

Supporting Information

For

Manipulation on the Electrical Characteristics of Nonvolatile Transistor-Type Memory Devices through the Acceptor Strength of Donor-Acceptor Conjugated Copolymers

Chien Lu,^a Wen-Ya Lee^{b*} and Wen-Chang Chen^{a*}

^{a.} Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan, R.O.C. E-mail: chenwc@ntu.edu.tw

^{b.} Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 106, Taiwan, ROC. E-mail: wenyalee@mail.ntut.edu.tw

Polymerization of PDTT-DPP.

The similar structure of PDTT-DPP with different alkyl chain length were developed by McCulloch group for photovoltaic devices.³⁸ Amounts of 261mg of 2,6-bis(tri-n-butylstannyl)dithieno[3,2-b:2',3'-d]thiophene (0.50 mmol), 452 mg of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.50 mmol), tri(o-tolyl)phosphine (16 mol% with respect to the monomer), and tris(dibenzylideneacetone)dipalladium(0) (2 mol % with respect to ditin monomer) were dissolved in 15ml of chlorobenzene. Then, the copolymer was synthesized by Pd(0)-catalyzed Stille coupling polymerization under microwave heating. After end-capped with trimethyl(thiophen-2-yl)stannane and bromothiophene (both 1.1 equiv. with respect to the monomers), the mixture was cooled and poured into methanol to afford a dark green solid (yield, 65%). ¹HNMR (CDCl₃), δ (ppm): 9.25-8.73 (br, Ar-H), 7.71-6.69 (m, br, Ar-H), 4.35- 3.62 (br,N-CH₂), 2.12-1.86 (m, br, -CH), 1.49-0.97 (m, br,-CH₂), 0.98-0.62 (m, br,-CH₃). Anal. Calcd for [C₅₆H₇₈N₂O₂S₅]: C, 69.23; H, 8.09; N, 2.88; O, 3.29; S, 16.50. Found: C, 67.02; H, 7.65; N, 2.48; O, 3.97; S, 18.88. Weight average molecular weight (Mw) and polydispersity index (PDI) estimated from GPC are 27550 g/mol and 1.62, respectively. The crude polymer was purified by methanol, acetone and hexane successively using a Soxhlet extraction to remove byproducts, oligomers and catalyst residues.

Table S1 Optical and electrochemical properties of the studied conjugated polymers.

polymer	UV-visible	Absorption		cyclic voltammetry		
	λ_{\max} (sol.) ^a (nm)	λ_{\max} (film) ^a (nm)	E_g^{opt} (eV)	HOMO (V/eV)	LUMO (V/eV)	E_g^{ec} (eV)
P4T-DTT	500	536	1.69	-5.14	-3.10	2.04
P4T-Q	528	546	1.83	-5.28	-3.22	2.06
P4T-BT	566	606	1.60	-5.04	-3.38	1.66
P4T-DPP	698	753	1.29	-5.17	-3.62	1.55
PDTT-DPP	702	705	1.36	-5.12	-3.56	1.56

^a DCB as processing solution.

Table S2 FET characteristics of the studied conjugated polymers.

Polymer		p-type mobility ^{avg} (cm ² V ⁻¹ s ⁻¹)	on/off ^{avg}	V _t ^{avg} (V)
P4T-DTT	P	(1.19±0.32)×10 ⁻¹	1.52×10 ⁵	-3
	N	-	-	-
P4T-Q	P	(3.05±0.24)×10 ⁻⁴	3.08×10 ³	-12
	N	-	-	-
P4T-BT	P	(2.70±0.73)×10 ⁻²	2.55×10 ³	15
	N	(3.22±0.43)×10 ⁻⁴	2.14×10 ²	84
P4T-DPP	P	(1.01±0.56)×10 ⁻¹	1.63×10 ⁴	-7
	N	(1.07±0.76)×10 ⁻³	1.33×10 ³	56
PDTT-DPP	P	(1.44±0.34)×10 ⁻¹	1.66×10 ³	-12
	N	(6.69±1.14)×10 ⁻³	2.07×10 ³	63

Table S3. The relationship between film thickness and memory window of P4T-BT, P4T-DPP and PDTT-DPP.

