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Manipulating Charge Transport in π-Stacked Polymer through Silicon Incorporation

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Content

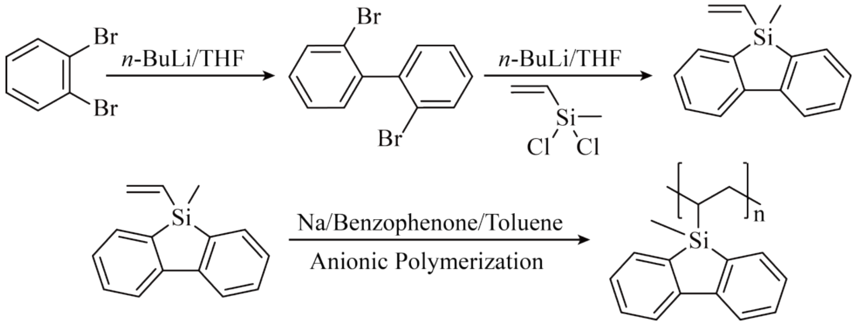
1. Materials

o-dibromobenzene, *n*-butyllithium (2.5 mol/ml) in hexane solution, methyl vinyl dichlorosilane, benzophenone were purchased from Sigma-Aldrich Co. and used without further treatments. All manipulations involving air-sensitive reagents were performed in an atmosphere of dry N_2. Toluene and tetrahydrofuran (THF) were refluxed with sodium and distilled.

2. Measurements

Nuclear magnetic resonance (NMR) spectra were collected on a Bruker Ultra Shield Plus 400 MHz instruments with chloroform-D as the solvent and tetramethylsilane (TMS) as the internal standard. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymer were measured by gel permeation chromatography (GPC) with Shim-pack GPC-80X columns, using polystyrene as standard and THF as eluent. Ultraviolet-visible (UV-Vis) spectra were recorded on an UV-3600 SHIMADZU UV-Vis-NIR spectrophotometer. Fluorescence spectra were obtained using a RF-5301PC spectrofluorophotometer with a Xenon lamp as a light source. The concentration of the homopolymer in THF solution was adjusted to be about 0.01 mg/ml or less. The thin solid films were prepared by spin casting the solution of the polymer on quartz substrates. The thickness of the nanofilm was measured by a Dektak surface profilometer. Powder X-ray diffraction (XRD) data were collected on a D/max-2500/PC diffractometer using Cu Kα radiation (λ=1.5405 Å).

3. Synthesis of the monomer and polymer



Scheme S1: Synthesis of poly (vinyl methyl silafluorene) (PVMSiF)

2, 2'-dibromobiphenyl[1]**:** To a stirred solution of *o*-dibromobenzene (0.233 g, 1 mmol) in 10 ml of dry THF at -78°C, was added 2.5 M *n*-butyllithium/hexane solution(0.4 ml, 1 mmol). The mixture proceeded at -78°C for 2 h and then allowed to warm to room temperature. After the reaction, the mixture was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel using petroleum as eluent, which gave a white solid. Yield: 41%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.30 (s, 2H), 7.45 (s, 2H), 7.60-7.66 (t, J=7.6 Hz, 2H), 7.79 (d, J=8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 123.60, 128.92, 129.81, 132.96.

Vinyl methyl silafluorene: To the mixture of 2,2'-dibromobiphenyl (3.1 g, 10 mmol) and dry THF (30 ml) was added a 2.5 M *n*-butyllithium/hexane solution(8 ml, 20 mmol) at -78°C. The resulting mixture was allowed to stir at this temperature for 2 h and then vinyl methyl dichlorosilane (0.65 ml, 5 mmol) was added into the mixture. After the addition, the mixture was warm to room temperature and stirred overnight. Then the reaction mixture was hydrolyzed with water and extracted with dichoromethane. The combined organic layers were collected, dried over anhydrous sodium sulfate (Na_2SO_4), filtered and evaporated to remove the solvent. The resulted crude product was chromatographed on a silica gel column with petroleum ether/ethylacetate as eluent. Recrystallize several times from ethanol or dichloromethane/hexane to afford the pure compound. Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 0.51 (s, 3H), 5.91-5.97 (m, 1H), 6.14-6.27 (m, 2H), 7.24-7.29 (m, 2H), 7.45 (t, J=7.6 Hz, 2H), 7.62 (d, J=7.6 Hz, 2H), 7.83 (d, J=7.6Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: -0.53, 126.1, 132.6, 136.6, 138.3, 139.2, 140.4, 142.3, 153.4.

