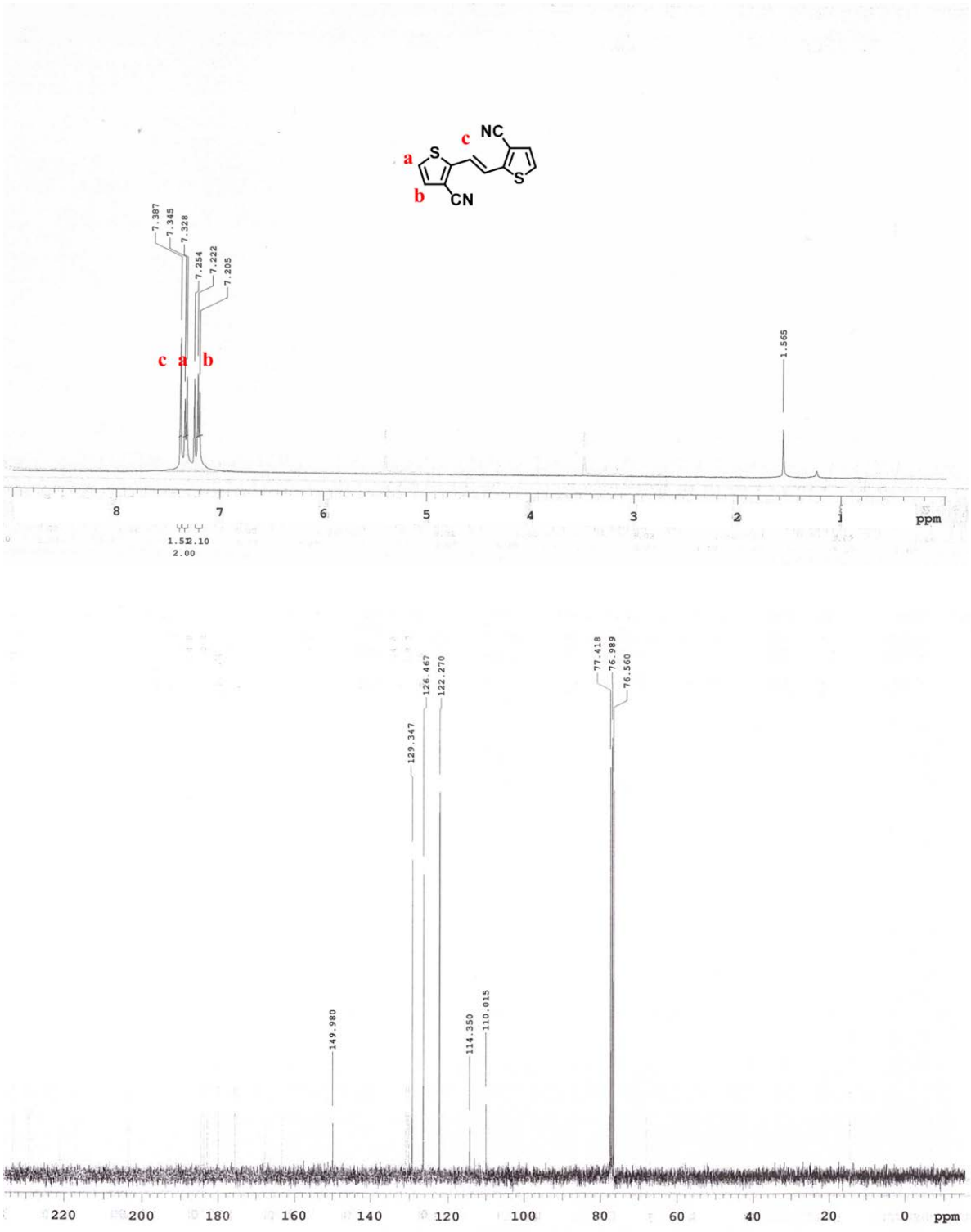