	Thickness (nm)	Positive V _t (V)	Negative V _t (V)	Memory window (V)	Memory Window ^{avg} (V)
P4T-BT	181	29.33	-21.04	50.37	
	122	31.66	-24.72	56.38	54.05
	67	30.78	-24.64	55.42	
P4T-DPP	173	37.78	-29.56	67.34	
	117	48.66	-29.31	77.97	74.81
	50	47.85	-31.27	79.12	
PDTT-DPP	166	37.89	-13.21	51.1	
	115	42.83	-12.33	55.16	53.63
	56	42.42	-12.21	54.63	

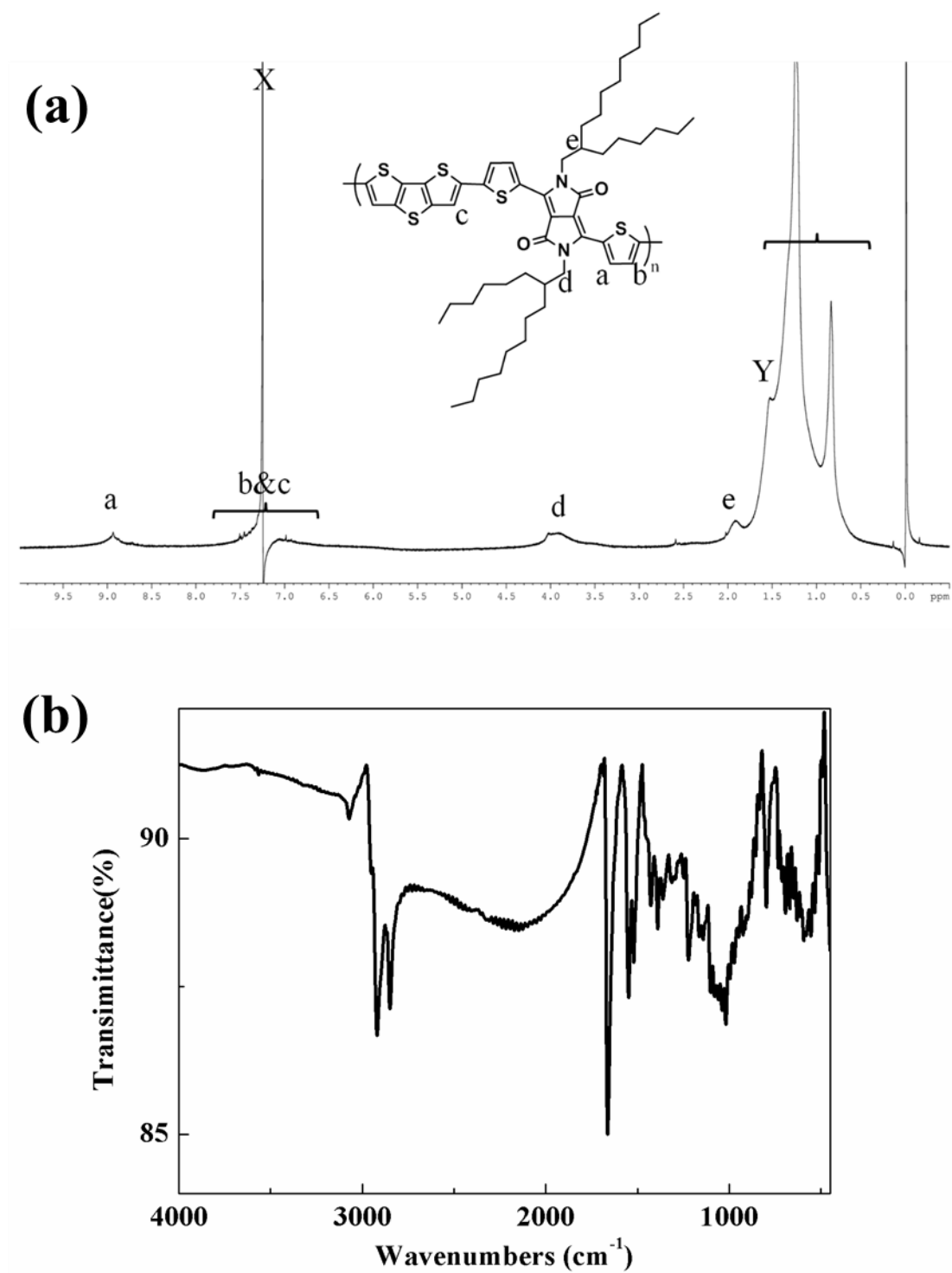


Fig. S1 (a) ^1H NMR spectrum of PDTT-DPP in CDCl_3 ($\text{X}=\text{CDCl}_3$, $\text{Y}=\text{H}_2\text{O}$) and (b) FTIR spectrum of PDTT-DPP powder.

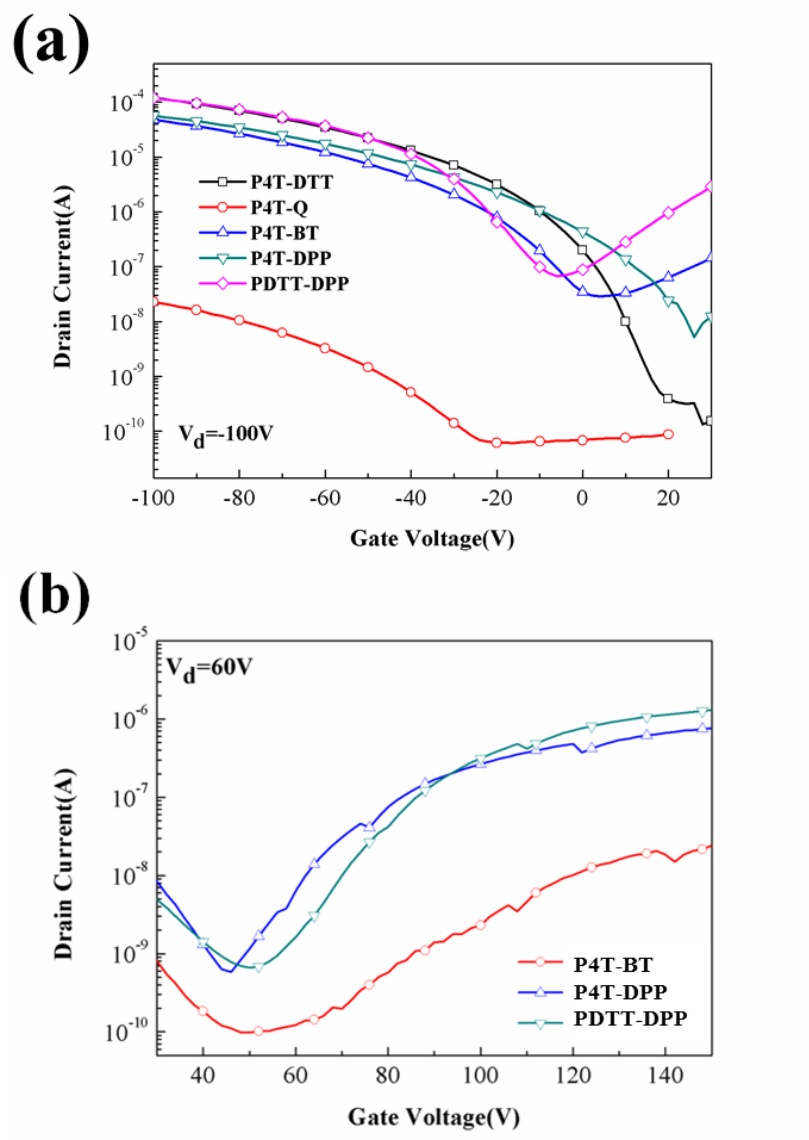


Fig. S2 The FET transfer characteristics of the polymers: (a) p-type and (b) n-type performance.

