# Nonvolatile memory organic field effect transistor induced by the steric hindrance effects of organic molecules<sup>†</sup>

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We report a nonvolatile memory organic field effect transistor (OFET) using ambipolar organic molecules as nano-interfaced semiconductor materials. Newly synthesized push-pull organic molecules (PPOMs) containing triarylamine as an electron donating group, thiophene as a spacer, and malononitrile as an electron withdrawing group are proposed. The tilted PPOMs with side chains could control the charge trapping of the conducting channel formed between pentacene and PPOMs. Quantum chemical calculations were carried out to estimate the dihedral angle at the neutral and electron charged anion molecules and to explain the charge mobilities of OFETs comprising the nano-interfaced PPOMs were affected by the dihedral angles derived from the steric hindrance of the bulky side chain of the spacer. The memory OTFT with higher dihedral angle material exhibited a wider memory window as well as reduced current flow. The memory OFET devices showed a memory window of -40 to +40 V, a memory ratio of 100 for "ON" to "OFF" currents, and long retention time for the nonvolatile memory.

## 1. Introduction

The organic field effect transistor (OFET) has attracted a great deal of attention given its potential application in low cost, flexible, and large area electronics.<sup>1</sup> Several OFET devices containing organic semiconducting materials exhibit high electronic performance comparable to or surpassing those with amorphous hydrogenated silicon (a-Si:H).<sup>2</sup> However, memory elements for OFET applications such as parts of radio frequency identification devices, smart cards, and disposable circuitry are less developed. Among organic memory devices, a memory based on the OFET is especially attractive because of its nondestructive readout and single transistor applications. Initial attempts at nonvolatile organic memory involved electrets, chargeable dielectrics, *etc.* Katz *et al.* demonstrated OFET memory with a polarizable gate insulator that induced floating-gate-like behavior,<sup>3</sup> while Singh *et al.* demonstrated OFET memory using poly(vinyl alcohol) as a gate electret.<sup>4</sup> Recently, Noh *et al.* reported simple electrets using a polymer for the memory dielectrics.<sup>5</sup> However, these devices still do not sufficiently satisfy the criteria demanded in order to compete with other types of memory devices with the electrets being generally limited to polymer materials.

However, until now, there has been no report on nonvolatile organic electrets using a nano-interfaced organic monomer layer as a semiconductor material, even though the use of organic monomer materials has become important for the development of molecularly interfaced memory and logic elements. Furthermore, to increase the retention time of nonvolatile organic memory devices, as well as to understand the intrinsic memory properties, molecular design of the organic materials is becoming an important issue.

In complement to demonstrate the concept of organic nonvolatile memory devices, we report an OFET memory device built on a silicon wafer and based on films of pentacene and a SiO<sub>2</sub> gate insulator that are separated by organic molecules acting as a gate dielectric. We propose push-pull organic molecules (PPOMs) containing triarylamine as an electron-donating group (EDG), thiophene as a spacer, and malononitrile as an electron-withdrawing group (EWG). The PPOMs were designed for charge transport control through differences of the dihedral angles induced by a steric hindrance effect of the side chains within the molecules. Therefore, we expect that these tilted PPOMs with potential energy barriers can save the charges that are transported to the nano-interfaced conducting channel formed between the semiconductor, pentacene, and SiO<sub>2</sub> used as the dielectrics. Finally, we also expect the charges to be contributed to the memory capacity of the memory OFET device.

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## 2. Experimental

Syntheses of the PPOMs (2-((5-(4-(naphthalen-1-yl(phenyl)amino)phenyl)thiophen-2-yl)methylene)malononitrile, QH, and 2-((4-methyl-5-(4-(naphthalen-1-yl(phenyl)amino)phenyl)thiophen-2-yl)methylene)malononitrile, QMe) as detailed in Supporting Information (ESI†) were performed under a nitrogen atmosphere in a dry box or by standard Schlenk techniques. Solvents were distilled from appropriate reagents. Detailed synthetic schemes and preparations of the PPOMs are provided in Supporting Information.