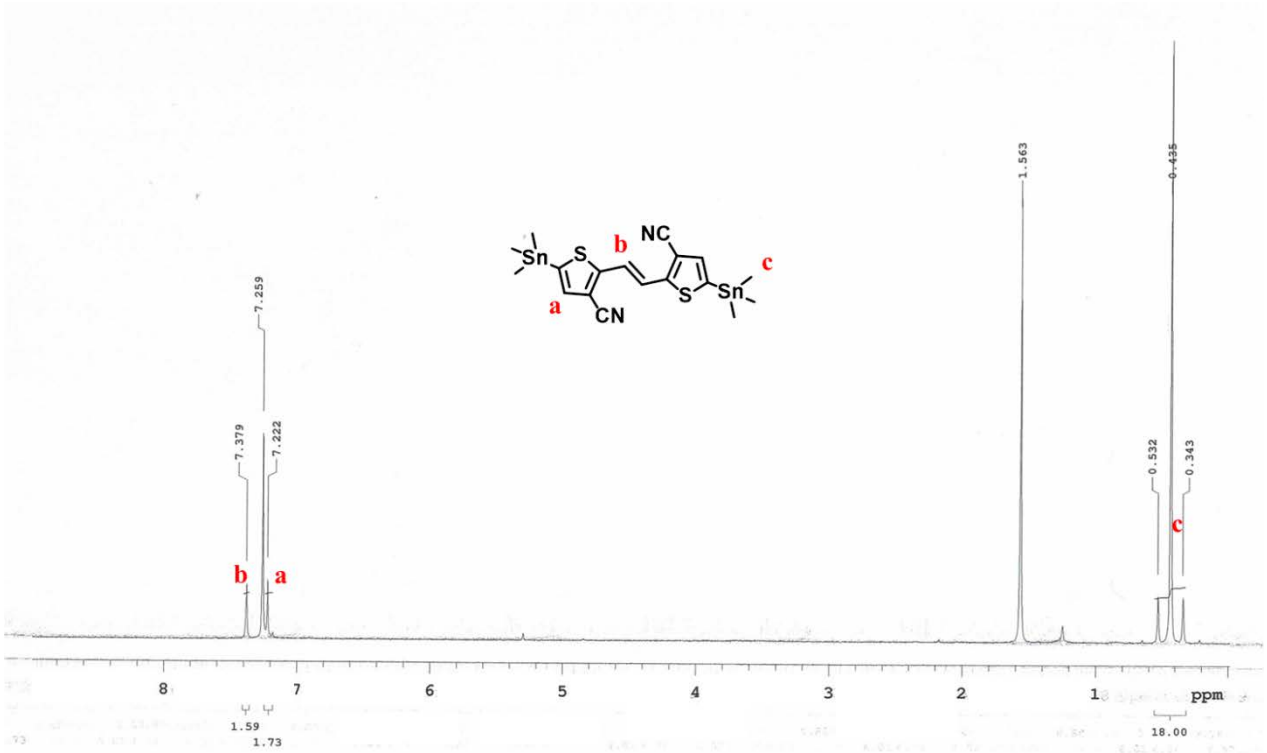


