

Supporting Information

Water-soluble Conjugated Polymers as Active Elements for Organic Nonvolatile Memories

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Instrumentation

¹H nuclear magnetic resonance (¹H NMR) spectra were measured at 300 MHz on a Bruker 300 AVANCE III spectrometer with *N,N*-Dimethylformamide (DMF-*d*₇) or dimethyl sulfoxide (DMSO-*d*₆) as the solvent. Fourier transform infrared (FT-IR) spectra were obtained with a Perkin Elmer Frontier spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu 2501 PC spectrophotometer at room temperature. The inherent viscosities were measured with an Ubbelodhe viscometer at 30 ± 0.1 °C in *N*-methyl-2-pyrrolidone (NMP) at a concentration of 0.5 g/dL. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 instrument under a nitrogen atmosphere with the gas-flow rate of 50 mL/min and a heating rate of 10 °C /min. Cyclic voltammetry (CV) measurements were carried out with a CHI 604E Electrochemical Workstation (CH Instruments, Shanghai Chenhua Instrument Corporation, China) under an argon atmosphere. The polymer film coated on a Pt plate (working electrode) was scanned at 1 mV/s in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) in anhydrous dichloromethane, with a Pt wire and platinum gauze as the reference and counter electrodes, respectively. The thickness of the polymer film was measured by a KLA Tencor *Alpha-Step Surface Profiler*.

The *I-V* characteristics were measured at room temperature by Keithley 4200 SCS semiconductor characterization system with voltage sweeping mode. During the measurement, a bias voltage was applied between the top (Au) and bottom (Pt) electrodes with the latter being grounded, unless otherwise specified.

Reagents for synthesis

2,5-Bis(trimethylstannyl)thiophene **2**, *N*-[3'-(*N,N*-dimethylamino)propyl]-3,6-dibromocarbazole **3**, and 2,7-Dibromo-9,9-bis(4-ethylbutyrate)fluorine **4** were prepared according to the reported procedures.[1-3] All starting chemicals, unless otherwise specified, were purchased from Alfa Aesar or Sigma-Aldrich and used as received. Solvents were purified by normal procedure before use. The other materials were common commercial level and used as received.

General procedure of copolymerization by Stille coupling. The equimolecular amount of 2,5-Bis(trimethylstannyl)thiophene and dibromide monomer(s), and Pd(PPh₃)₄ (~1.6 mol%) were dissolved in anhydrous *N,N*-dimethylformamide (DMF) under argon. The solution was bubbled with argon for 30 min. The mixture was vigorously stirred at 110 °C under an argon atmosphere for 48 hours. After cooling to room temperature, the mixture was poured into acetone. After washing with acetone for 24 hours in a Soxhlet apparatus to remove oligomers and catalyst residues and tetrahydrofuran for another 24 hours, the resulting polymer was dissolved in DMF. The solution was filtered with a 0.45 μm PTFE filter, concentrated and precipitated from acetone to yield the neutral precursor polymer.

P1: Monomer 1 (0.1191 g, 0.4 mmol), monomer 2 (0.4097 g, 1.0 mmol) and monomer 3 (0.2461 g, 0.6 mmol) were used in this copolymerization. Yield 450 mg purple powder. P1 shows an inherent viscosity of 0.72 dL/g in NMP. ¹H NMR (DMF-*d*₇, 300 MHz), 9.257 (s), 8.85-8.80 (m), 8.33-7.36 (m), 4.80-4.73 (m), 4.00-3.90 (m), 2.56-2.52 (m), 2.32-2.20 (m), 1.80-1.75 (m).

P4: Monomer 1 (0.0894 g, 0.3 mmol), monomer 2 (0.4097 g, 1.0 mmol) and monomer 3 (0.3866 g, 0.7 mmol) were used in this copolymerization. Yield 400 mg dark green powder.

P2 shows an inherent viscosity of 0.62 dL/g in NMP. ¹H NMR (DMSO-*d*₆, 300 MHz), 8.14 (s), 7.91-7.67 (m), 7.29 (m), 7.66 (m), 6.11 (t), 5.30 (t), 3.15 (s), 2.07 (br), 1.17 (m), 0.90 (m).