Poly (vinyl methyl silafluorene) (PVMSiF): A small amount of sodium blocks in toluene was evacuated three times and refilled with dry N_2 each time. The reaction was heated to 110°C in oil bath until sodium blocks become sodium sand. Then the toluene was removed and washed the sodium sand with dry THF for three times. The solution of benzophenone (5 mg, 0.025 mmol) in THF was dropped into the reaction and the colour of the mixture was dark blue. Then vinyl methyl silafluorene (0.222 g, 1 mmol) in THF was quickly added into and stirred for 10 minutes at room temperature. The mixture was further stirred at 60°C for 48 h. After the anion polymerization, the solution was dropped slowly into methanol to obtain the poly(vinyl methyl silafluorene). The precipitated polymer was filtered, collected and dried under vacuum. Yield: 75%. M_n = 45,700; M_w=48,500; polydispersity index (PDI) = 1.06 as measured by GPC (see Figure S1), showing typical narrow molecular distribution (M_w/M_n=1.06) of anionic polymers.

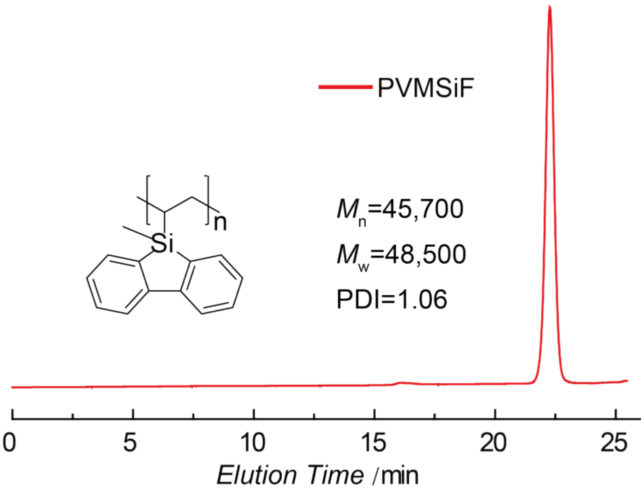


Figure S1: GPC chromatogram of PVMSiF

4. DSC and TGA

Thermogravimetric analyses (TGA) were conducted on a DTG-60 Shimadzu thermal analyst system under a heating rate of 10°C/min and a nitrogen flow rate of 50 cm^3/ min. Differential scanning calorimetry (DSC) was run on a Pyrisl DSC (PERKIN ELMER Co.) thermal analyst system under a heating rate of 20°C/min and an argon flow rate of 50 cm^3/min.