Top contact OFETs with the PPOMs as depicted in Fig. 1b were constructed on heavily n-doped Si substrates with a 300 nm SiO<sub>2</sub> layer. The PPOMs were deposited at  $4.9 \times 10^{-7}$  Torr, maintaining a substrate temperature of 70 °C. PMMA was spin-coated as a 60-80 nm thick film from a toluene solution onto the SiO<sub>2</sub> layer. The films were kept in an oven at 70 °C overnight and subsequently annealed at 100 °C for a period of 3 h. The PPOMs (20 nm thickness) were vacuum deposited onto the PMMA/SiO<sub>2</sub>/Si substrate. Pentacene films (50 nm thickness) were vacuum deposited on the PPOM deposited substrates and kept at 30 °C at a deposition rate of 0.1 Å/s and 10<sup>-7</sup> Torr. Finally, gold electrodes as source and drain contacts were deposited onto the organic layers through a shadow mask. The channel length and width were 100 and 10 000  $\mu$ m, respectively. The *I*-V curves were measured using a Keithley 4200 semiconductor parameter analyzer. Writeread-erase cycle tests, as well as switching time measurements, were carried out using an Agilent pulse generator (model HP81104A-80MHz or a homemade pulse generator) with a Tektronix oscilloscope (model TDS-3014). All electrical measurements were conducted at a constant temperature, 25 °C, and relative humidity, 50%, under air atmosphere without any device encapsulation. Atomic force microscopy (AFM) measurements were carried out on a Multimode XE-100 instrument (PSIA Inc., City, State, Country), operating in non-contact mode with silicon cantilevers (resonance frequency in the range of 204-259 kHz and an integrated Si tip with a typical curvature radius of 10 nm).

### 3. Results and discussion

The newly synthesized PPOMs were composed of triarylamine as an EDG, thiophene as a spacer, and malononitrile as an



**Fig. 1** (a) Molecular structure of the PPOMs (QH and QMe). (b) Schematic of the OFET memory device.

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EWG in the molecular backbone. Herein, two types of molecules: R = H (2-((5-(4-(naphthalen-1-yl(phenyl)amino)phenyl)thiophen-2-yl)methylene)malononitrile),  $OH: R = CH_3$ (2-((4-methyl-5-(4-(naphthalen-1-yl(phenyl)amino)phenyl)thiop hen-2-yl)methylene)malononitrile), QMe, The intermediate thiophene spacer of QH, 2-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, was successfully synthesized from 5-bromothiophene-2-carbaldehyde through protection of the aldehyde group and borylation in 86% overall yield, and in a similar manner the thiophene spacer of QMe, 2-(5-(5,5dimethyl-1,3-dioxan-2-yl)-3-methylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, was synthesized from 2-bromo-3-methylthiophene in 77% overall yield. And then the electron donor, N-phenylnaphthalene moiety, and acceptor, malononitrile moiety, were added to the intermediate thiophene spacer through Suzuki coupling and condensation reactions in overall 25% and 29% yield for QH and QMe, respectively. The detailed organic synthesis and characterization of QH and QMe are reported in the Supporting Information. This conclusion is also consistent with Fourier transform infrared spectroscopy (FTIR) spectra of the PPOMs (Fig. S1 in the Supporting Information).

As mentioned earlier, the thiophene spacer was designed for controlling the charge transport properties from triarylamine to malononitrile and vice versa. The charge transport would be affected by the dihedral angles derived from the steric hindrance of the side chains of the thiophene spacer as shown in Fig. 1a.

For realization of the OFET memory device as shown in Fig. 1b, a top contact OFET with the PPOMs was constructed on the heavily n-doped Si substrates with a 300 nm SiO<sub>2</sub> layer. Poly(methyl methacrylate) (PMMA) was used as the dielectric layer. PMMA is a hydroxyl-free polymer that decreases the number of electron traps, providing the gate dielectric interface buffered to the organic molecules.<sup>6</sup> Gold electrodes, as source and drain contacts, were deposited onto the organic layer through a shadow mask (Device I). The channel length and width



Fig. 2 Potential energy surfaces for: neutral QH (a) and QMe (b); anionic QH (c) and QMe (d), scanned at the  $B3LYP/6-31+G^*$  level of theory.

were 100 and 10,000  $\mu$ m, respectively. An OFET device without organic molecules (Device II) was prepared as a control for the OFET memory device bearing organic molecules (Device I).