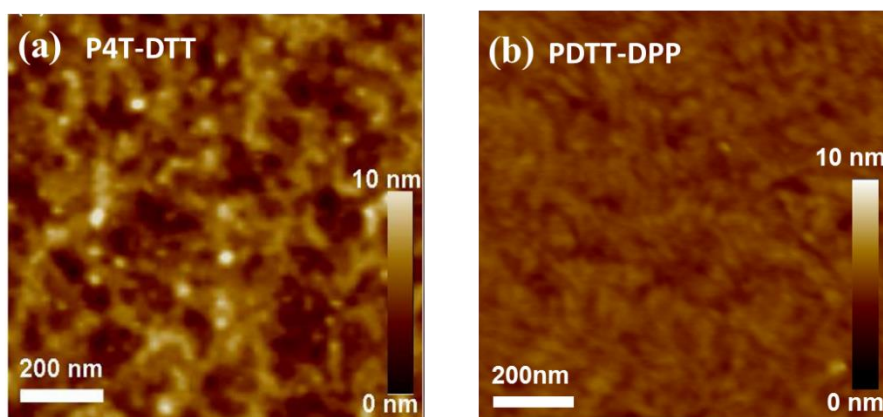


Fig. S3. AFM height images of (a) P4T-DTT and (b) PDTT-DPP films.