General procedure of quaternization. Quaternization reagent was added to a solution of neutral precursor polymer **P1** (100 mg) in DMF (5 mL). The mixture was heated with stirring under an argon atmosphere. After the quaternization reaction was finished, the reaction mixture was cooled to room temperature and precipitated from ethyl acetate. The precipitates were collected by centrifugation, washed with chloroform and THF, and dried overnight in a vacuum at 80 °C.

P2: the quaternization reagent was 1,4-butane sultone (0.2 mL), and the reaction mixture was heated to 70 °C for 3 days. Yield 104 mg purple powders. ¹H NMR (DMF-*d*₇, 300 MHz), 9.273 (s), 8.82-8.75 (m), 8.33-7.36 (m), 4.80-4.73 (m), 4.01-3.90 (m), 3.256-2.52 (m), 2.20 (br), 1.78 (br), 1.56 (br).

P3: the quaternization reagent was iodomethane (0.2 mL), and the reaction mixture was heated to 50 °C for 10 days. Yield 100 mg purple powders. ¹H NMR (DMF-*d*₇, 300 MHz), 9.30 (s), 8.93-8.77 (m), 8.34-7.36 (m), 4.81-4.71 (m), 4.04-3.90 (m), 3.17 (s), 2.57-2.53 (m), 1.40 (s), 1.27 (s).

Hydrolysis of Neutral Carboxylate-Containing polymer.

Neutral carboxylate-containing polymer **P4** (120 mg) was added to a solution of sodium hydroxide in methanol; the mixture was refluxed for 20 hours. After cooling to room temperature, the methanol was removed by rotary evaporation. The obtained mixture was purified by dialyzing against water (Millipore Nanopure™) using a 3400-Da MWCO cellulose membrane for two days in a Soxhlet apparatus. After dialyzing, a kelly-green solution was obtained. This solution was proceeded with two methods. One part was dried after removal of the solvent under reduced pressure in vacuum at 80 °C overnight. However,

the dried polymer was difficult to dissolved in water again. The other part was concentrated to ~20 mg/mL, filtered with a 0.45 μm PTFE filter and then used directly to prepare to devices by spin-coating.

Fabrication and characterization of memory devices

The Si/SiO₂/Ti/Pt substrates were pre-cleaned with ethanol, H₂SO₄:H₂O₂ = 7:3 (v/v) and water sequentially in an ultrasonic bath for 20 min. A 0.1 mL aqueous solution of **P2**, **P3** or **P5**, or DMF solution of **P1** and **P4** (1.0 wt % polymer) was spin-coated onto the substrates at a spinning speed of 400 rpm for 12 s and then 2000 rpm for 40 s, followed by a vacuum-drying at 100 °C for 8 h. Before spin-coating, the solution was filtered through polytetrafluoroethylene (PTFE) membrane micro-filters with a pore size of 0.45 μm . The thickness of the polymer films are 82, 94, 91, 87 and 83 nm for **P1-P5**, respectively, as measured by spectroscopic ellipsometer (model M2000DI, Woollam). To construct the Au/polymer/Pt structures, Au top electrodes with a diameter of 100 μm and thickness of 100 nm were deposited at room temperature by thermal evaporation with a metal shadow mask. The current–voltage (I – V) characteristics of the Au/polymer/Pt devices were measured in an ambient atmosphere on Keithley 4200 SCS semiconductor characterization system in voltage sweeping mode. The sweeping step is 0.01 V.

References

- [1] Kohsuke Kawabata and Hiromasa Goto, *J. Mater. Chem.* **2012**, 22, 23514.
- [2] R.-H. Lee, J.-K. Liu, J.-H. Ho, J.-W. Chang, B.-T. Liu, H.-J. Wang, R.-J. Jeng, *Polym. Inter.* **2011**, 60, 483.
- [3] B. Bao, L. Yuwen, X. Zhan, L. Wang, *J. Polym. Sci. Part A Polym. Chem.* **2010**, 48, 3431.