Figure S12. ^{1}H NMR and ^{13}C NMR spectrum of (*E*)-1,2-bis(5-(trimethylstannyl)-3-cyanothiophene-2-yl)ethene.



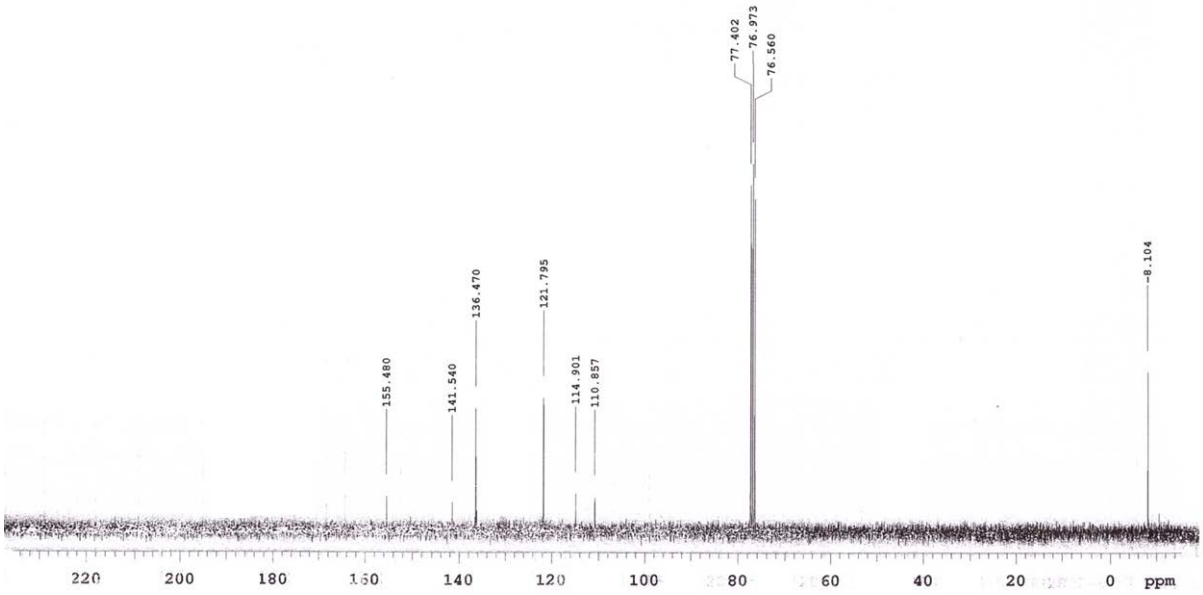


Figure S13. ^{1}H NMR spectrum of 2,5-bis(2-dodecylhexadecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione.