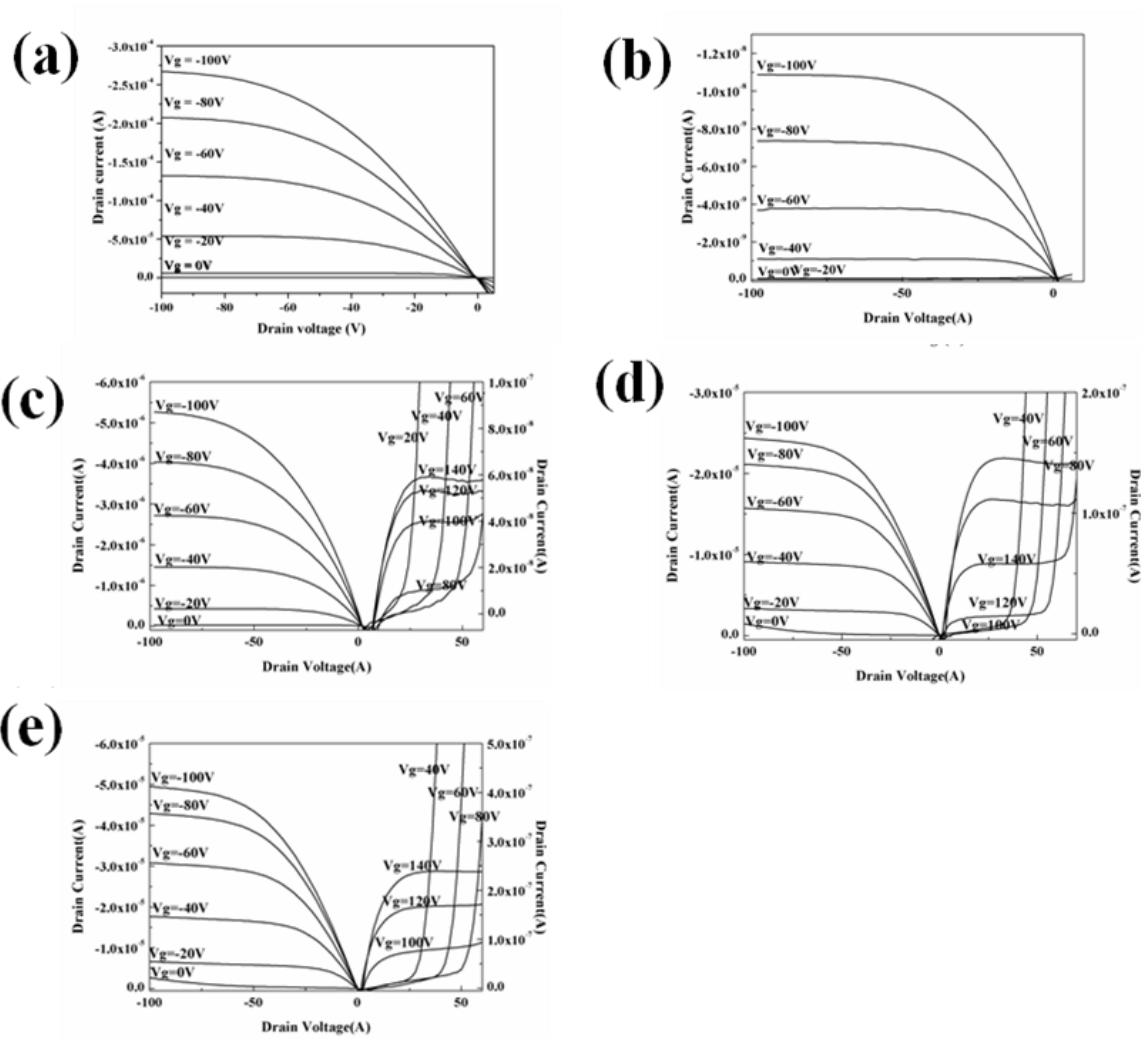


Fig. S4 The FET output characteristics of (a) P4T-DTT, (b) P4T-Q, (c) P4T-BT, (d) P4T-DPP, and (e) PDDT-DPP.

