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Manipulating Charge Transport in π -Stacked Polymer through Silicon Incorporation

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Given the fundamental importance in charge transport engineering for device operation in molecular electronics, the manipulating strategies and material design principles for a desired application are highly expected. In stark contrast to conventional organic electronic devices, designing organic semiconductors that perform effectively as molecular nanofuse remains a challenge. Based on a novel silicon-containing π -stacked polymer of silafluorene (PVMSiF), we successfully fabricated a molecular nanofuse device with high ON/OFF ratio up to 4×10^6 for the first time. Using a combination of absorption and photoluminescence (PL) spectra, X-ray techniques (XRD), and micro-PL analysis supported by theoretical insights into unit and backbone geometries and wave function delocalizations provided by density functional theory (DFT) and molecular dynamics (MD) simulations, we demonstrate the fundamental correlations between the polymer structures and the spectacular fuse-like resistive switching behaviors. It was shown that the manipulation of charge transport in π -stacked polymer is applicable via silicon incorporation to realize the molecular nanofuse device of the π -stacked polymers, following a silicon-stimulated filament mechanism with breakable π - π stacking at charged states. These findings may have important consequences on future material studies and device applications.

Introduction

Manipulating charge transport behaviours of organic semiconductors^[1] has been the focus of a growing body of investigations in organic electronics, ranging from organic light emitting diodes (OLEDs) and organic photovoltaic (OPV) to field-effect transistors, bio-/chemo-/photo-sensors, and electronic memories.^[2] The π -conjugated molecules with vast adoptable structures^[3] have critical properties for conductance tuning, such as adjustable the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), band-gap (E_g), and delocalization pattern of the π -systems. However, charge transport occurs both within and between the π -systems, whose regular align and proper assembly are highly preferred.^[4] Alternatively, the π -stacked polymers,^[5] in which the aromatic pendant groups are arranged in a face-to-face conformation (π - π stacking) that induced,

regulated, and stabilized by the covalent bonds among the polymer backbone, offer additional π -orbital channels^[6] for charge transport with mobilities up to $0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$,^[7] which are highly attractive for molecular electronics.^[4,8,9] Nevertheless, compared to the massive systems and sophisticated design strategies of conventional π -conjugated small molecules and polymers for optoelectronic applications, there are rare rules^[10] for π -stacked polymers to follow, which greatly hinders their progress with limited molecular species of polyvinylcarbazoles (PVK) and poly(di)benzofulvenes,^[5] let alone their varied applications.

Introducing heteroatoms such as silicon into the π -conjugated organic systems to replace the carbon atoms at desired sites in conjugation skeletons, has demonstrated its success in effectively constructing new series of functional molecules with tunable optoelectronic structures and properties,^[11] despite the elaborated synthetic efforts and difficulties. As a typical example, silafluorene, formed by replacing the sp^3 hybridized carbon of fluorene with silicon, was reported to be an excellent building block for OLEDs with high stability,^[12a] for OPV with improved cell efficiency,^[12b] and for chemosensors with high sensitivity,^[12c] by taking advantage of the particular orbital interactions between the Si

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($\sigma^*-\pi^*$ conjugation etc.) and the π -conjugated framework.^[13] Encouraged by these merits brought by Si incorporation, we intend to introduce Si into the π -stacked polymers; this may offer new opportunities to control the optoelectronic properties and electrons and/or holes flows for the improved or, more importantly, the innovated device performances.

Particularly, the nanofuse device,^[14] which emulates macroscopic electronic device of fuse working in the *on/off* sense with an irreversible behavior to voltage, could (i) detect an overvoltage to protect complex electronic systems, (ii) trigger other processes in a controlled manner, and (iii) act as binary component of read-only memories. However, designing such a kind of molecular switch with organic semiconductors remains a challenge. Dialkoxybenzene/quinone bisketal pairs were reported to be among the few successful ones,^[15] where the initial aromatic conductor can be electrochemically transformed into the insulator quinone bisketal at a controlled voltage. Nanofuses based on conformational molecular changes have been theoretically proposed^[16] but never been experimentally explored, because most of the aromatic groups have a stronger tendency to form face-to-face conformation at charged states,^[17] resulting in increased conductivity under applied voltages to function as *off/on* molecular switches for write-once read-many-times memory (WORM),^[18,19] dynamic random access memory (DRAM),^[20] or nonvolatile flash memory.^[21]

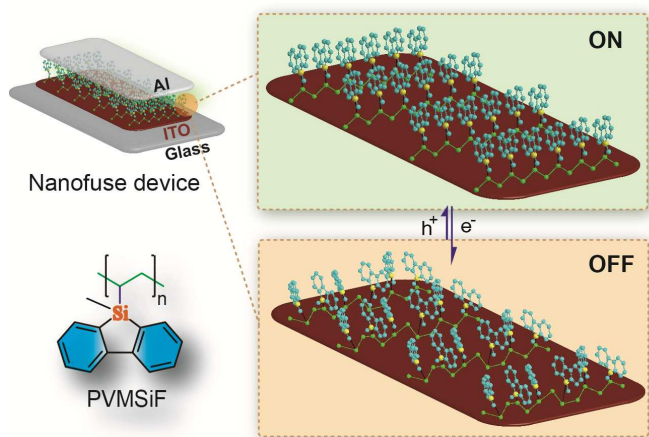


Figure 1. Schematic illustration and possible operation mechanism of the nanofuse device (ITO/PVMSiF/Al).