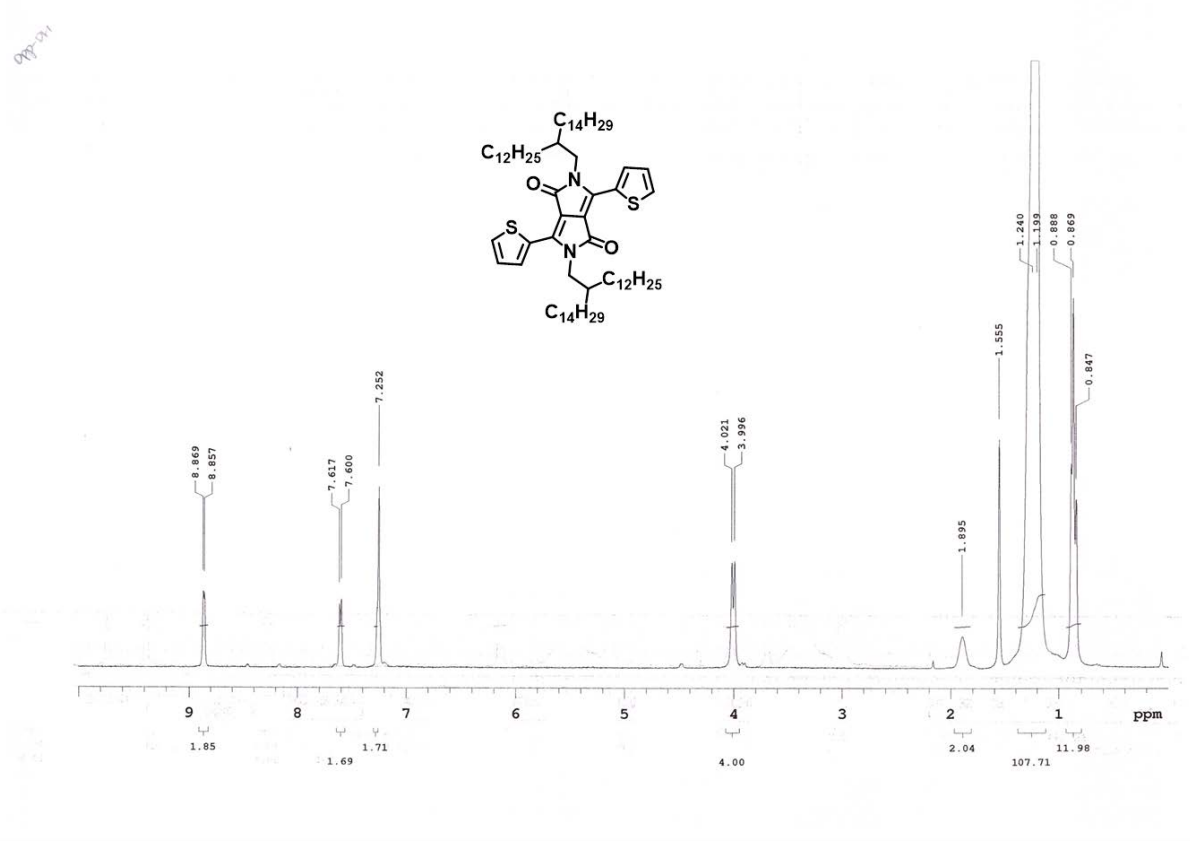


Figure S14. ^{1}H NMR spectrum of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-dodecylhexadecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione.

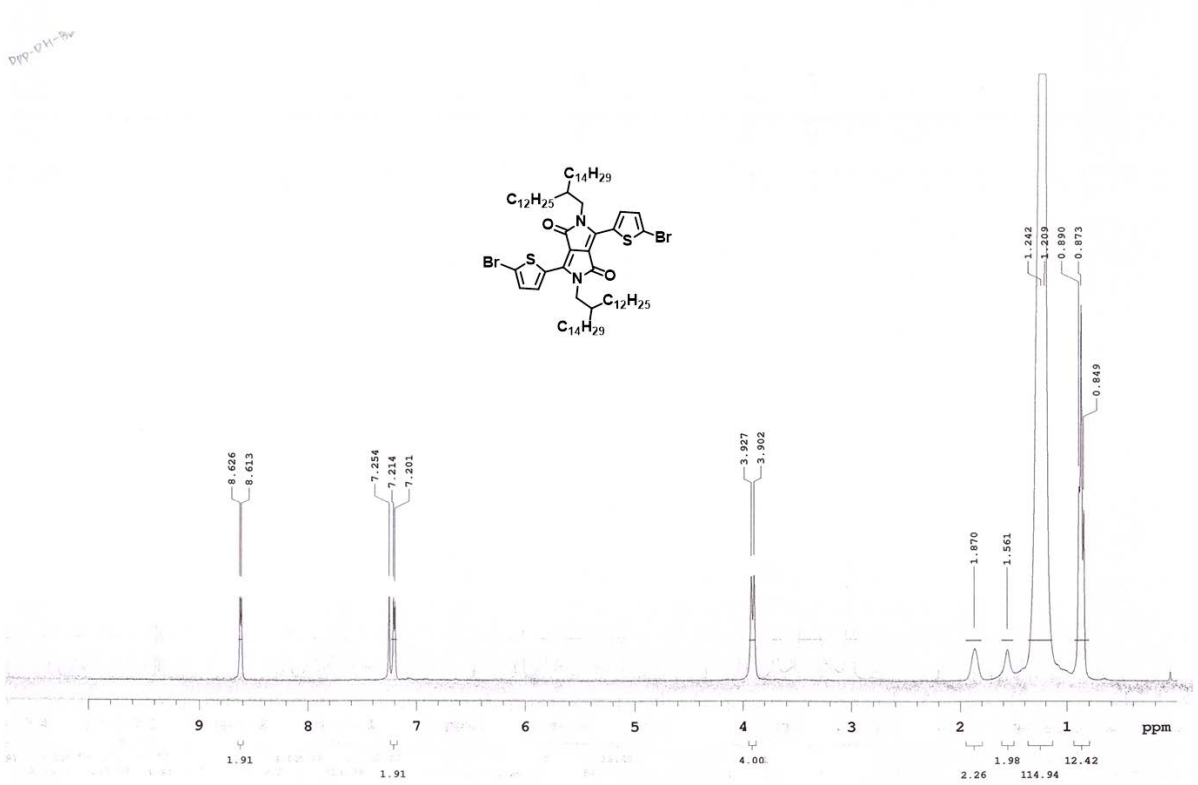


Figure S15. ^{1}H NMR spectrum of 2,5-bis(7-dodecylhenicosyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione.