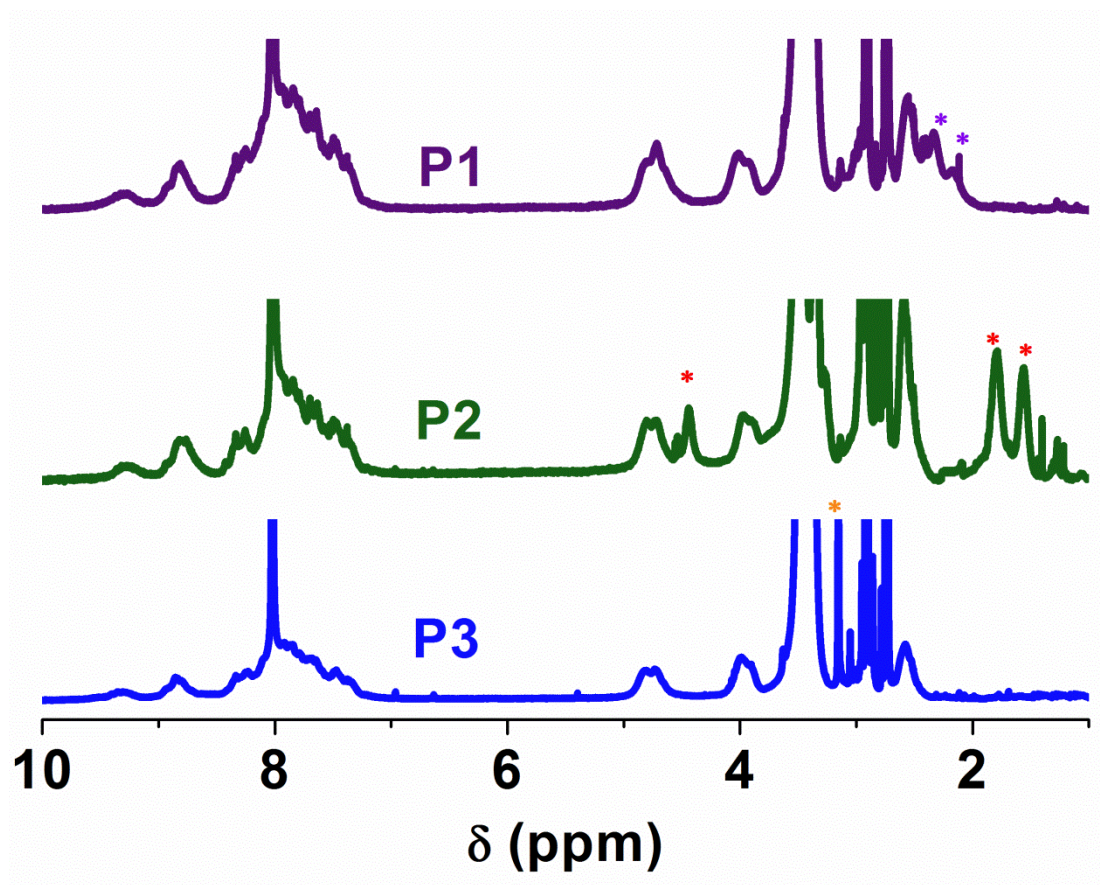


Figure S1. The ^1H NMR spectra of **P1-P3**. The stars indicate the changes from the quaternization.