Herein, we report the first experimental approach to realize a high-performance *on/off* molecular nanofuse device of π -stacked polymer with ON/OFF ratio up to 4×10^6 . Our strategy involves the manipulation of charge transport behaviors of the novel π -stacked polymer of polyvinylsilafuorene (PVMSiF) via silicon incorporation (**Figure 1**), which results in: (i) the partially π -stacked pendant group, that has aromatic silafuorene^[22c,23] for π - π stacking and high conductive ON-states, (ii) methyl substituent and sp^3 hybridized Si to prevent the full π - π stacking, (iii) long C-Si bond length (*c.a.* 1.9 Å) to accommodate the twisted partial π - π stacking architecture, and

(iv) spectacular interactions between Si and the π -conjugated system, which leads to unstable and breakable π - π stacking at anionic states after electron injection for transition to the low conductive OFF-states. This unique fuse-like resistive switching of PVMSiF induced by breakable π - π stacking at charged states demonstrates great potentials of π -stacked polymers in charge transport engineering for advanced molecular optoelectronic devices.

Results and discussion

Material design, synthesis and characterization

The silicon-incorporated π -stacked polymer (PVMSiF) was designed by replacing sp^3 hybridized C of fluorene with Si to form the monomer of vinyl methyl silafuorene,^[22a,22b] which was further polymerized to obtain the target material (**Scheme S1**). The monomer can be synthesized in a two-step synthetic route of lithium mediated C-C coupling and C-Si formation from *o*-dibromobenzene according to the previously reported methods in high yield.^[24-25] However, the vinyl silafuorenes cannot be polymerized via free radical mechanism due to the feasible radical transfer to silicon atoms.^[22c] These difficulties in the chemical incorporation of silicon into the π -stacked polymer were eventually overcome via the anionic living polymerization. The obtained novel silicon-containing π -stacked homopolymer (PVMSiF) show typical narrow molecular distribution ($M_w/M_n=1.06$) of anionic polymers with the number-average (M_n) and weight-average (M_w) molecular weight of 45,700 and 48,500 respectively, as revealed by gel permeation chromatography (GPC) analysis (**Figure S1**). PVMSiF with *c.a.* 205 aromatic silicon-incorporated repeating units ($n=205$) and flexible polyethylene backbone, show high thermostabilities (**Figure S2**) and excellent solubility in a variety of organic solvents. Good morphology of the spin-coated PVMSiF nano-film was observed by atom force microscopy (AFM, **Figure S3**). Therefore, devices can be facilely fabricated with nanoscale thin films (50 nm) of PVMSiF (HOMO = -6.13 eV, LUMO = -2.51 eV, **Figure S4**) as active layer, and aluminum (Al, 100 nm) and indium tin oxide (ITO) as top and bottom electrodes respectively (**Figure 2**).^[26]

Nanofuse device performance

The current-voltage (*I-V*) characteristics of the ITO/PVMSiF/Al device were measured at room temperature and ambient atmosphere. From **Figure 2**, when a positive voltage is applied from 0 to 8 V (1st sweep), the device is initially ON with high current density, then an abrupt decrease in the current occurs at 5.35 V (which corresponds to $V_{c,OFF}$, the critical voltage to switch the device off), indicating that the device undergoes a sharp electrical transition from a high conductivity state (ON-state) to a low conductivity state (OFF-state). This ON-to-OFF transition can function in a memory device as a writing process. Once the device has reached its OFF-state, it remains there even after the power is turned off. A subsequent positive sweep (2nd sweep) shows that the device