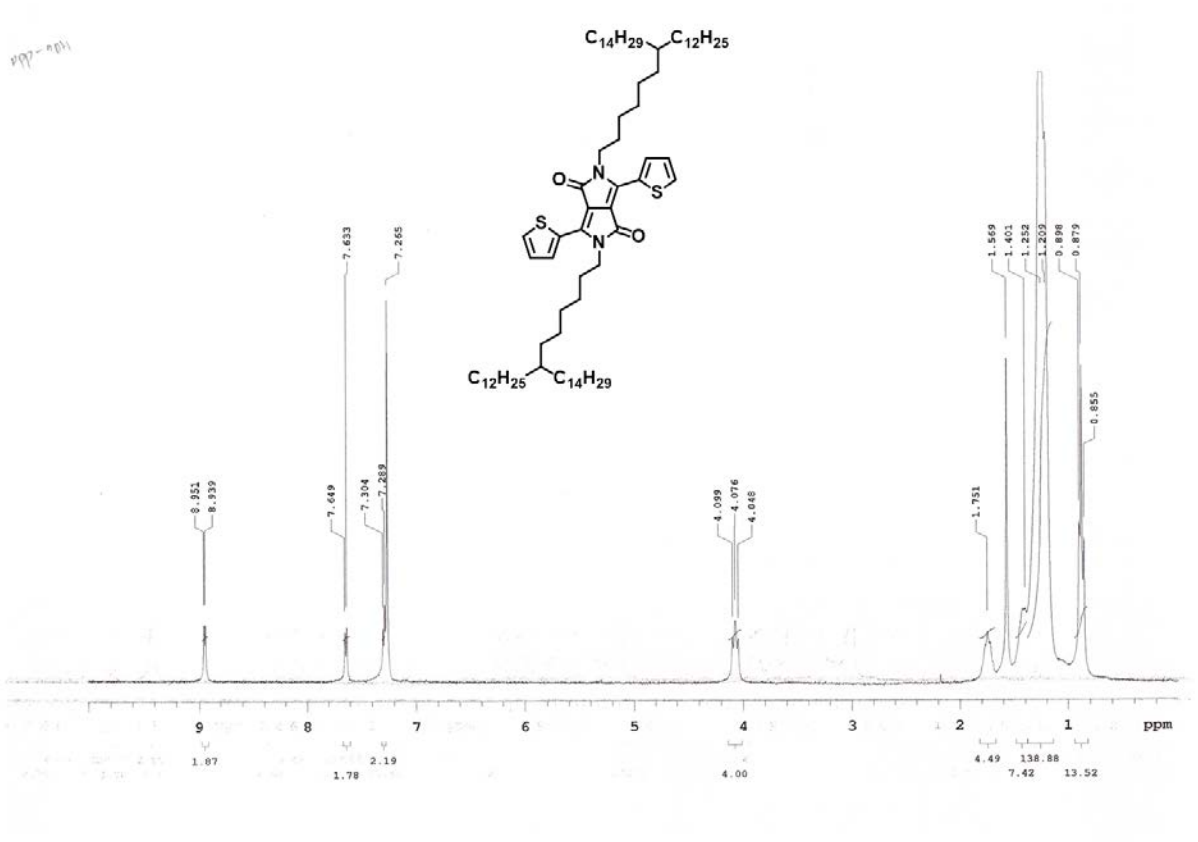


Figure S16. ^{1}H NMR spectrum of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(7-dodecylhenicosyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione.