To understand the molecular structure of the OFET memory devices at the molecular level, DFT calculations were performed with a B3LYP exchange functional and 6-31+G\* basis sets using the Gaussian 03 suite of programs.<sup>7</sup> Potential energy surface (PES) curves were plotted by changing the dihedral angles  $(C_1-C_2-C_3-C_4)$  from -90 to 90 degrees, with every 10 degree step to predict the relationship between the charge variation and dihedral angle as shown in Fig. 2. Fig. 2a shows that the neutral QH molecule was the most stable state at a dihedral angle of -20.8 degrees. The rotation energy barrier was relatively small (0.4 kcal/mol) when the dihedral angle changed from negative to positive. Nevertheless, for the neutral QMe molecule, the rotation energy barrier was as large as 8.5 kcal/mol, due to the steric hindrance effect of the methyl group attached to C4, for which in the most stable dihedral angle reached up to -38.3 degrees as depicted in Fig. 2b. When the molecules become anions, QH was the most stable state at -0.7 degrees and had a symmetrical PES curve as depicted in Fig. 2c. In contrast, the QMe molecule had an unsymmetrical PES curve with -21.1 degrees in the most stable position as shown in Fig. 2d. Based on the optimized results of both neutral and electron charged anion states, the dihedral angle of the OMe was about 20 degrees larger than that of QH, due to the large steric hindrance of the C4 methyl group. Therefore, when the molecules reached a - 1 charge, the dihedral angles of both the OH and OMe changed by about 20 degrees. As a result, the QH turned out to be completely planar with QMe also experiencing a change in conformation of -20 degrees closer to the planar.

The optimized structures and dihedral angles ( $C_1$ - $C_2$ - $C_3$ - $C_4$ ) of the neutral and electron charged anion species of QH and QMe are shown in Fig. 3. It is well known that a planar structure is more efficient for electron transport than a tilted structure in conjugated systems.<sup>8,9</sup> Furthermore, as noted from the dihedral angle, QH should give higher conductance than QMe, which is exactly the same as in a previous study <sup>10</sup> In other words, it is expected that the charge mobility of the OFET device should be reduced due to charge trapping on both QMe and QH layers. Furthermore, according to the tilt angles, the charge trapping on

∠ (C1-C2-C3-C4)

= 38.3

Neutral

QMe

 $\angle (C_1 - C_2 - C_3 - C_4)$ 

=0.70

Anion

 $\angle$  (C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub>-C<sub>4</sub>)

= 21.1°

Anion

Fig. 3 B3LYP/6-31+G\* optimized structures and dihedral angles  $(C_1-C_2-C_3-C_4)$  of neutral and electron charged anionic QH and QMe.

QH

∠ (C1-C2-C3-C4)

= 20.8

Neutral



Fig. 4 AFM topographs of pentacene films on: a) SiO<sub>2</sub>; b) QH; c) QMe.

the QMe layer should be higher than that on the QH layer in both neutral and electron charged anion states.

