

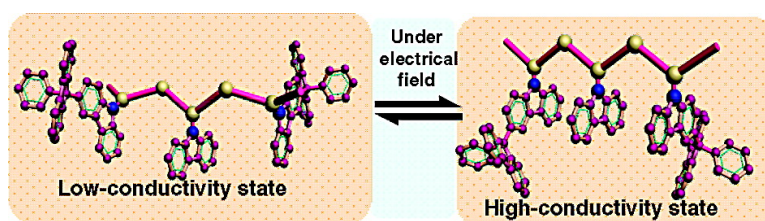
Communication

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An Effective Friedel–Crafts Postfunctionalization of Poly(*N*-vinylcarbazole) to Tune Carrier Transportation of Supramolecular Organic Semiconductors Based on π -Stacked Polymers for Nonvolatile Flash Memory Cell

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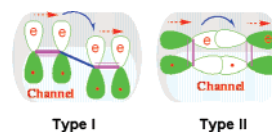
Carrier-transporting channels of organic semiconductors have two fundamental configurations via π -orbital combination: π -conjugated configuration (type I)¹ and π -stacked configuration (type II),² as shown in Scheme 1. Organic semiconductors based on type I have attracted considerable interest in a wide variety of applications such as light-emitting diodes,³ transistors,⁴ lasers,⁵ sensors,⁶ solar cells,⁷ and memory devices.⁸ However, π – π stacking interaction plays a vital role in improving the mobility of OFET,⁹ the self-assembly of disk liquids,¹⁰ and the formation of aggregates.¹¹ One typical class of supramolecular organic semiconductors (SOSs) is π -stacked polymers such as poly(*N*-vinylcarbazole) (PVK),¹² whose hole-transporting properties are attributed to the intrachain π – π stacking alignment. PVK has been exploited in applications such as organic photoconductive materials,¹³ host materials for WOLEDs and phosphorescent OLEDs,¹⁴ and conductance switching materials.¹⁵ However, there are only few reports on the development of an essential strategy for tuning the semiconducting properties of SOSs.

In this Communication, we offer a general method to utilize the steric effect of bulky moieties for tuning carrier behaviors in PVK SOS system and explore their applications in nonvolatile flash memory. To construct this unique system, a useful Friedel–Crafts postfunctionalization of PVK to incorporate nonplanar phenylfluorene moieties (PFM) is also developed.

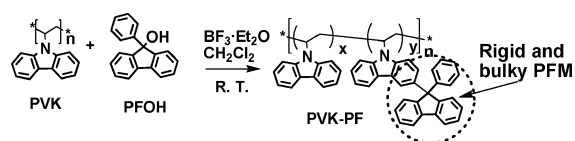
PVK–PF, as a typical SOS model, was prepared via Friedel–Crafts reaction between PVK and tertiary alcohol PFOH, using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ complex as a Lewis acid catalyst, as reported in our previous work (Scheme 2).¹⁶ GPC measurement revealed the M_n of PVK to be 42 226, with a PDI of 2.09. After the covalent attachment of PFM, the M_n of PVK–PF increased to 59 095, with a comparable PDI of 2.25.

In the UV–visible absorption spectra (Figure 1a and 1b), the modified PVK–PF shows a broad profile, significantly different from the three strong absorption bands at 295, 330, and 345 nm observed in that of PVK. PVK and PVK–PF also exhibit different light-emitting behaviors, as shown in Figure 1c and 1d. There are two emission peaks at ca. 371 and 450 nm for PVK. The intensity of the peak at 450 nm tends to be increased with the number of scans, indicating the formation of photoinduced π -stacked face-to-face conformations among the carbazole (Cz) moieties.¹¹ A broad, structureless band attributable to excimer emission was also detected at about 411 nm in solid state. In contrast, PVK–PF exhibits a single, stable emission peak at about 380 nm in both solution and solid film (Figure 1d). The results indicate that rigid PFMs can prevent Cz groups from undergoing π -stacking alignments. In addition, the introduction of bulky PFMs into PVK also

Scheme 1. Two Fundamental Types of π Orbital Combination: π -Conjugated Configuration (Type I) and π -Stacked Configuration (Type II)



Scheme 2. Friedel–Crafts Postfunctionalization of π -Stacked PVK–PF SOS



improves the thermal stability, but does not affect the hole-injecting ability of PVK–PF, as revealed by TGA and cyclic voltammetric (CV).

The electrical characteristics of the polymers are demonstrated by the current–voltage (I – V) curves of an ITO/PVK or PVK–PF (50 nm) /Al sandwich device. For PVK, no conductance switching behavior is observed when the voltage across the device is swept from 0 to -3.0 V or 0 to 3.0 V (see Supporting Information). For PVK–PF, the device was initially at a low-conductivity state when swept negatively from 0 to -3 V. However, when it was swept positively from 0 to 3 V, a sharp increase in the measured current occurred at about 2.2 V (the second sweep in Figure 2a), indicating the device transition from a low-conductivity state ($\sim 10^{-11}$ A, OFF state) to a high-conductivity state ($\sim 10^{-7}$ A, ON state). The transition from the OFF state to the ON state is equivalent to the “write” process. The device in its high-conductivity state exhibited good stability during the subsequent positive sweep (the third sweep). It remained in the ON state even after the power was turned off (the fourth sweep). One of the most important features in this system is the “erase” process in which the ON state can be recovered by the simple application of a reverse voltage at about -2.0 V (the fifth sweep). The sixth sweep shows a stable OFF state same as that of the first sweep, which allows the application of PVK–PF in a rewritable flash memory device. An ON/OFF current ratio of more than 10^4 has been achieved (Figure 2b). The effect of continuous read pulses of -1 V on the ON and OFF states was investigated (Figure 2c). No degradation was observed of the OFF and ON states after 10^8 read cycles, indicating that both states are insensitive to read cycles. There was no significant degradation in the device currents of both the OFF and ON states after 6 h of continuous stress test (Figure 2d), demonstrating the stability of both the material and the electrode/polymer interfaces.