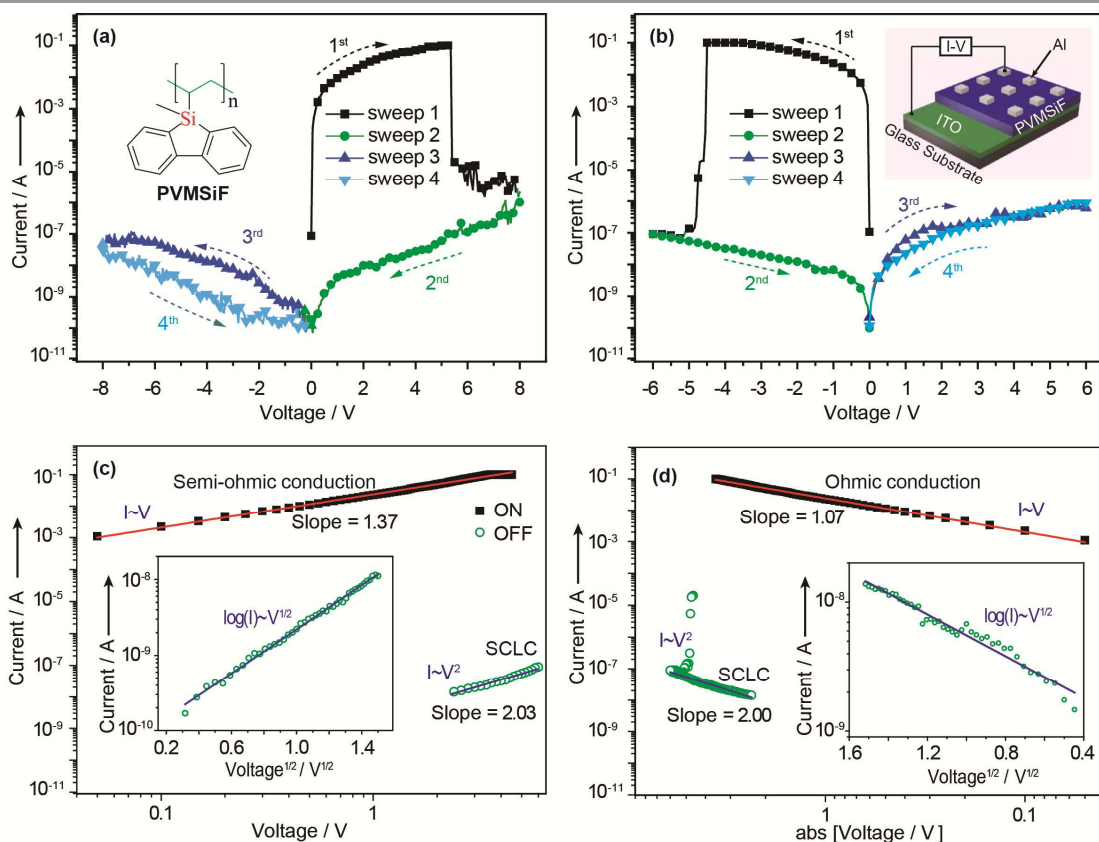


Figure 2. Typical I - V curves of the ITO/PVMSiF/Al device: (a) positive and reverse voltage sweeps; (b) negative and reverse voltage sweeps; $\ln(I)$ vs $\ln(V)$ plots in OFF- and ON-states under (c) positive and (d) negative voltage sweeps (inset: $\ln(I)$ vs $V^{1/2}$).

remains in its low conductivity state. After reverse sweeps (3rd and 4th sweeps) was applied, the device remains at its low conductivity (OFF) state, suggesting a WORM memory behavior.^[27] The ON/OFF state current ratio in the first (before writing) and second (after writing) sweeps remains constant (3×10^6) until the turn-off voltage of 5.35 V is reached (Figure S5a) with high ON/OFF-states stabilities (Figure S6). Interestingly, when a negative voltage is applied, similar WORM memory behavior of the device was also observed (Figure 2b). The ON/OFF ratio is close (4×10^6), while the turn-off voltage is slightly lower (-4.50 V) (Figure S5b). This ON-to-OFF WORM memory at bilateral bias based on the homopolymer presents an example of rudimentary molecular fuse.^[13] When the voltage applied to the molecular circuit is either high enough (>5.35 V) or low enough (<-4.50 V), PVMSiF-based device is irreversibly turned to OFF state, which breaks the circuit and stops the electrical conduction. This interesting property might be particularly important in molecular electronics, protecting against voltage surges, or serving as components in memory storage systems, when situated in a molecular circuit.^[28]

In order to identify the particular conductance switching of the molecular fuse, the transport behaviors of charge carriers of the polymer under electric fields were investigated. The measured I - V curves at different states of the PVMSiF device

were fitted with appropriate charge transport models. When positive voltage is applied (Figure 2c), the plot of $\ln(I)$ versus $\ln(V)$ was well fitted to a line in the voltage range from 0 to 5.35 V (ON state) before the electrical transition. However, the slope of such a linear relation is not around 1.0 as in ohmic conduction mechanism but an accelerated one of 1.37, *i.e.* a semi-ohmic conducting mode.^[26] The I - V curve at the OFF state was fitted to a linear relationship between I and V^2 in the voltage range from 5.35 to 2.28 V, indicating the space-charge-limited current (SCLC) model.^[27] When the voltage is sweeping from 2.28 to 0 V, a linear relation at the OFF state was observed between $\ln(I/V)$ and $V^{1/2}$ that can be fitted by the Schottky emission model^[27] (Figure 2c inset). When negative voltage is applied (Figure 2d), similar behaviors of the I - V curves were observed, except that the slope of the $\ln(I)$ versus $\ln(V)$ is 1.07, which can be satisfactorily attributed to Ohmic conduction mechanism.