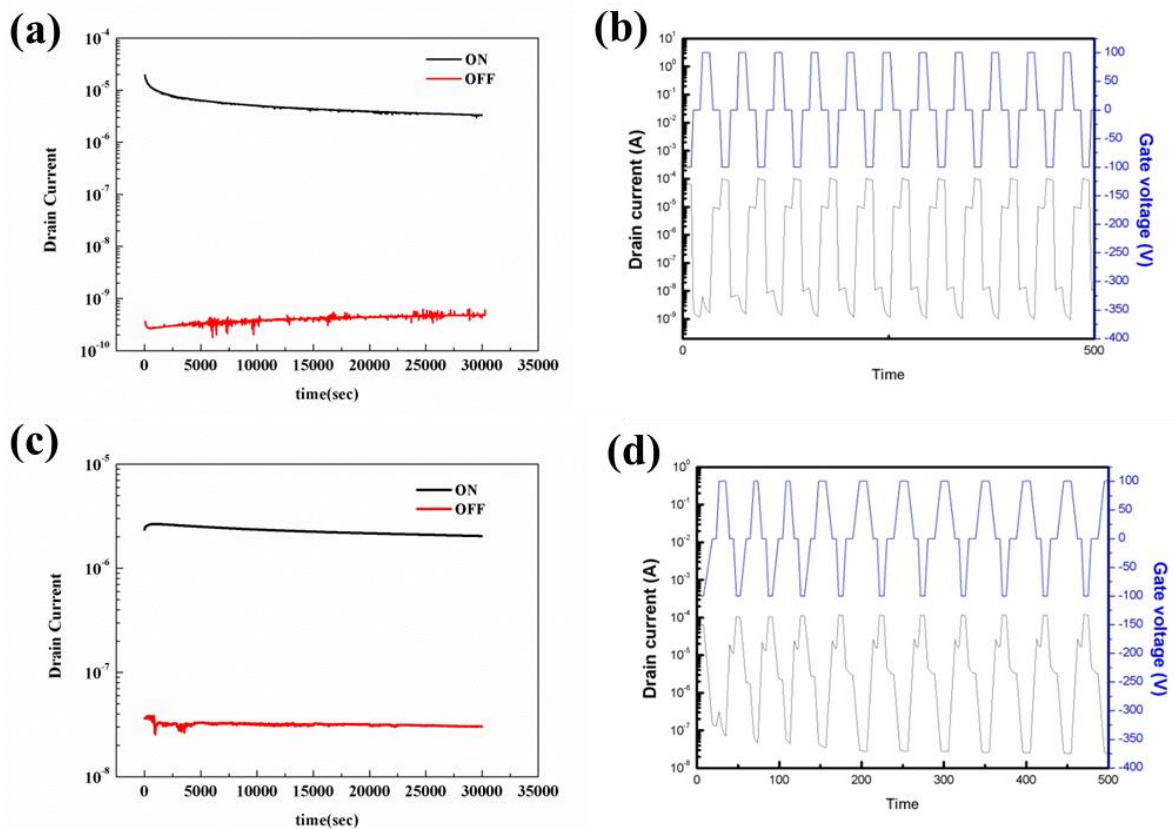


Fig. S5 Retention time and WRER curves of the conjugated polymer-based OFET memory devices with (a, b) PDDT-DPP and (c, d) P4T-BT as active layers. The retention time of the devices were operated at a read voltage of 10 V longer than 30000s. The drain current of WRER cycles was measured at $V_d = -100$ V and The writing, reading and erasing are set to the gate voltage of 100, 0 and -100 V, respectively, up to 200 cycles.