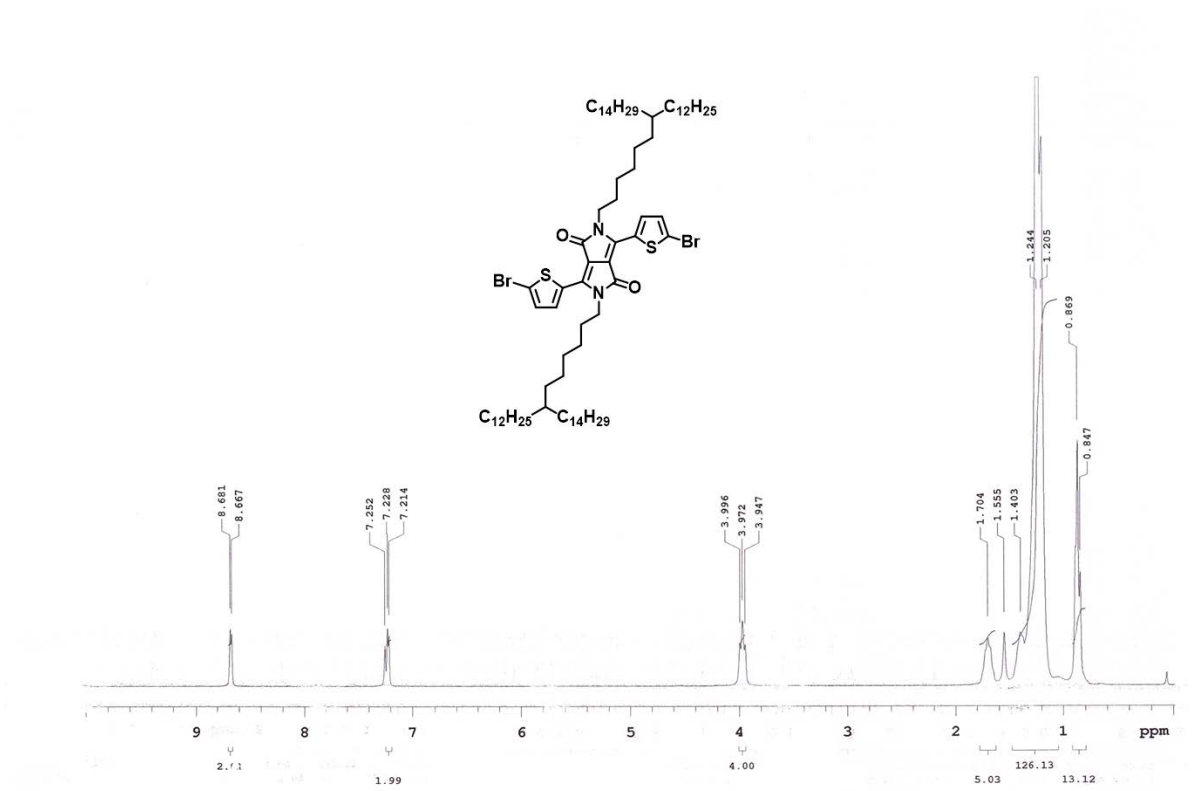


Figure S17. ^{1}H NMR spectrum of 2DPP-TVT.

