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Electronic Supporting Information

Flexible Memory Devices with Tunable Electrical Bistability via Controlled Energetic in Donor-Donor and Donor-Acceptor Conjugated Polymers

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Experimental Section

Materials: The CPs **CP1-CP4** were prepared according to a previously reported procedure.[13] Bottom electrode ITO (15±1 nm; surface resistivity 300 Ω/sq) coated PET (177.8 μm) was used as commercially purchased. All other reagents were used as received from commercial sources.

Fabrication of the Flexible Memory Device: The memory devices were fabricated with the configuration of ITO coated PET/polymer CPs/Al shown in Figure 1b. The ITO coated PET used for memory device was pre-cleaned by ultra-sonication with water, acetone, and isopropanol each for 15 min. A 150 μl $CHCl_3$ solution of CPs (15 mg/ml) was spin-coated onto the ITO coated PET at a rotation rate of 1000 rpm for 60 s and heated at 100 ^{o}C for 10 mins under Argon. The film thickness was determined and controlled to be around 160 nm. Finally, a 100-nm-thick Al top electrode was thermally evaporated through the shadow mask at a pressure of 2×10^{-7} torr with a depositing rate of 1-3 Å/s.

Measurements: Electrochemistry was performed with a CH Instruments 612C electrochemical analyzer. Voltammograms were presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry (CV) was conducted with the use of a three-electrode cell in which glassy carbon was used as working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken by using an Ag/AgCl, KCl (sat.) reference electrode. The absorption spectra were measured using a Varian Cary 500 UV-Vis-near infrared (NIR) spectrophotometer. The electrical characterization of the memory device was performed by a computer-controlled Keithley 236 Series Source-Measure Units and tested inside an Argon-filled glove box. ITO was used as common electrode and Al was the electrode for applying voltage during the sweep. The probe tip of a gold shaft with a point radius <0.1 μm was attached to 10 μm diameter gold wire (GGB Industries, Inc.). The Gaussian 09 program package is used for theoretical calculation in this research, and the basic units were optimized by means of the density functional theory (DFT) method at the B3LYP level of theory (Beckesstyle three-parameter density functional theory using the Lee-Yang-Parr correlation functional) with the 6-31G(d) basic set. The thickness of the polymer thin films was measured by Bruker Dektak XT contact profilometer.

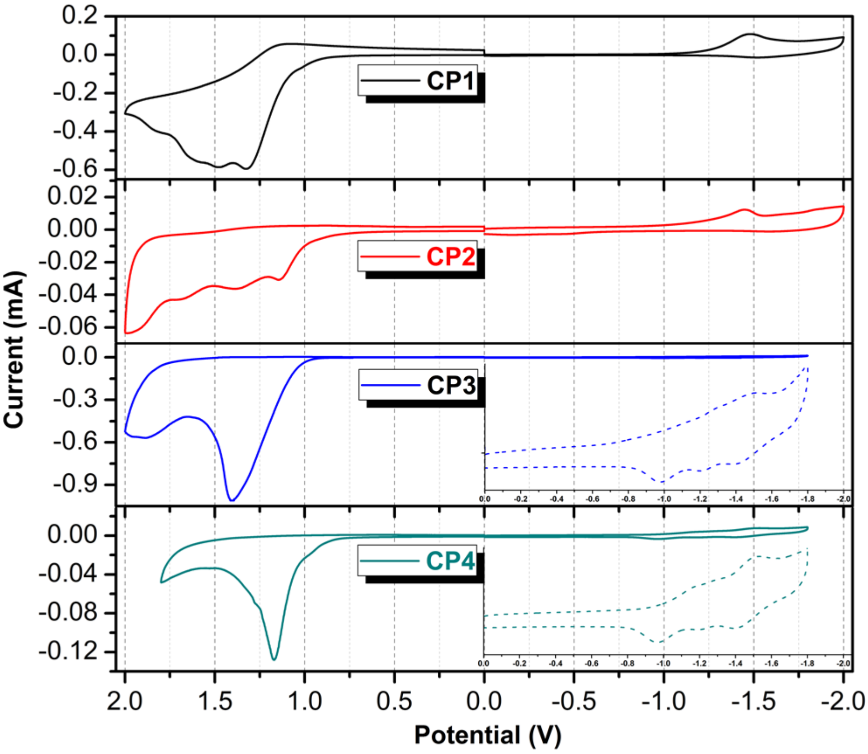

Figure S1. Cyclic voltammetric diagrams of polymers in 0.1 M TBAP at a scan rate of 100 mV/s. The inset figures show the enlarged reduction diagrams for **CP3** and **CP4**.