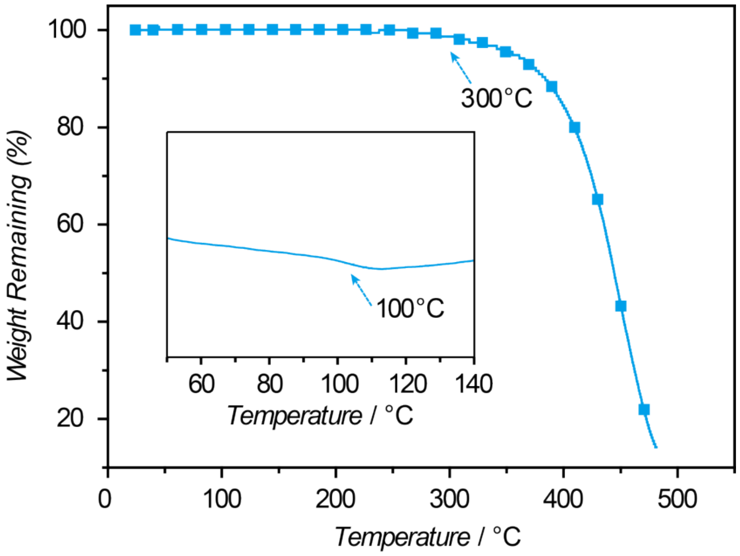


Figure S2: TGA and DSC (inset) curves of PVMSiF

5. Atom force microscopy

Atomic force microscope (AFM) images were obtained using a Bruker Dimension Icon AFM equipped with Scanasyst-Air peak force AFM tips. The measurement was carried out at room temperature in a tapping mode.

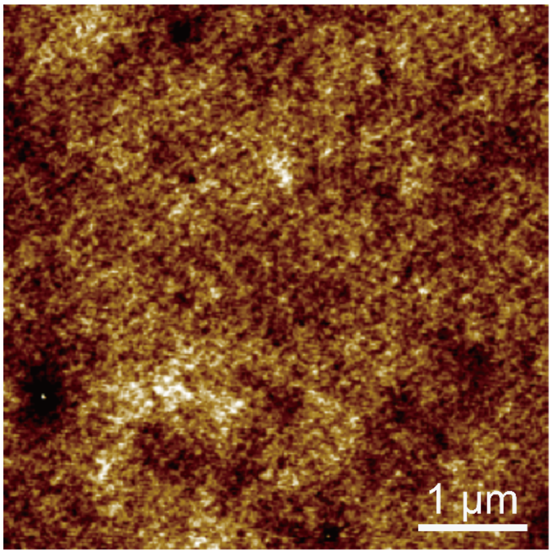


Figure S3: The AFM height image (5×5 µm^2) of the annealed PVMSiF thin film for molecular nanofuse.

6. Cyclic voltammetry

The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and the energy gap between them (E_g) were measured by cyclic voltammetry (CV). The CV measurements were performed at room temperature on a CHI660E system in a typical three-electrode cell with a working electrode (glass carbon), a reference electrode (Ag/Ag$^+$, referenced against ferrocene/ferrocenium (FOC)), and a counter electrode (Pt wire) in an acetonitrile solution of Bu_4NPF_6 (0.01 M) at a sweeping rate of 100 mV/s. The HOMO energy levels of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): E_{HOMO}= -[E_{onset}-(-0.05)]-4.8 eV, where the value of 0.05 V is for FOC *vs* Ag/Ag$^+$ (E_{FOC}=-0.05 eV) and E_{onset}^{Ox} and E_{onset}^{Red} are the onset potential of the oxidation and the reduction respectively. The HOMO and LUMO energy levels of PVMSiF were measured to be at -6.12 and -2.51 eV respectively.