From XRD measurements, the intermolecular d-spacings of the QH and QMe/PMMA/SiO<sub>2</sub>/Si substrates were 1.166 ( $2\theta = 32.86$ ) and 1.179 Å ( $2\theta = 32.84$ ) as shown in Fig. S2. Amazingly, the intermolecular d-spacing of OMe was larger than that of OH due to the larger dihedral angle. To improve OFET performance, an understanding of the role of the organic semiconductor/gate dielectric interface is crucial since the field effect mobility is largely determined by the morphology of the semiconductor film at the interface with the gate dielectric.<sup>11</sup> In general, gate dielectric surface properties have been modified with self assembled monolayers (SAM). For example, SiO<sub>2</sub> dielectrics treated with octadecyltrichlorosilane (OTS) or hexamethyldisilazane (HMDS) improve the mobility and decrease the gate leakage of most OFETs.<sup>12</sup> Pentacene shows a preferred orientation of the crystalline domain dependent on the chemical and physical properties of the gate insulator controlled by the end functional group in the SAM. A nonpolar surface modified by a CH<sub>3</sub>-terminated SAM was beneficial for improving hole mobility by enabling effective ordering of the pentacene crystalline lamellae.13 The topographs of the pentacene films on the PPOM surfaces were observed by AFM. No obvious orientation was detected with the pentacene layer that formed on the SiO<sub>2</sub> surface, as shown in Fig. 4a, which indicates that the pentacene film consisted of either mostly amorphous grains or crystalline grains with an in-plane texture, where the layered stacks were perpendicular to the surface. In the case of hydrocarbon functionalized PPOMs, every pentacene nucleation site was sufficiently stabilized by hydrophobic interactions with the PPOM surface to grow and form a large number of small grains, as shown in Fig. 4b and c. The RMS roughness was changed from 30.36 nm for the pentacene/SiO<sub>2</sub> to 7.85 nm and 7.28 nm for the pentacence/QH/SiO<sub>2</sub> and pentacene/QMe/ SiO<sub>2</sub> films, respectively. Consequently, the difference of the memory OFET performance can be mainly attributed to the chemical nature of the nano-interfaced PPOMs since the surface roughness and gate leakage current were nearly identical regardless of surface modification.

Fig. 5 shows transfer characteristics of the OFET devices. The dielectric pristine SiO<sub>2</sub> and PMMA polymer layers<sup>14</sup> used as control experiments herein have been shown to retain injected charge. In our results, the pristine OFET with a SiO<sub>2</sub> layer, as depicted in Fig. 5a, or PMMA, as shown in Fig. 5b, shows only weak hysteresis with a memory window ( $\Delta V_T$ ) less than 5 V. The memory window is defined as the difference between the threshold voltages in the up and down steps of the gate voltages. Amazingly, the transfer characteristics of the PPOM-FET devices show that



Fig. 5 Transfer characteristics of the OFET with  $V_{ds} = -40$  V demonstrating the nonvolatile OFET memory device. Each measurement was carried out with an integration time of 1 s.

there is a clearly visible hysteresis between the two source-drain currents for gate voltage sweep in the negative and positive directions shown in Fig. 5c and d. In the transfer characteristics of the OFET with QH (OFET-QH device) and QMe (OFET-QMe device), the memory window of the OFET-QMe was wider than that of OFET-OH and as expected, the drain current of OFET-QMe decreased more than that of OFET-QH. For OFET-QMe, the ON/OFF ratio was about 10<sup>2</sup> (two orders of magnitude difference in current between the high conductance ON state and low conductance OFF state). The "ON" current was 30 nA at a gate voltage of -50 V. The "OFF" current appeared to be 0.6 nA at the gate voltage of 50 V. This result corresponds to a memory ratio of at least 50, a very competitive value, even when compared to inorganic ferroelectric transistors.15 The "ON"-"OFF" switching phenomenon was achieved by the conversion of the "anion" and "neutral" states. When a gate voltage is applied to the neutral QH and QMe, they undergo a gradual conformational change from the neutral ("OFF" state) to the anion ("ON" state) species. Then, when the gate voltage is turned off, the anionic species ("ON" state) of OH and OMe gradually change to neutral ("OFF" state) species. The difference in QH and QMe is the response time as QH changes more quickly and the operation voltage range of QMe is wider than that of QH. This property can be explained by the vertical electron affinity (VEA) values of QH and QMe. The calculated VEA values for QH and QMe were -1.774 and -1.699 eV, respectively, implying that QH becomes more stabilized than QMe by receiving one electron. Thus, QH can be changed from the "OFF" to the "ON" state more easily than QMe, which is consistent with the experimental observations shown in Fig. 5. For the reverse change from "ON" to "OFF", the reason for the faster change of QH is that the "ON" state of QH is a more efficient charge transport medium than the "ON" state of QMe. Therefore, it is assumed that due to charge trapping, the main effect of the nano-interfaced QMe and QH reduced the charge mobility of the conduction channel formed between pentacene and the QMe (QH) layer, generating a hysteresis effect. It is certainly true that the hysteresis becomes more obvious in the

transfer characteristics of the devices comprising an additional QH or QMe layer. It is believed that the hysteresis effect in pentacene-based OTFTs is due to charge (electron) trapping and detrapping. In partial summary, the larger tilted structure caused by the steric hindrance gives higher charge trapping and reduces the charge mobility more and finally produces higher hysteresis. Thus, the memory window of QMe is larger than that of QH.