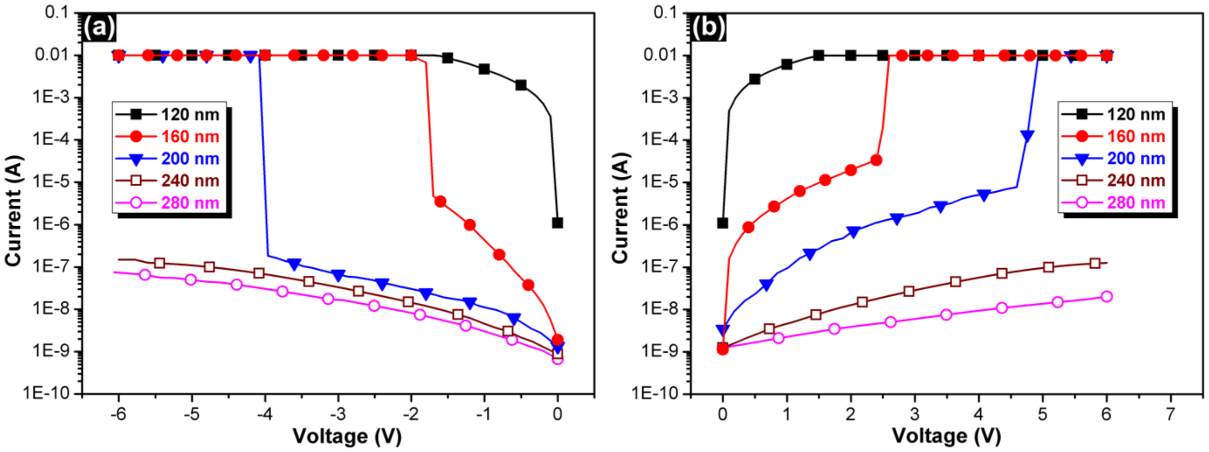

Figure S2. Current-voltage (*I*-*V*) characteristics of the ITO/ **CP4** (120-280 nm)/Al memory device with the first sweep performed (a) negatively and (b) positively.

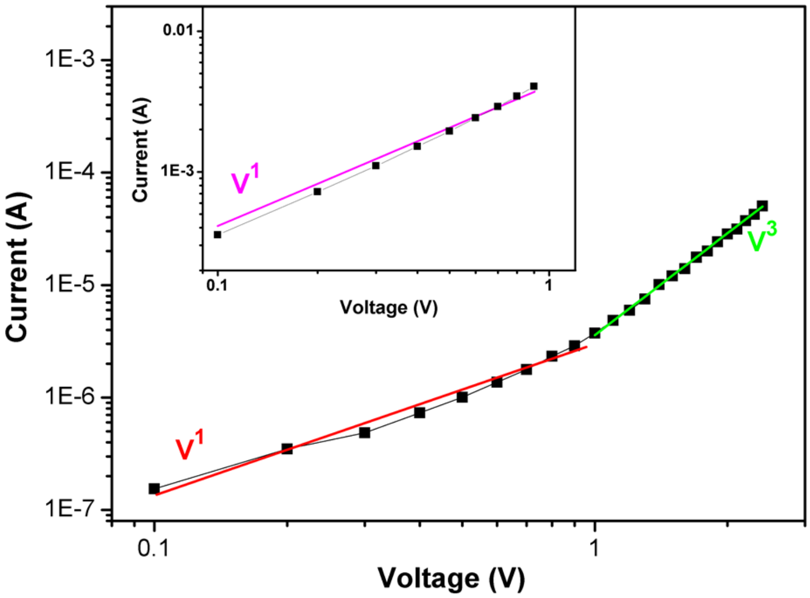

Figure S3. Experimental (symbols) and fitted (solid lines) *I–V* curves of the ITO/ **CP4** (160 nm)/Al memory device: OFF-state with the Ohmic (below 1.0 V) and the trap-limited SCLC (above 1.0 V) conduction model and (inset) ON-state with the Ohmic current model.

Table S1. Redox Potentials and Energy Levels of Conjugated Polymers

code	λ_{onset} [nm]	Redox Potentials [V] a)		Energy Levels [eV]				
		$E_{ox,onset}$	$E_{red,onset}$	E_g^{opt} b)	E_g^{ec} c)	HOMO d)	LUMO^{opt} e)	LUMO^{ec} f)
CP1	637	1.05	-1.27	1.95	2.32	-5.48	-3.53	3.16
CP2	633	0.97	-1.21	1.96	2.18	-5.40	-3.44	3.22
CP3	772	1.04	-0.91	1.61	1.95	-5.47	-3.86	3.52
CP4	783	1.01	-0.97	1.58	1.98	-5.44	-3.86	3.46

a) From cyclic votammograms vs. Ag/AgCl in CH_3CN.

b) The data were calculated from polymer films by the equation: $E_g^{opt} = 1240/\lambda_{onset}$ (energy gap between HOMO and LUMO).

c) E_g^{ec}, electrochemical band gap is derived from the difference between $E_{ox,onset}$ and $E_{red,onset}$.

d) The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV ; onset = 0.37 V).

e) The LUMO energy levels were calculated from HOMO - E_g^{opt}.

f) The LUMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV ; onset = 0.37 V).