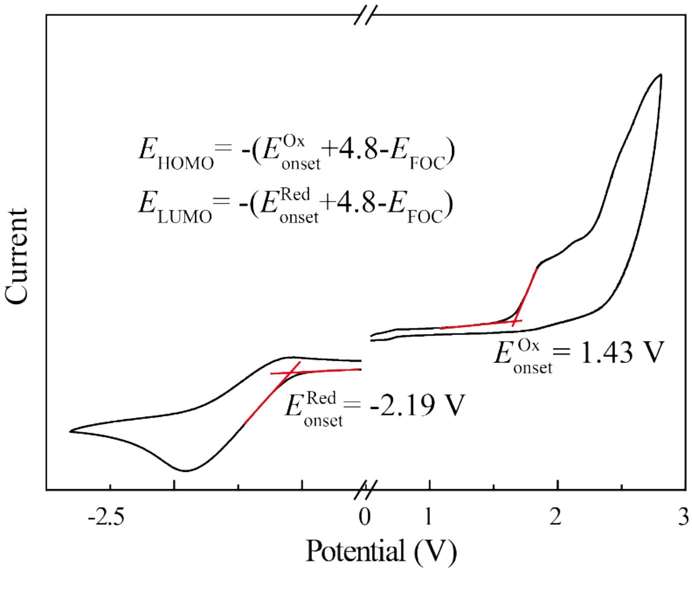


Figure S4: Cyclic voltammogram of PVMSiF film on a glassy carbon electrode (0.01 M Bu_4NPF_6 in acetonitrile, scanning rate of 100 mV/s).

7. Device fabrication and characterization

The indium-tin oxide (ITO) glass was pre-cleaned in ultrasonic bath for 15 min each in detergent, deionized water, acetone, and ethanol. Then toluene solution of PVMSiF (10 mg/ml) was spin-coated onto the ITO-glass substrate at a rotational speed of 1500 rmp for 10 s. The resulting film was annealed at 90°C in a vacuum over for 8 h. Finally, Al was thermally evaporated onto the film surface at 8×10^{-4} Pa through a shadow mask to yield top Al electrodes with area of 0.78 mm^2. The devices were characterized under ambient conditions at room temperature, using Agilent B1500A. The current-voltage (I-V) characteristics of the ITO/PVMSiF/Al device were measured at room temperature and ambient atmosphere, where the voltage was applied to the top electrode (Al) and the bottom electrode (ITO) was grounded.

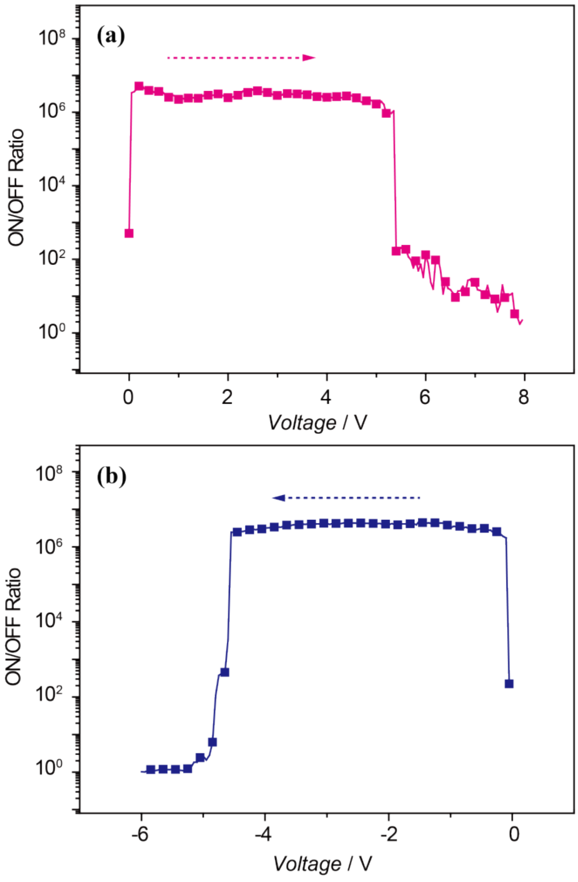


Figure S5: ON/OFF current ratio of the ITO/PVMSiF/Al device: **(a)** Positive sweep from 0 to 8 V, and **(b)** negative sweep from 0 to -6 V; Both sweeps switch the device from ON to OFF states.