For devices exhibiting memory performances, the ability for write-read-erase-read pulse cycles, retention time, and reliability, required for usage as nonvolatile memory devices, was further investigated. Fig. 6 presents a representative result of write-read-erase-read cycle tests of QH- and QMe-based organic molecular devices. In the write-read-erase-read cycle, writing (ON state) was achieved by applying a negative voltage pulse whose amplitude (-60 V) was higher than V<sub>c,ON</sub>, and erasing (OFF state) through erasing the ON state by applying a positive voltage pulse whose amplitude (60 V) was higher than V<sub>c,OFF</sub>. A small probe voltage (0 V) pulse was employed to read the states [ON state (write) and OFF state (erase)] of the device. The QMe device showed higher ON current and lower OFF current, compared to the QH device.

Fig. 7 shows a representative result of the retention tests carried out on the PPOM devices under ambient conditions. Once the device was switched to the ON state by applying a negative voltage pulse with an amplitude (-100 V) higher than the V<sub>c,ON</sub>, the ON state was retained without any degradation for over 30 min, which is applicable for nonvolatile memory. When the ON state was switched back to the OFF state by applying a positive voltage pulse with an amplitude of 100 V, higher than the V<sub>c,OFF</sub>, the OFF state was retained without any degradation for over 30 min. The QMe devices showed that the ON current for the current decay was still more than one order of magnitude larger than the OFF current, even after 30 min.

The mechanism is proposed by charge trapping in the organic molecules as charge tunneling through the semiconductor



**Fig. 6** Switching performance of the OFET device based on the PPOMs a) QH and b) QMe during continuous "write-read-erase-read" sequences. The ON state was induced ("write") by a -60 V pulse, and the OFF state ("erase") by +60 V. Between switching, the states were probed ("read") by measuring the current under a small voltage (0 V).





**Fig. 7** Retention times at the ON and OFF states of the OFET devices based on QH and QMe.

organic molecules is possible. During the charge transfer process, some of the carriers would be trapped due to the charge trapping sites generated by the dihedral angle differences of the steric hindrance effects of the PPOMs. Even when the gate field was withdrawn, these trapped charge carriers remained in the organic molecules because of the tunneling barrier of the organic molecules. In addition, there was also an effect of the potential energy barrier for the conformational change from the electron charged anion to the neutral state, as noted from the potential energy surface (Fig. 2). It is demonstrated that a higher potential energy barrier gives longer time for the de-trapping of the injected charge on the PPOMs. As a result, memory characteristics were increased only when the PPOM layers existed, and their hysteretic I-V characteristics and memory window sizes were directly related to the difference between the dihedral angles. Therefore, it is contended that the memory behavior originated from the modulation of the gate field by charges stored in the novel organic molecules. The modulation of the nano-interfaced and sterically hindered organic molecules between the semiconducting channel and dielectric materials may be considered to be the cornerstone of the organic nonvolatile memory device.

#### 4. Conclusions

In conclusion, a nonvolatile memory OFET with a gate insulator based on nano-interfaced organic molecular materials has been presented. The proposed electron donor-spacer-acceptor PPOMs were successfully synthesized and characterized. The observed memory effect occurred due to a charge trapping on the conduction channel comprising PPOMs and charge detrapping with high potential energy barrier caused by the steric hindrance effect of the nano-interfaced organic semiconductor, PPOMs. As a matter of fact, the memory window of the OFET-QMe was wider than that of the OFET-QH. The OFET memory device presented herein may be applied to a variety of potential applications, including novel, nonvolatile organic memory, which would be useful for low-cost, lightweight, flexible, low duty data storage media, logic display driver and flash memory.

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