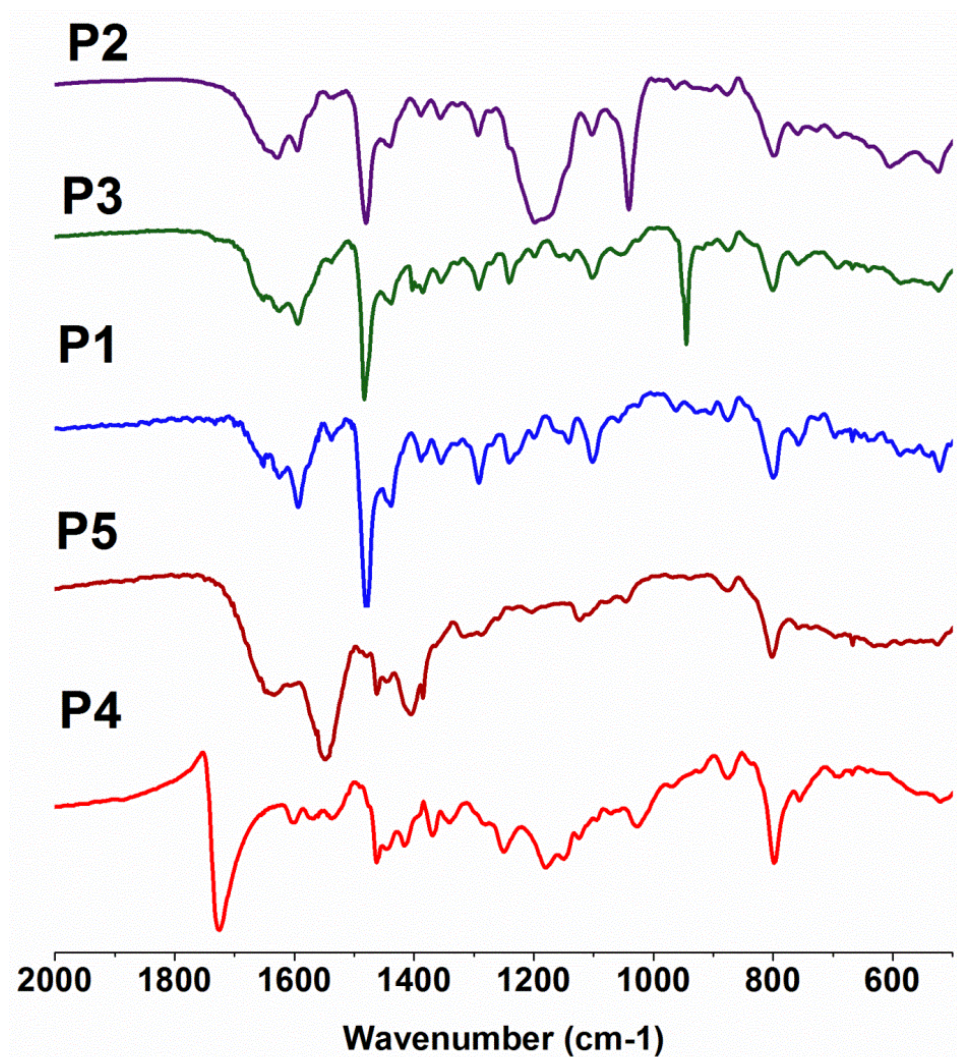


Figure S2. The FT-IR spectra of **P1-P5**.

The peaks at 1200 and 1040 cm^{-1} of **P2** are the characteristic peaks of $-\text{SO}_3\text{Na}$.

The peaks at 1730 and 1080 cm^{-1} of **P4** are the characteristic peaks of $-\text{COOR}$.

The peaks at 1630, 1550 and 1410 cm^{-1} of **P5** are the characteristic peaks of $-\text{COOR}$.