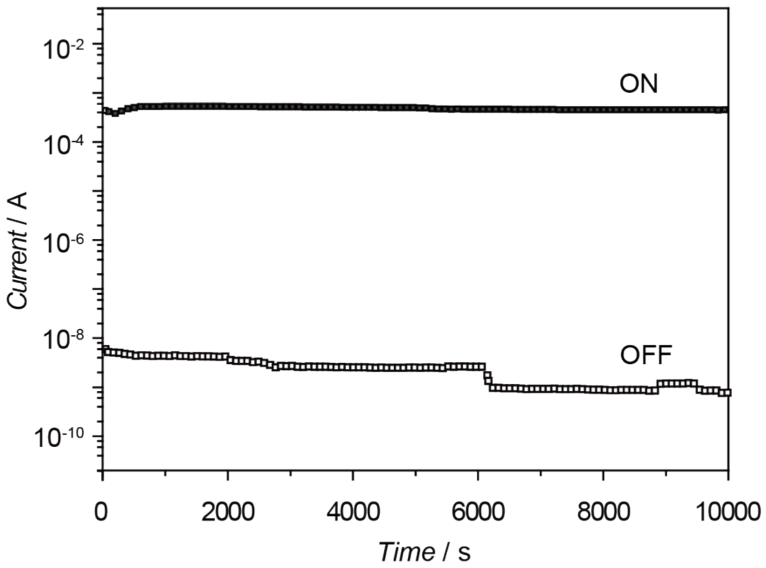


Figure S6: Long-time responses (retention times) of the ON- and OFF- states (read at 1.0 V) of the ITO/PVMSiF/Al device

8. Micro-PL spectrum

The micro-PL spectra were acquired on an inverted microscope (eclipse Ti-U, Nikon, Japan) equipped with a dark-field condenser (0.8 < NA < 0.95), a 100 W halogen lamp, a 75W Xenon Lamp, a true-color digital camera (Nikon DS-fi2), and a monochromator (Acton SP2300i) equipped with a grating (grating density: 300 L/mm; blazed wavelength: 500 nm) and a spectrograph CCD (PIXIS 400BR: excelon, Princeton Instruments). The micro-PL spectrum measurement (Excitation light: 340-380 nm; Acquisition time: 10 s) was performed to probe the PL shift of the active layer in collection zone (A) during the operation of the device (Figure S7). In a controlled measurement, PL spectrum in collection zone (B) where no electrical field can be applied was also collected for the comparison investigation.

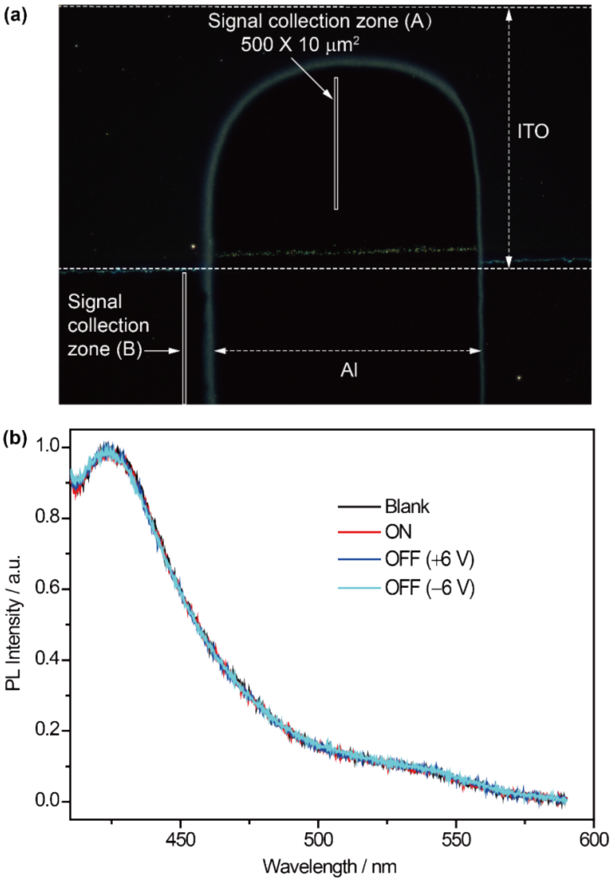


Figure S7: The micro-PL spectrum measurements: (a) micrograph of the nano-fuse device and PL signal collection zones, where zone (A) is on the active layer of the device, while zone (B) with the same area (500*10 µm^2) of zone (A) is close to but outside of the device; (b) PL spectra of PVMSiF collected from zone (B) for control (Blank) and zone (A) at ON and OFF states.