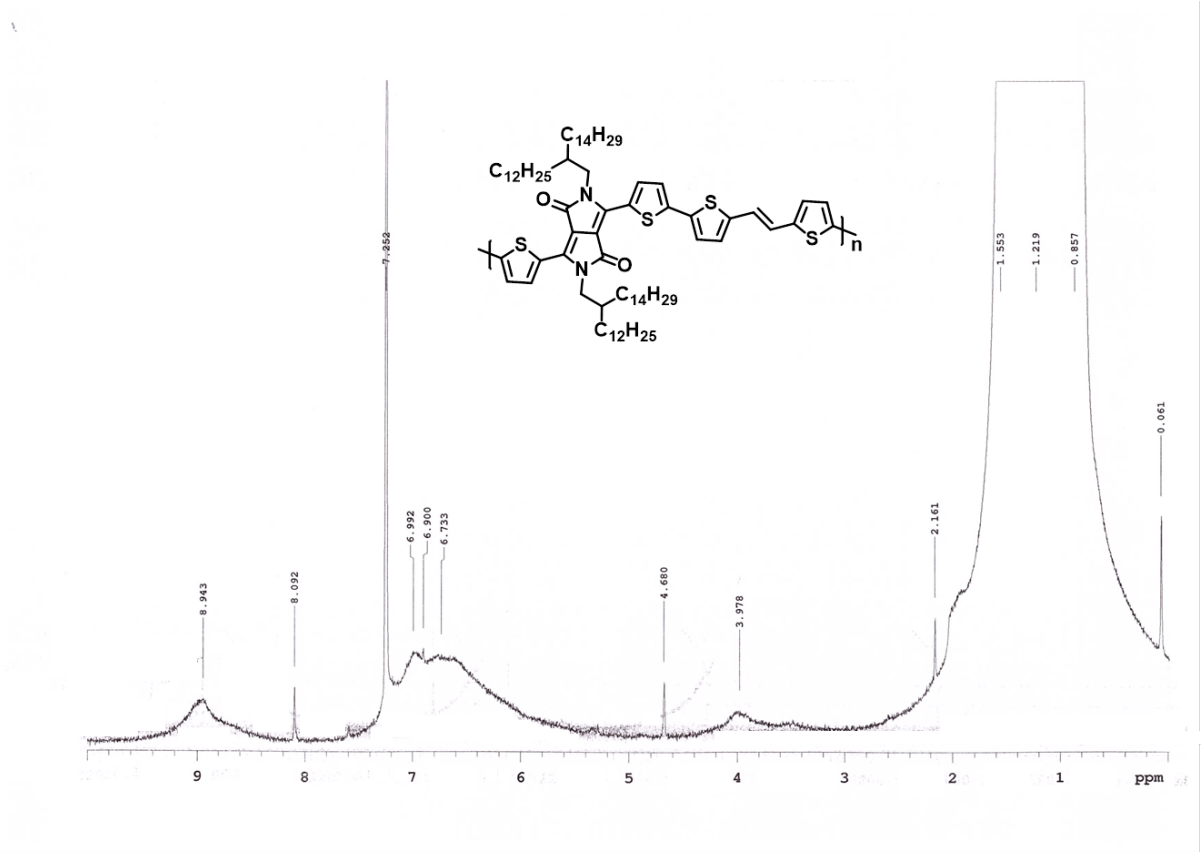


Figure S18. ^{1}H NMR spectrum of 2DPP-2CNTVT.