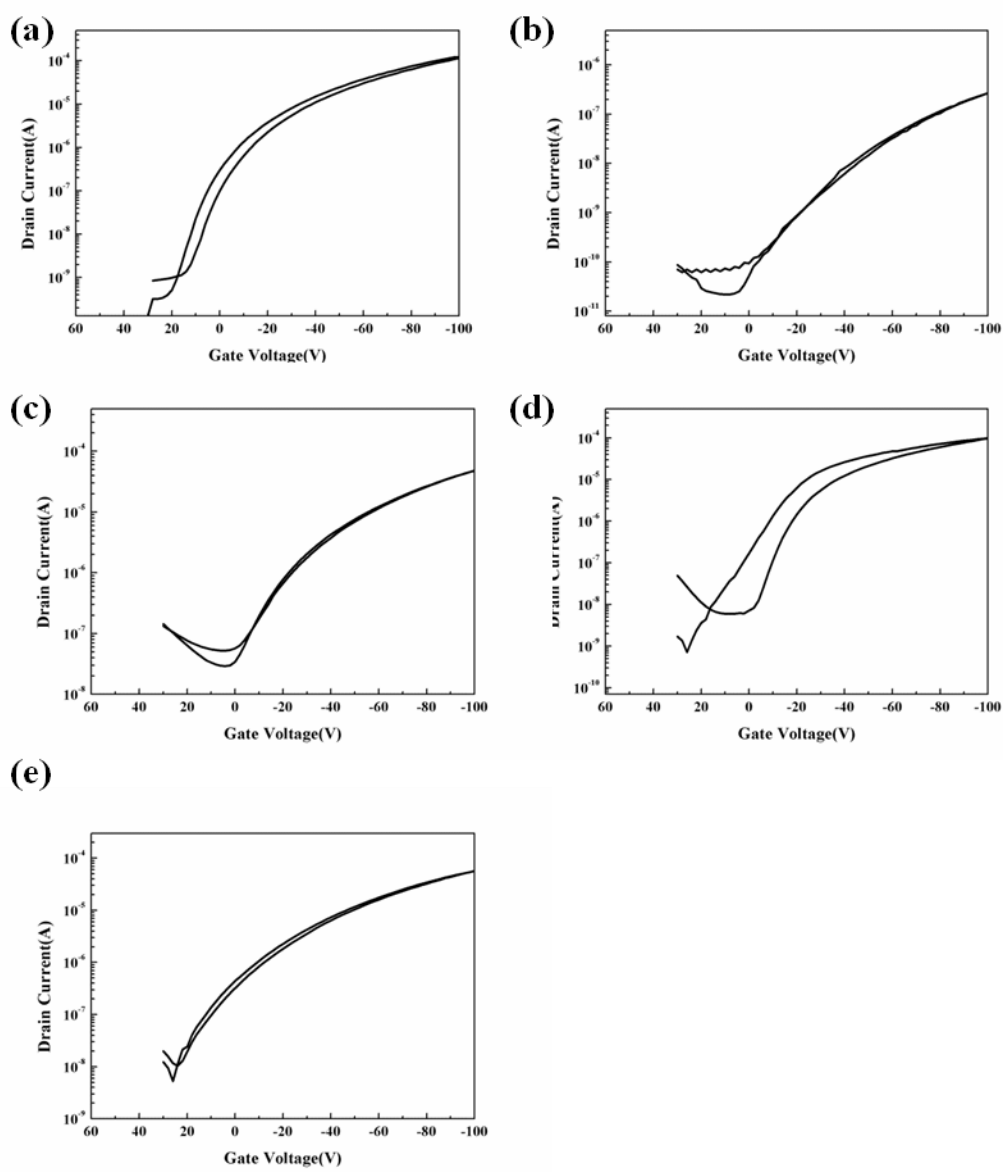


Fig. S6 The initial dual sweep of (a) P4T-DTT, (b) P4T-Q, (c) P4T-BT, (d) P4T-DPP, and (e) PDTT-DPP.

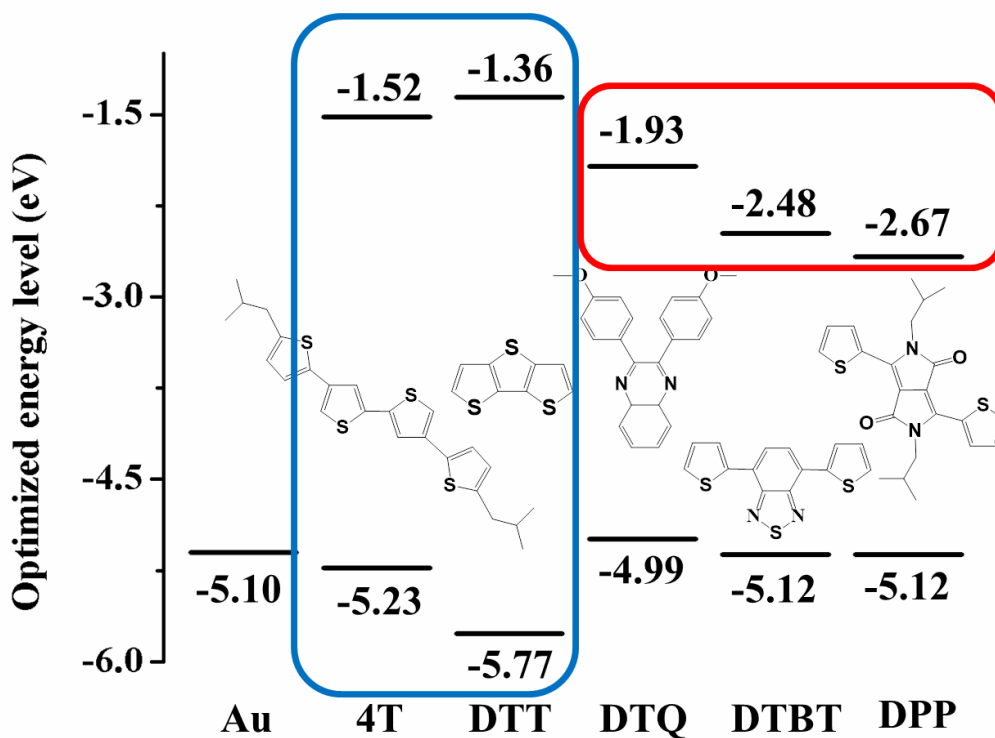


Fig. S7 DFT molecular simulation results (B3LYP/6-31G(d) level): LUMO and HOME energy levels for the basic unit of donor and acceptor moieties with the work function of Au electrodes.