9. Theoretical calculations

The theoretical DFT calculations were performed on Gaussian 09 program package with different parameters for structure optimizations and vibration analysis. The ground state geometries of the monomer and dimmers were optimized with restricted and unrestricted formalisms of M062X/cc-PVDZ to consider the long range π-π interactions for neutral and ion states respectively. The symmetric constraint was not used for geometry optimization. These optimized stationary points were further characterized by harmonic vibration frequency analysis to ensure that real local minima had been found. Based on the optimized structures, the molecular energy levels, such as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, energy gaps (E_g) were further calculated at B3LYP/6-31G level. The ionization potentials (IP), electron affinities (EA), reorganization energy (λ) were calculated by B3LYP/6-31G (see Table S1) directly from the relevant points on the potential energy surfaces following the standard procedures in the literature.[2, 3] The molecular electrostatic potential (ESP) was generated using ChemBio-3D, where green color stands for positive electrostatic potential while yellow stands for negative electrostatic potential.

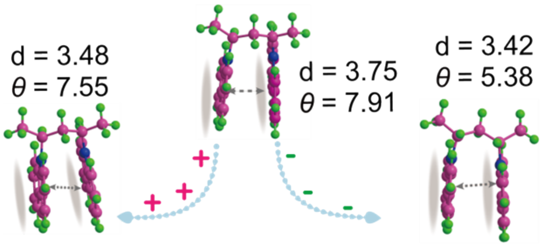


Figure S8: The π-π stacking structures of the dimer of PVK at cationic (left), neutral (middle), and anionic (right) states (d in Å; θ in º)

The stable (energy-minimized) conformation of the homopolymer was obtained by mechanical dynamic (MD) simulation using NAMD (version 2.9) in NPT ensemble at atmospheric pressure and room temperature (300℃). The general amber force field (GAFF) is chosen and the bond and angular parameters of Si were obtained by DFT calculations at B3LYP/6-31G(d) level while its dihedrals were parameterized by mimicking that of C. A cutoff of 10 Å for non-bonded interactions and a 70 ps equilibration with the time step of 1 ps were adopted for the MD simulation. The polymer conformation was found to be stable after 30 ps of equilibration to form the energy-minimized conformation of PVMSiF shown in Figure S7. The molecular graphics software VMD was used to visualize all the trajectories. The distances and angles between the repeating units of PVMSiF were measured by self-written TCL codes run in VMD.

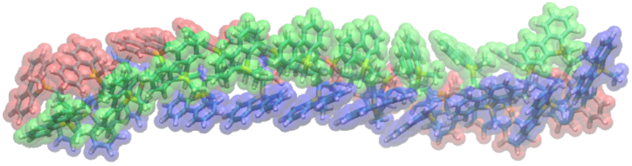
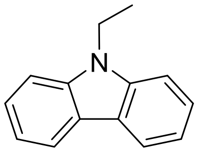
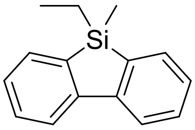
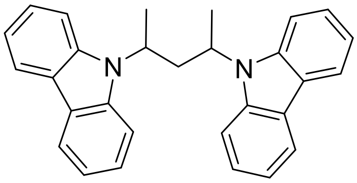
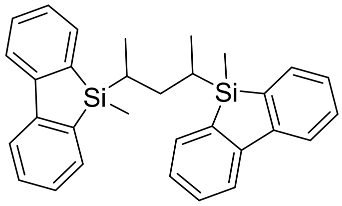


Figure S9: The energy-minimized conformation of PVMSiF (n=30) predicted by mechanical dynamic (MD) simulation.