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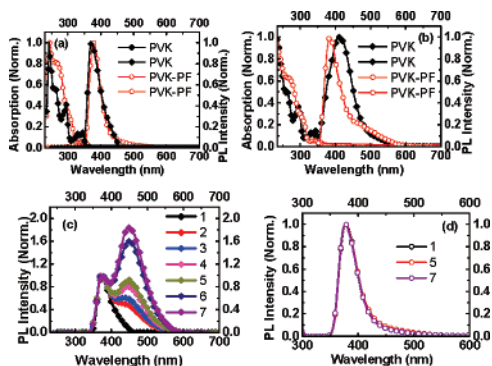


Figure 1. UV-visible absorption spectra and fluorescence spectra ($\lambda_{\text{ex}} = 330$ nm) of PVK and PVK-PF in solution and solid film: (a) in diluted CH_2Cl_2 solution (1.0×10^{-5} mol/L); (b) in solid film spin-coated from toluene solution; (c) PL of PVK in different number of scan in diluted solution; (d) PL of PVK-PF in different number of scan.

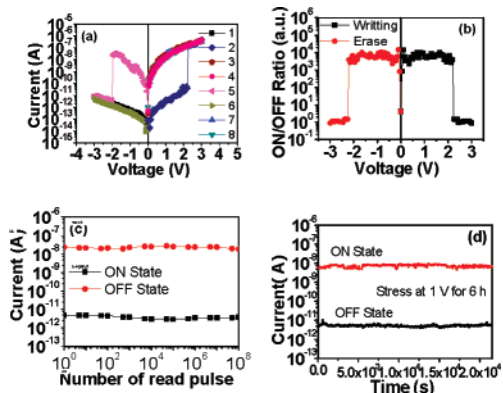


Figure 2. (a) Current–voltage (I – V) characteristics of a memory device: ITO/PVK–PF (50 nm)/Al (390 nm) (0.2×0.2 mm²); (b) ON- to OFF-state current ratio as a function of applied voltage; (c) effect of -1 V read pulses on the device current in the OFF and ON states; (d) effect of operation time (at 1 V) on the device current in the OFF and ON states tested under ambient conditions.

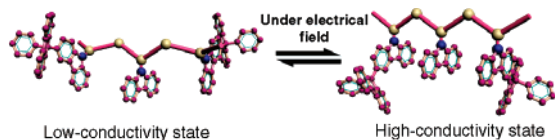


Figure 3. Schematic diagram for the switching transition from low-conductivity to high-conductivity states.

Although pristine PVK has only a single conductivity state (ON) in solid state,^{15b} flash memory based on the filament conduction effect can be observed in impurity PVK.^{15d} In the PVK–PF SOS system, the ON-state current increased with the increase of temperature and the linear dependence of current magnitude on the active area of the device ruled out the filament conduction effect (see Supporting Information).

Memory effects of PVK derivatives with flexible spacers between the carbazole pendant group and the polymer backbone,^{15c} in which regiorandom and regioregular alignments corresponds to the low- and high-conductivity states, only showed WORM or volatile features. The nonvolatile flash memory effect of PVK–PF is essentially involved with the unique steric effects of rigid and bulky PFMs and their field-induced alignment, as schematically illustrated in Figure 3. The ON state of PVF–PF consists of nearly full face-to-face conformation but the resultant arrangement is still less regular than that of PVK, as indicated by their different current

densities. The nonvolatile feature of the device can probably be attributed to the rigidity and adaptability of the bulky PFM to π -stacked surroundings. This leads to a highly stable conformation at the ON state with intrachain alignments, which is supported by optimized geometric conformations (see Supporting Information). A reversal of the electric field breaks the stacks due to thermal injecting at the electrode/polymer interface, causing the sample to switch back to its initial state.^{15a} The nonvolatile feature and “erase” process are expressively different from the electrical behaviors of other PVK derivatives with flexible spacers.^{15c}

In summary, we proposed a concept of SOSs based on π -stacked polymers and developed an effective Friedel–Crafts postfunctionalization of PVK to construct the PVK–PF SOS system. At the same time, we demonstrated the first nonvolatile flash memory device based on conformation change effects, in which the rigid PFMs play a crucial role, not only in the ON/OFF current ratios but also the nonvolatility of the memory device, by controlling intrachain π -stacked interaction.

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Supporting Information Available: Detailed synthetic procedures, TGA, DSC, CV curves, J – V curve, enlarged Figure 1 and 2, and optimized geometries. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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