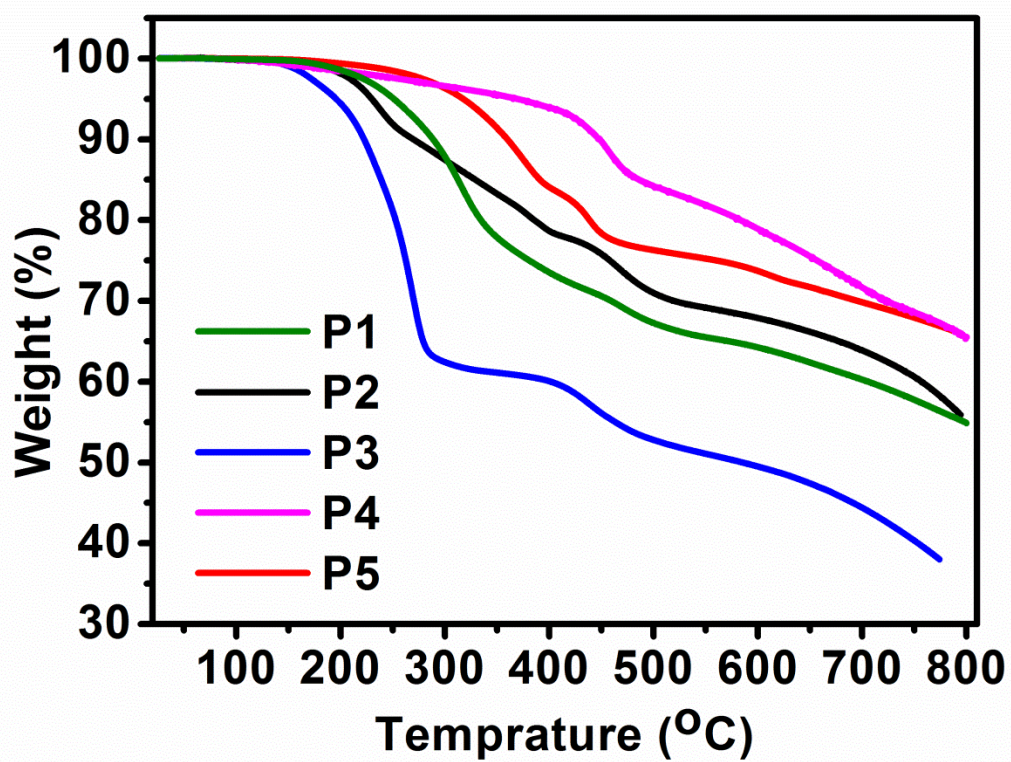


Figure S3. TGA curves of P1-P5.

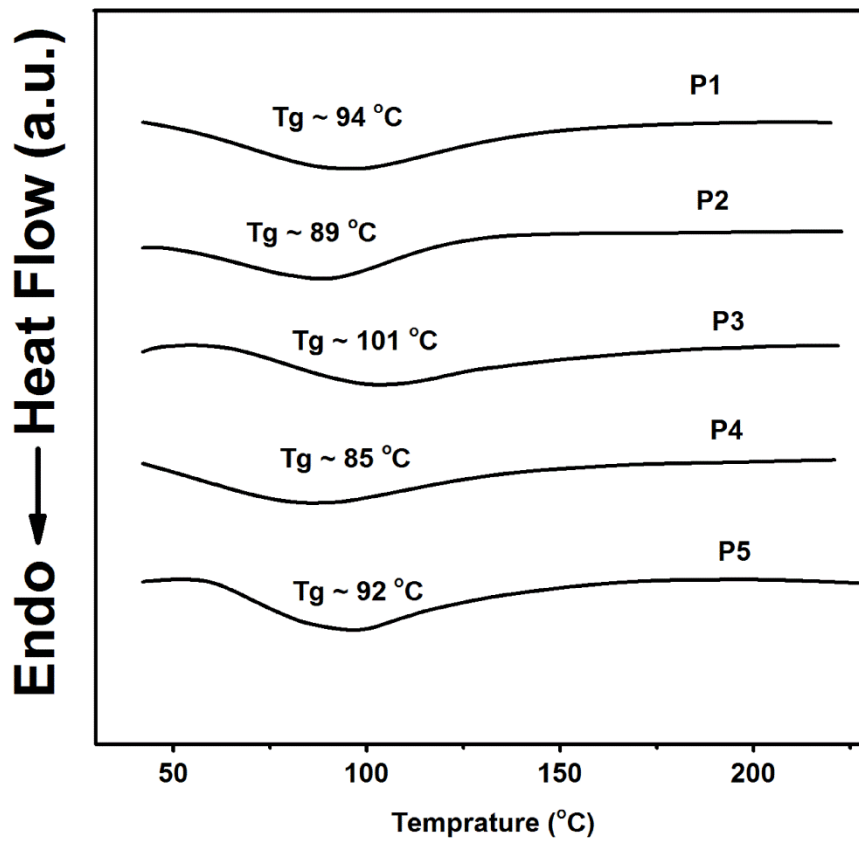


Figure S4. DSC curves of P1-P5.