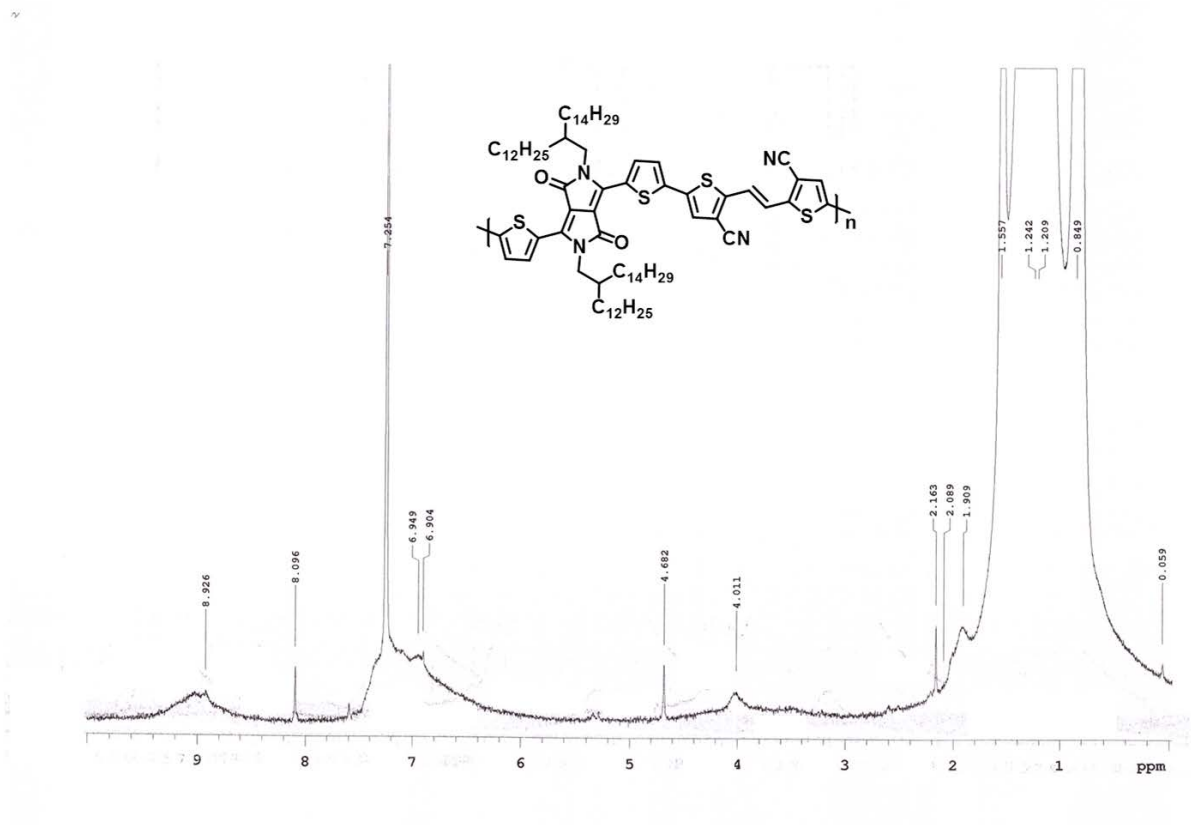


Figure S19. ^{1}H NMR spectrum of 7DPP-TVT.

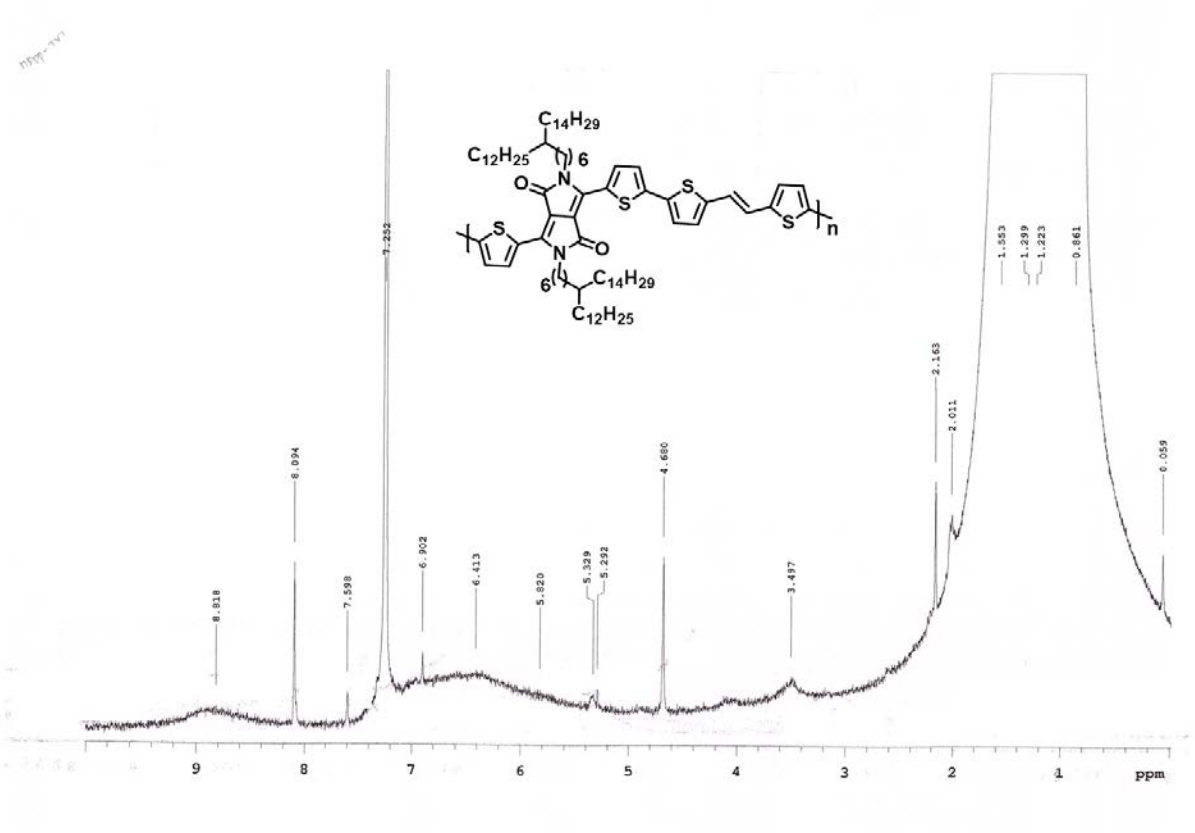


Figure S20. ^{1}H NMR spectrum of 7DPP-2CNTVT.