Optical Properties

The UV-visible absorption and photoluminescence (PL) spectra of PVMSiF in dilute tetrahydrofuran (THF) and thin film before and after annealing were investigated (Figure 3) to understand the fuse-like electronic switching mechanism of PVMSiF. In THF, the chromophore of silafluorene is well solvated and shows one narrow absorption band around 278 nm

and one luminescence band around 348 nm.^[25,29] However, in the solid film, silafluorenes in PVMSiF are aggregated due to π - π stacking, resulting in the appearance of the absorption shoulder around 319 nm and PL peak at 417 nm even in the as-spun films. After annealing at 90°C for 8 h, the PL peak around 360 nm corresponding to the emission of single molecule of silafluorene unit disappears; the absorption and emission band become further red-shifted and broadened with enhanced absorption around 325 nm and red-shifted PL peak at 424 nm, suggesting the almost complete π - π stacking of the whole polymer chain after thermal relaxation. Considering that the PVMSiF layer was annealed at 90 for 8 h before the vacuum-deposition of Al electrode, the π -stacked polymer should be well self-assembled with complete and stable π - π stacking. As found in PVK, the neighboring carbazole groups have a high tendency to form the face-to-face conformations (π - π stacking) in the ground state and increased tendency in charged states, leading to high conductivity,^[18] these π - π stacked silafluorenes of PVMSiF can also serve as highly conductive channels for charge carriers, which should be responsible for the ON-state of the memory device.

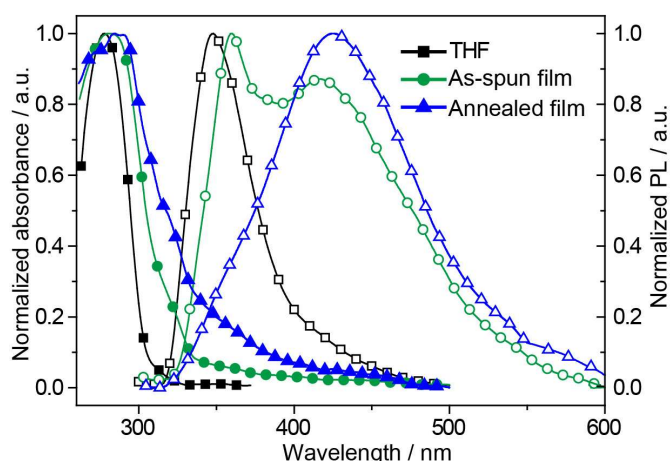


Figure 3. UV-vis absorption (solid symbols) and PL (open symbols) spectra of PVMSiF in THF and in as-spun and annealed films.

Micro-PL spectrum measurement was performed to probe the PL shift of the active layer of PVMSiF during the device operation (**Figure S7**). The PL spectra at either ON or OFF states are similar to that of blank film with a peak around 424 nm, which is also very close to that of annealed film in **Figure 3**, suggesting that the supra-conjugated polymer of PVMSiF remains optically identical at both ON and OFF states. It is possible that the supra-conjugation is sufficiently long for high charge mobility at ON state, while at OFF state, the supra-conjugation is partially broken that it cannot support for long conducting channel with high conductivity, but it is still longer than the effective conjugation length of the supra-conjugated polymer, leading to identical photoproperties regardless of the minor change of the chain structure.

DFT calculations

For in-depth understanding of this extraordinary molecular electrical behavior, quantum chemical calculations (M062X/cc-PVDZ) considering the long-range π - π interaction^[30] were performed to identify the relations between the electronic states and structures of the π - π stacking. The DFT calculations of the monomer and dimer models of PVMSiF were compared with that of the well-known π -stacked polymer of PVK^[8] (**Figure 4** and **Table S1**). The unmodified PVK and its synthetically developed derivatives have exhibited excellent memory effects^[26, 31] with an ON/OFF resistivity ratio of about 10^6 ; initially the devices are at the OFF state; when a voltage exceeding V_c is applied, the current in the device abruptly increases and the devices are switched to the ON state. Compared to the carbazole units in PVK, silafluorene shows lower HOMO and LUMO energy levels due to its unique σ^* - π^* conjugation. Higher electron affinity (EA) and closer reorganization energy of hole and electron (λ_h and λ_e) of silafluorene than that of carbazole suggests facilitated electron injection and balanced carrier transportation of silafluorene.^[32] Same trends were observed in their dimers, except for that of λ_e . The decreased λ_e in the di-silafluorene may be due to the strong interaromatic interaction of LUMO.^[11b] As illustrated in **Figure 4**, the isosurface of LUMO delocalizes between the π -stacked silafluorene, and this delocalization is even more apparent along the π -stacked polymer chain, indicating the facilitated electron transportation with low λ_e . Continuous positive electrostatic potentials (ESP) (in green color) along the polyethylene backbone can be also observed in **Figure 4**, offering high conductive open channels for charge carriers to migrate through. The DFT optimized dimer of PVK exhibits good face-to-face conformation of π - π stacking with low tilt angle of 7.91° and short unit distance of 3.75 Å at ground state (**Figure S8**).^[27] In comparison with PVK, units in PVMSiF were partially stacked with a larger tilt angle of 25.15° and an