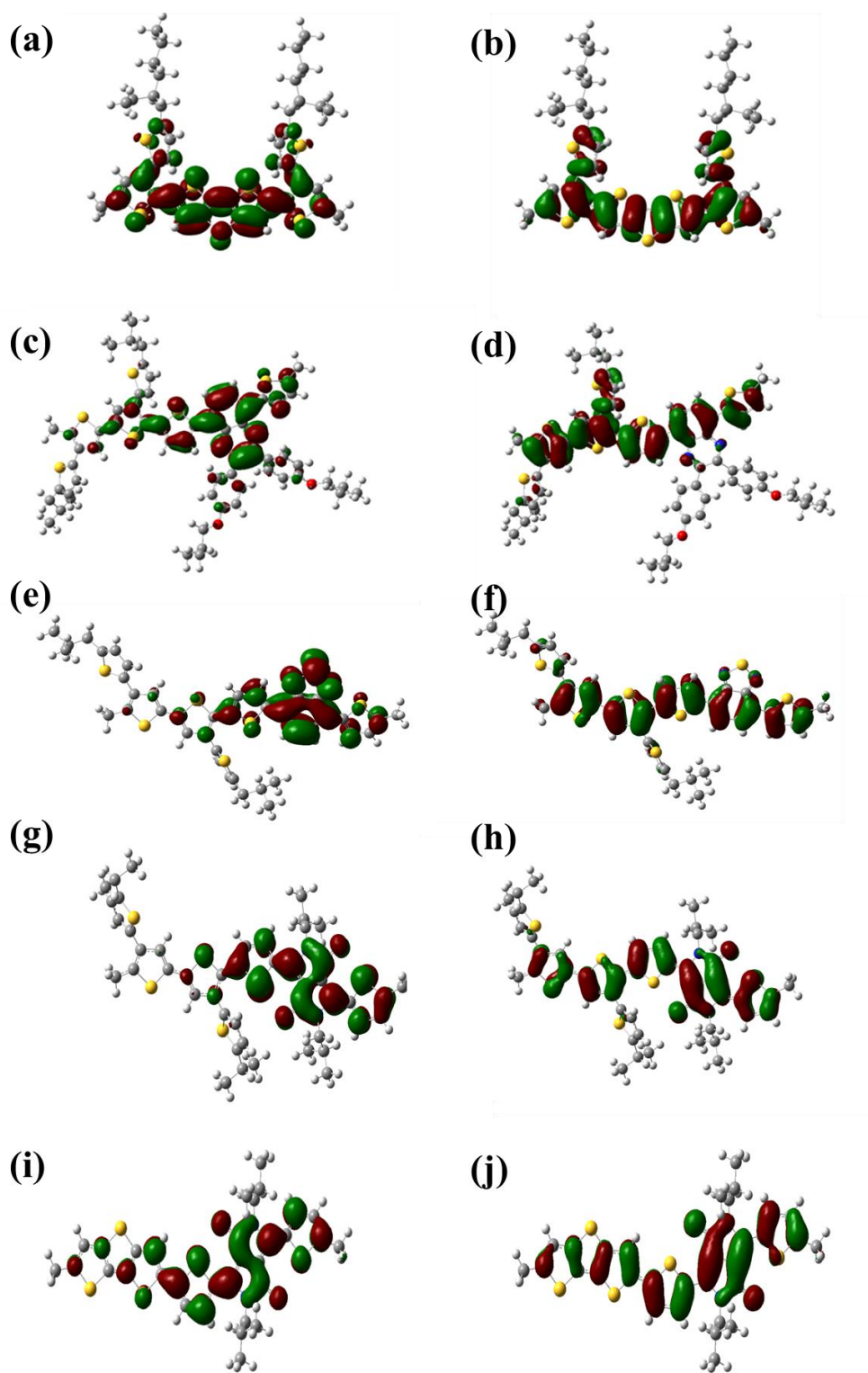


Fig. S8 Molecular orbitals of the LUMO levels of (a) P4T-DTT, (c) P4T-Q, (e)P4T-BT (g)P4T-DPP, (i) PDTT-DPP ,and HOMO levels of (b) P4T-DTT, (d) P4T-Q, (f)P4T-BT (h)P4T-DPP, (j) PDTT-DPP.