The model polymer with the polymerization degree of 30 was constructed for MD simulations. After the equilibration, the partial π-π stacking is obvious in the middle of the polymer chain. Three strips (in blue, green, and red) of π-π stacked silafluorene units can be observed to be twisted together along the backbone. As a result, the middle 12 units of PVMSiF were chosen for the further DFT calculations of HOMO, LUMO, and ESP to mimic the optoelectronic properties of the polymer.

Table S1: HOMO and LUMO, IP, EA, and λ calculated at the B3LYP/6-31G level for monomers and dimers of PVK and PVMSiF (in eV).

Molecular	HOMO	LUMO	IP	EA	λ_h	λ_e
	-5.32	-0.57	6.93	-1.02	0.11	0.29
	-5.85	-0.84	7.42	-0.67	0.34	0.41
	-4.94	-0.42	6.23	-0.85	0.22	0.41
	-5.68	-0.82	6.90	-0.36	0.47	0.35

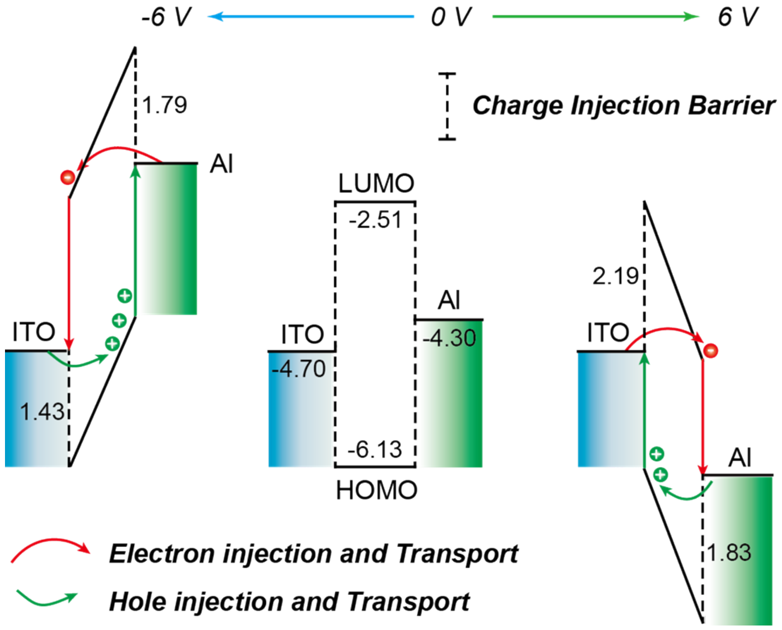


Figure S10. Schematic diagrams of the electronic structures corresponding to the operating mechanism of the ITO/PVMSiF/Al device at -6 V (left), 0 V (middle), and 6 V (right) respectively.