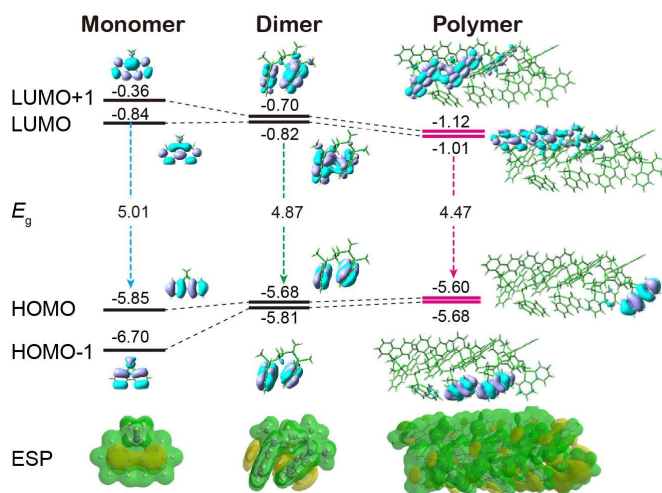


Figure 4. HOMO, LUMO, and ESP isosurfaces of monomer, dimer, and polymer ($n=12$) of PVMSiF from DFT calculations.

increased unit distance of 4.16 Å at the neutral ground state (**Figure 5**). The less significant π - π stacking in PVMSiF is due to the sp^3

hybridization of Si and the spatial hindrance of methyl substituent in silafluorene. When the dimers were charge injected, the tilt angle and unit distance of PVK further decrease to $7.55^\circ/3.48 \text{ \AA}$ and $5.38^\circ/3.42 \text{ \AA}$ for hole and electron injection, respectively. This means that the π - π stacking in PVK strengthens after charge injection and cannot be broken at applied driven voltages, resulting in higher conductivity at both biases as found experimentally^[26]. However in PVMSiF, the π - π stacking is not as strong as in PVK. The tilt angle and unit distance decrease to 16.93° and 3.70 \AA after hole injection; after electron injection, they increase to 28.62° and 4.28 \AA , suggesting that the π -stacked motif of PVMSiF is stabilized at cationic state but destabilized at anionic state. The unstable π - π stacking upon electron injection of the partially π -stacked silafluorene in PVMSiF may destroy the conductive channel at high driving voltages, which might be the main reason for the decreased conductivity at high bias (OFF-state).

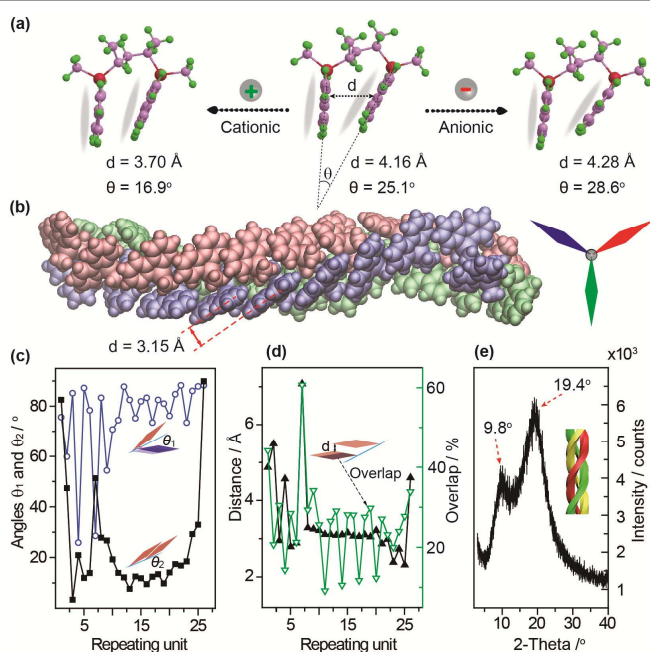


Figure 5. DFT calculations, MD simulations, and XRD measurements: (a) The π - π stacking distance (d , in \AA) and tilt angle (θ in $^\circ$) in the dimer of PVMSiF at cationic (left), neutral (middle), and anionic (right) states; (b) The energy-minimized conformation of PVMSiF ($n=30$) predicted by mechanical dynamic (MD) simulation; (c) The angle between the nearby (θ_1 in $^\circ$) and every three (θ_2 in $^\circ$) silafluorene units; (d) The distance (d in nm) and overlap ratio (in %) of every three silafluorene units; (e) X-ray diffraction pattern of PVMSiF powder.