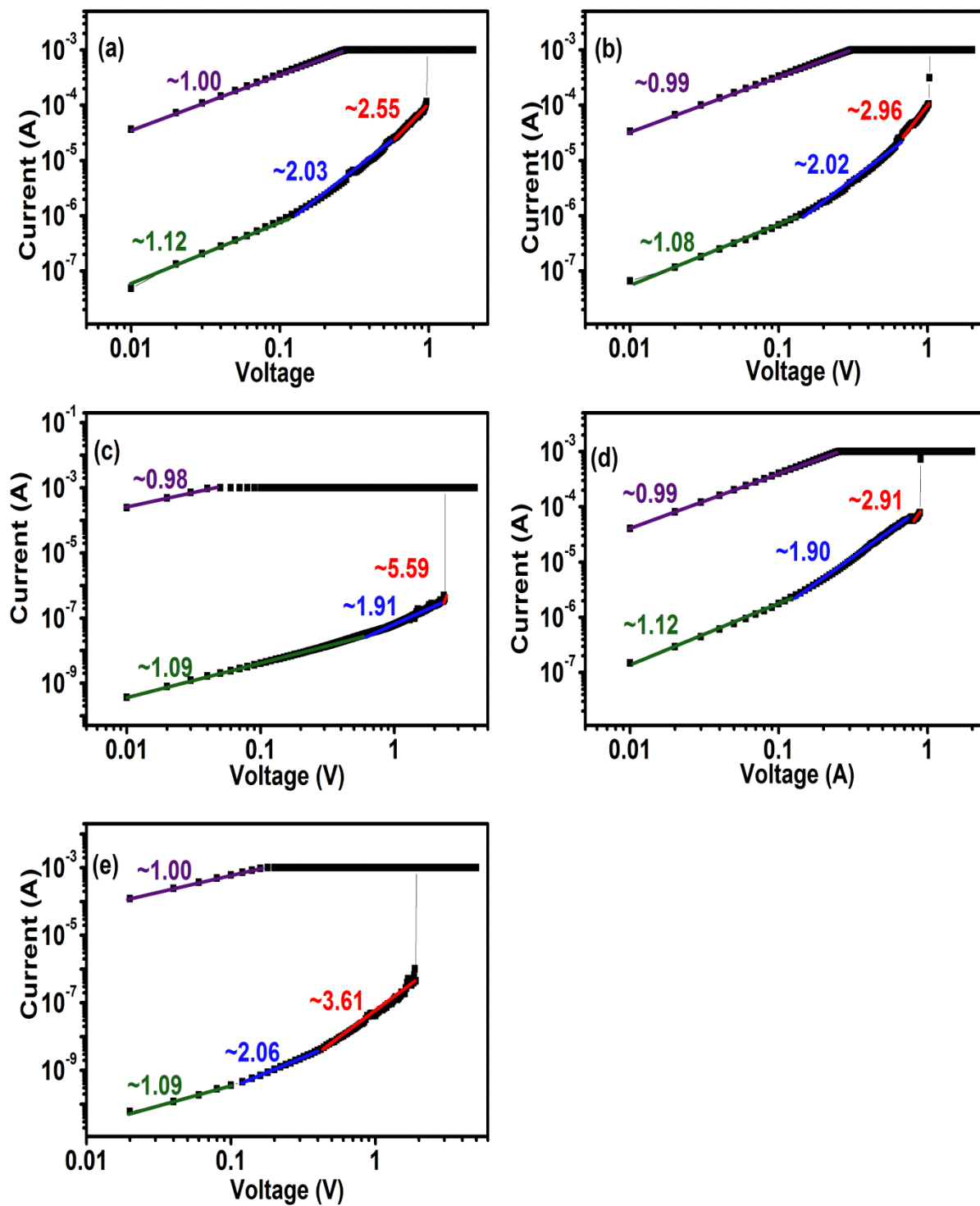


Figure S5. The I - V curves of the Au/Polymer/Pt memory cells plotted in log-log scale and the linear fitting results in both ON and OFF states in the processes of SET, (a) **P2**, (b) **P3**, (c) **P1**, (d) **P5** and (e) **P4**. The corresponding slopes for different portions are also shown.