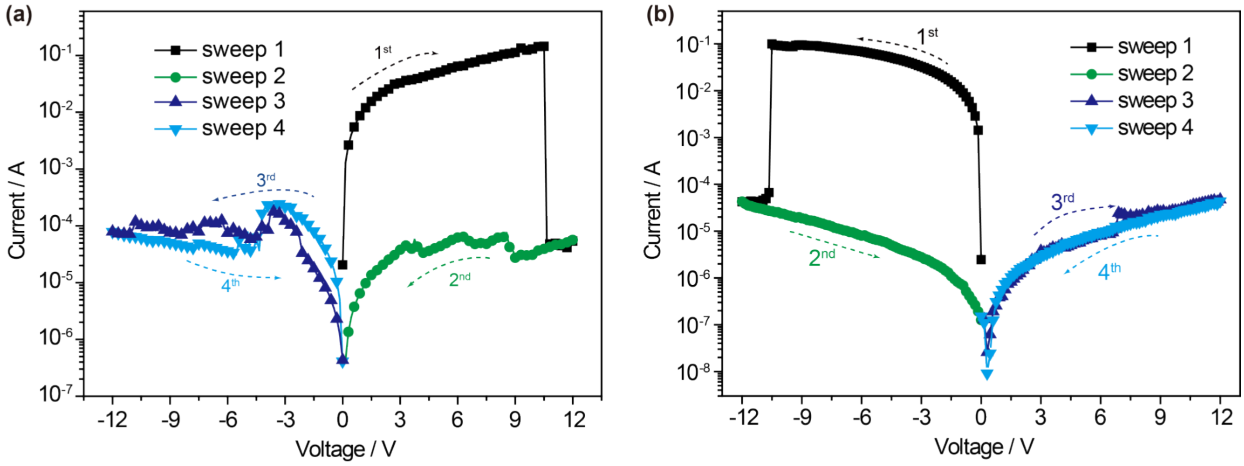


Figure S11. The I-V curves of the ITO/PVMSiF (110 nm) /Al device: (a) positive and reverse voltage sweeps; (b) negative and reverse voltage sweeps.

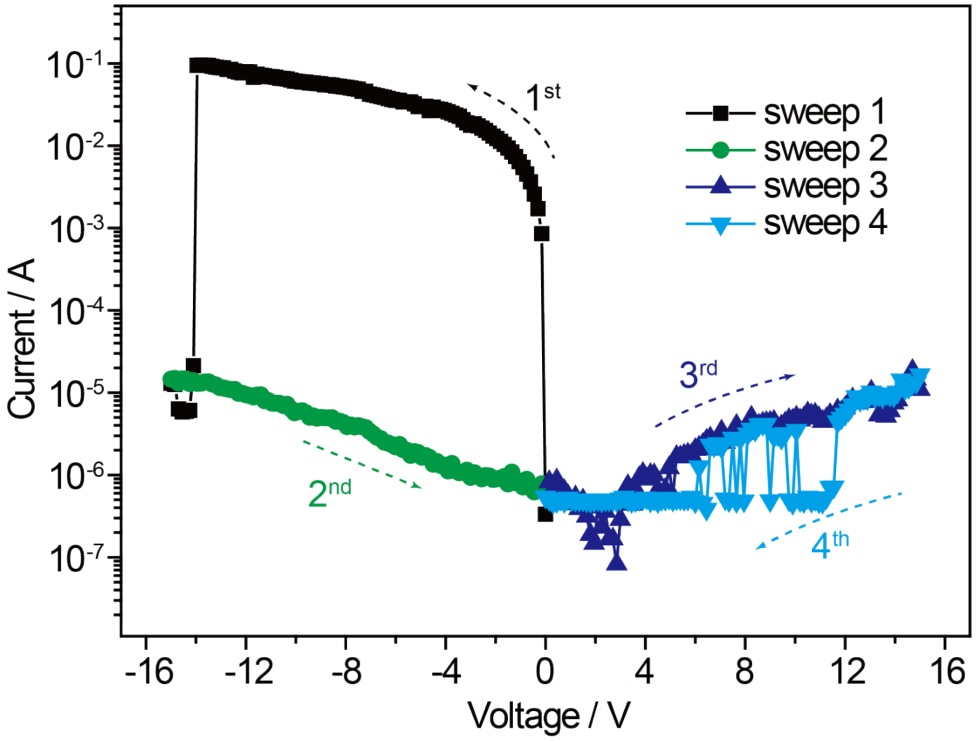


Figure S12. The I-V curves of the thermally recovered ITO/PVMSiF (110 nm) /Al device. The ITO/PVMSiF (110 nm) /Al device is firstly turned to be at OFF state. Then, it was treated by thermal annealing at 90°C for 10 h. Interestingly, the device was at ON state after thermal treatment, which can act as a nano-fuse device again.

10. References

1. H. Gilman, R. D. Gorsich, *J. Am. Chem. Soc.* **1955,** 77, 6380.
2. R. F. Chen, C. Zheng, Q. L. Fan, W. Huang, *J. Comput. Chem.* **2007,** 28, 2091.
3. J. Yin, S. L. Zhang, R. F. Chen, Q. D. Ling, W. Huang, *Phys. Chem. Chem. Phys.* **2010,** 12, 15448.