MD simulations

The polymer conformations of PVMSiF were further investigated with mechanical dynamic (MD) simulations^[33,34] (Figure S9). The stable PVMSiF ($n=30$) conformation after 70 ps equilibration (Figure 5b) exhibits three strips of π - π stacking that twisted together along the polyethylene backbone, resulting in a rigid spiral 1D π -stacked polymer. In the middle of the polymer chain where the effects of the chain ends were minimized, the nearby two silafluorene units are almost vertical to each other ($\theta_1 = 80 \pm 5^\circ$) without π - π stacking, while the angle (θ_2) between every three silafluorene units are lower than 15° (Figure 5c) with distance

around 3.15 \AA (Figure 5d), indicating the typical π - π stacking of silafluorenes. However, the π - π stacking is not complete but shifted with an offset about one phenyl. As further assessed by the overlapping ratio defined by the area ratio of the vertical projection of the two nearby silafluorene groups (Figure 5d), the major π - π stacking overlapping ratio is about 30%, i.e. the partial π - π stacking. The π -stacked motif of the polymer was also confirmed by X-ray diffraction (XRD) measurements (Figure 5e). The strongest diffraction peak appears at $2\theta=19.4^\circ$ corresponding to the face-to-face distance about 4.57 \AA , which may be related to the intramolecular periodic strip-to-strip distance between the three strips of π - π stacking.^[22c] The 1D rigid polymer conformation offers the high conductance of the π -stacked silafluorene-based polymer for molecular devices. Meanwhile, the semi-stable partial π - π stacking provides increased possibility for tuning the conductance via conformational changes upon external stimuli.

Discussions

Based on both experimental and theoretical investigations, a possible mechanism for this unusual molecular nanofuse device of the partially π -stacked polymer of PVMSiF can be proposed (Figure S10). After thermal annealing, PVMSiF chains were well assembled in rigid rod-like π -stacked conformation on ITO surface for the initially ON-state of the device. When positive voltage was applied, holes were injected from Al into HOMO of PVMSiF due to the lower hole injection barrier (1.83 eV) than that of electron (2.19 eV) injected from ITO into LUMO of PVMSiF. And, the hole injection leads to closer packing of silafluorenes, resulting in accelerated ohmic conduction model at ON-state (Figure 2). When the applied positive voltage further increases, the ratio of electron injection will gradually increase, leading to gradual breakage of the π - π stacking motif. At $V_{c,OFF}$, the destruction effects of the electron injection prevails the construction effects of hole injection, leading to completely destroyed conductive channel of π - π stacking, which turns the device to the OFF-state. Similarly, when negative voltage was applied on Al, holes were injected from ITO into HOMO of PVMSiF due to lower injection barrier (1.43 eV) of hole than that of electron (1.79 eV). At more negative applied voltages, electron injection from Al into LUMO of PVMSiF will increase and thus breaks the π - π stacking. Because of the higher electron injection barrier at positive voltage (2.19 eV) than that at negative voltage (1.83 eV), the $V_{c,OFF}$ at positive sweep is higher than that at negative sweep as found experimentally. On the OFF-state, the continuous π - π stacking conductive filaments were eliminated, resulting in typical Schottky emission and SCLC models as in most organic materials. The high conductivities at low voltages and low conductivities at high voltages suggest typical fuse-like electronic switching behavior for molecular circuitries. The conducting channel destruction due to silicon incorporation serve as a trigger for ON-to-OFF switching of the device, which could offer important clue for charge transport manipulation of organic semiconductors.

The breakage of π - π stacking is also possible to be resulted from the structural rearrangements of the oxidized and reduced

silafluorenes at applied voltages^[35]. However, this degradation mechanism through silafluorene radical cations or anions rearrangements seems to be not in line with several experimental observations: (1) The device is very stable that it can last over 10000 s at both ON and OFF states (Figure S6), suggesting that these radical cations or anions responsible for the high current density at ON state are quite stable without rearrangement reactions; (2) When we increased the thickness of PVMSiF film up to 110 nm (Figure S11), the fuse-like function was also observed but with increased ON-OFF transition voltage (up to 10.5 V) and decreased ON/OFF ratio (around 10^3), which is in contradictory to the degradation mechanism which depends on a characteristic bias voltage above a fixed threshold for electrochemical oxidation or reduction. Also, in such a thick polymer film, Al atom cannot diffuse deep enough to responsible for the memory effect, supporting that the fuse function is originally from the molecular structure effects; (3) After careful annealing of the device that is turned off electrically, the fuse function can be recovered thermally (Figure S12), which provides a direct proof that PVMSiF is not degraded irreversibly during the device operation.

Conclusions

Summarily, in stark contrast to conventional π -conjugated and π -stacked polymers, the newly prepared silicon-containing π -stacked polymer of PVMSiF exhibits extraordinary molecular nanofuse as well as excellent WORM memory behaviors with high ON/OFF ratios (up to 4×10^6) under ambient air conditions. The conductivity switching mechanism of the polymeric nanofilm, understood in a silicon-stimulated filament theory, was proposed to be related to the π - π stacking conductive filaments formation and deformation control upon electron/hole injection realized by silicon incorporation strategy, based on a combinational analysis of UV-Vis and PL spectra, XRD, micro-PL and joint theoretical investigations of DFT and MD simulations. It is for the first time that the 1D π -stacked homopolymer of vinyl silafluorene has been achieved via anionic living polymerization; the semi-stable partially π - π stacked conformation of the regioregular silicon-incorporated π -stacked polymer results in unique on/off irreversible switching behavior for molecular nanofuse. The strategy to realize the fuse-like charge transport behavior via breakable π - π stacking at charged states through silicon incorporation could be highly valuable not only for understanding the charge transfer and charged states manipulating principles in π -conjugated and π -stacked polymers but also for providing new clues in designing high-performance π -stacked materials for molecular electronics.

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Notes and references

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- 1 A. J. Heeger, *Chem. Soc. Rev.* **2010**, *39*, 2354.
- 2 A. Batra, G. Kladnik, H. Vazquez, J. S. Meisner, L. Floreano, C. Nuckolls, D. Cvetko, A. Morgante, L. Venkataraman, *Nat. Commun.* **2012**, *3*, 1086.
- 3 H. L. Dong, H. F. Zhu, Q. Meng, X. Gong, W. P. Hu, *Chem. Soc. Rev.* **2012**, *41*, 1754.
- 4 Y. G. Wen, Y. Q. Liu, *Adv. Mater.* **2010**, *22*, 1331.
- 5 a) T. Nakano, K. Takewaki, T. Yade, Y. Okamoto, *J. Am. Chem. Soc.* **2001**, *123*, 9182; b) T. Nakano, *Polym. J.* **2010**, *42*, 103.
- 6 a) I. Diez-Perez, J. Hihath, T. Hines, Z. S. Wang, G. Zhou, K. Mullen, N. J. Tao, *Nat. Nanotechnol.* **2011**, *6*, 226; b) J. Vura-Weis, S. H. Abdelwahed, R. Shukla, R. Rathore, M. A. Ratner, M. R. Wasielewski, *Science* **2010**, *328*, 1547.
- 7 T. Uemura, N. Uchida, A. Asano, A. Saeki, S. Seki, M. Tsujimoto, S. Isoda, S. Kitagawa, *J. Am. Chem. Soc.* **2012**, *134*, 8360.
- 8 J. R. Pinzon, A. Villalta-Cerdas, L. Echegoyen, *Top. Curr. Chem.* **2012**, *312*, 127.
- 9 a) B. Zhang, Y. Chen, Y. Zhang, X. Chen, Z. Chi, J. Yang, J. Ou, M. Q. Zhang, D. Li, D. Wang, M. Liu, J. Zhou, *Phys. Chem. Chem. Phys.* **2012**, *14*, 4640; b) K. Watanabe, T. Sakamoto, M. Taguchi, M. Fujiki, T. Nakano, *Chem. Commun.* **2011**, *47*, 10996.
- 10 a) L. Xie, Q. Ling, X. Hou, W. Huang, *J. Am. Chem. Soc.* **2008**, *130*, 2120; b) J. Yin, R. Chen, S. Zhang, H. Li, G. Zhang, X. Feng, Q. Ling, W. Huang, *J. Phy. Chem.C.* **2011**, *115*, 14778.
- 11 a) C. Zheng, Y. Tao, J. Z. Cao, R. F. Chen, P. Zhao, X. J. Wu, W. Huang, *J. Mol. Model.* **2012**, *18*, 4929; b) M. X. Wang, *Chem. Commun.* **2008**, *0*, 4541; c) R. S. Klausen, J. R. Widawsky, T. A. Su, H. Li, Q. Chen, M. L. Steigerwald, L. Venkataraman, C. Nuckolls, *Chem. Sci.* **2014**, *5*, 1561.
- 12 a) K. L. Chan, M. J. McKiernan, C. R. Towns, A. B. Holmes, *J. Am. Chem. Soc.* **2005**, *127*, 7662; b) M. J. Yuan, P. Y. Yang, M. M. Durban, C. K. Luscombe, *Macromolecules* **2012**, *45*, 5934; c) J. C. Sanchez, A. G. DiPasquale, A. L. Rheingold, W. C. Trogler, *Chem. Mater.* **2007**, *19*, 6459.
- 13 R. Emanuelsson, A. Wallner, E. Ng, J. R. Smith, D. Nauroozi, S. Ott, H. Ottosson, *Angew. Chem. Int. Edit.*, **2013**, *52*, 983; *Angew. Chem.* **2013**, *125*, 1017.
- 14 a) N. Fuentes, A. Martin-Lasanta, L. Alvarez De Cienfuegos, M. Ribagorda, A. Parra, J. M. Cuerva, *Nanoscale* **2011**, *3*, 4003; b) S.

- Rodriguez-Bolivar, F. M. Gomez-Campos, L. Alvarez De Cienfuegos, N. Fuentes, D. J. Cardenas, E. Bunuel, J. E. Carceller, A. Parra, J. M. Cuerva, *Phys. Rev. B.* **2011**, *83*, 125424.
- 15 a) N. Fuentes, L. A. de Cienfuegos, A. Parra, D. Choquesillo-Lazarte, J. M. Garcia-Ruiz, M. L. Marcos, E. Bunuel, M. Ribagorda, M. C. Carreno, D. J. Cardenas, J. M. Cuerva, *Chem. Commun.* **2011**, *47*, 1586; b) L. Wang, Z. Su, C. Wang, *Appl. Phys. Lett.* **2012**, *100*, 213303.
- 16 A. J. Mota, L. Alvarez De Cienfuegos, S. P. Morcillo, N. Fuentes, D. Miguel, S. Rodriguez-Bolivar, F. M. Gomez-Campos, D. J. Cardenas, J. M. Cuerva, *ChemPhysChem.* **2012**, *13*, 3857.
- 17 A. Cappelli, M. Paolino, G. Grisci, G. Giuliani, A. Donati, R. Mendichi, A. C. Boccia, C. Botta, W. Mroz, F. Samperi, A. Scamporrino, G. Giorgi, S. Vomero, *J. Mater. Chem.* **2012**, *22*, 9611.
- 18 Y. Liu, N. Li, X. Xia, Q. Xu, J. Ge, J. Lu, *Mater. Chem. Phys.* **2010**, *123*, 685.
- 19 B. Zhang, G. Liu, Y. Chen, C. Wang, K. Neoh, T. Bai, E. Kang, *ChemPlusChem.* **2012**, *77*, 74.
- 20 N. Kang, B. Cho, B. Kang, S. Song, T. Lee, J. Lee, *Adv. Mater.* **2012**, *24*, 385.
- 21 C. Liu, J. Hsu, W. Chen, K. Sugiyama, A. Hirao, *ACS Appl. Mater. Inter.* **2009**, *1*, 1974.
- 22 (a) I. M. Gverdtsiteli, O. K. Zhurnal, *J. Gen. Chem. USSR (Engl. Transl.)*. **1966**, *36*, 114; (b) J. C. Sanchez, A. G. DiPasquale, A. L. Rheingold and W. C. Trogler, *Chem Mater.* **2007**, *19*, 6459. (c) R. Chen, Q. Fan, S. Liu, R. Zhu, K. Pu, W. Huang, *Synthetic Met.* **2006**, *156*, 1161.
- 23 R. Shintani, H. Otomo, K. Ota, T. Hayashi, *J. Am. Chem. Soc.* **2012**, *134*, 7305.
- 24 R. F. Chen, Q. L. Fan, C. Zheng, W. Huang, *Org. Lett.* **2006**, *8*, 203.
- 25 R. Chen, R. Zhu, C. Zheng, Q. Fan, W. Huang, *Sci. China. Chem.* **2010**, *53*, 2329.
- 26 Q. Ling, D. Liaw, C. Zhu, D. S. Chan, E. Kang, K. Neoh, *Prog. Polym. Sci.* **2008**, *33*, 917.
- 27 Q. D. Ling, D. J. Liaw, E. Teo, C. X. Zhu, D. Chan, E. T. Kang, K. G. Neoh, *Polymer* **2007**, *48*, 5182.
- 28 S. W. Lee, S. J. Park, E. E. B. Campbell, Y. W. Park, *Nat. Commun.* **2011**, *2*, 220.
- 29 C. W. Keyworth, K. L. Chan, J. G. Labram, T. D. Anthopoulos, S. E. Watkins, M. McKiernan, A. White, A. B. Holmes, C. K. Williams, *J. Mater. Chem.* **2011**, *21*, 11800.
- 30 E. G. Hohenstein, S. T. Chill, C. D. Sherrill, *J. Chem. Theory. Comput.* **2008**, *4*, 1996.
- 31 Y.-S. Lai, C.-H. Tu, D.-L. Kwong, J.S. Chen, *App. Phys. Lett.* **2005**, *87*, 122101
- 32 (a) J. Wang, C. Q. Zhang, C. M. Zhong, S. J. Hu, X. Y. Chang, Y. Q. Mo, X. W. Chen, H. B. Wu, *Macromolecules* **2011**, *44*, 17. (b) R. Chen, C. Zheng, Q. Fan, W. Huang, *J. Comput. Chem.* **2007**, *28*, 2091.
- 33 F. May, M. Al-Helwi, B. Baumeier, W. Kowalsky, E. Fuchs, C. Lennartz, D. Andrienko, *J. Am. Chem. Soc.* **2012**, *134*, 13818.
- 34 A. Balijepalli, J. Robertson, J. E. Reiner, J. J. Kasianowicz, R. W. Pastor, *J. Am. Chem. Soc.* **2013**, *135*, 7064.
- 35 Brook, MA, *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, 2000.