

Simultaneous Protection of Organic p- and n-Channels in Complementary Inverter from Aging and Bias-Stress by DNA-Base Guanine/ Al_2O_3 Double Layer

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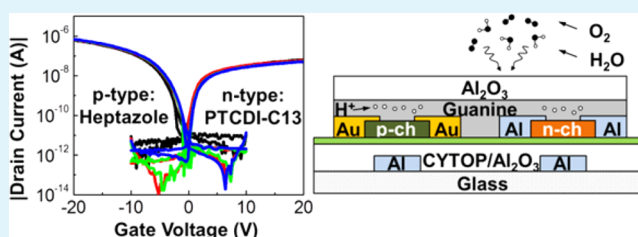
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Supporting Information

ABSTRACT: Although organic field-effect transistors (OFETs) have various advantages of lightweight, low-cost, mechanical flexibility, and nowadays even higher mobility than amorphous Si-based FET, stability issue under bias and ambient condition critically hinder its practical application. One of the most detrimental effects on organic layer comes from penetrated atmospheric species such as oxygen and water. To solve such degradation problems, several molecular engineering tactics are introduced: forming a kinetic barrier, lowering the level of molecule orbitals, and increasing the band gap. However, direct passivation of organic channels, the most promising strategy, has not been reported as often as other methods. Here, we resolved the ambient stability issues of p-type (heptazole)/or n-type (PTCDI-C13) OFETs and their bias-stability issues at once, using DNA-base small molecule guanine ($\text{C}_5\text{H}_5\text{N}_5\text{O}$)/ Al_2O_3 bilayer. The guanine protects the organic channels as buffer/and H getter layer between the channels and capping Al_2O_3 , whereas the oxide capping resists ambient molecules. As a result, both p-type and n-type OFETs are simultaneously protected from gate-bias stress and 30 days-long ambient aging, finally demonstrating a highly stable, high-gain complementary-type logic inverter.

KEYWORDS: organic field-effect transistors, guanine, Al_2O_3 , passivation, complementary inverter



INTRODUCTION

Organic field-effect transistors (OFETs) have been developed for more than a decade with various benefits of light weight, low cost, and mechanical flexibility.^{1–4} The development of electrical property has been of particular concern and nowadays the mobility of several organic semiconductors becomes to exceed that of amorphous Si-based FET, which is used in the display industry.^{5–9} What makes practical application of OFETs still problematic is, however, operational-bias and long-term environmental stability. The factors to determine the stability are generally categorized into four parts; semiconductor channel, dielectric, channel/dielectric interface, and semiconductor channel surface. For the issues of dielectric and interface, the most detrimental factor is thought to be charge trapping phenomena originating from hydroxyl functional group ($-\text{OH}$) or other ionic impurity.^{10–12} Those trapping effect can be dramatically reduced using polymer dielectric such as fluoropolymer CYTOP, or self-assembled monolayers (SAMs) treatment on conventional inorganic oxide.^{13–19} The other issues of organic semiconductor and its surface, on the other hand, have not been cleared out yet; such issues are about the vulnerability of charge carriers (especially electrons for n-channel OFETs) to penetrated ambient oxygen and water molecules, which causes detrimental effects on device perform-

ance and stability.^{20–22} To protect OFET from such ambient molecule-induced instabilities, several strategies were previously introduced: formation a kinetic barrier by more compact packing, lowering the level of molecule orbitals below oxidation energy level, and increasing the band gap for defending even from energetic photons.^{23–27} However, passivation related works in OFET have not been reported as much as other methods,^{28–33} although finding a proper passivation layer is the most apparent strategy to protect the organic semiconductor from penetrated atmospheric species and has thus been well-developed in organic light emitting devices (OLEDs).^{34,35} In particular, the direct passivation was not much successful for n-type organic channels.³³

Here, we propose DNA-base small molecule guanine ($\text{C}_5\text{H}_5\text{N}_5\text{O}$)/ Al_2O_3 bilayer as a unique passivation layer to solve above issues at once, simultaneously covering the aging and bias stress stabilities of both n- and p-channel OFETs in an air ambient. Although the Al_2O_3 layer shows very low oxygen and water permeability by itself,³⁶ direct deposition of such an inorganic insulator on organic material usually causes serious

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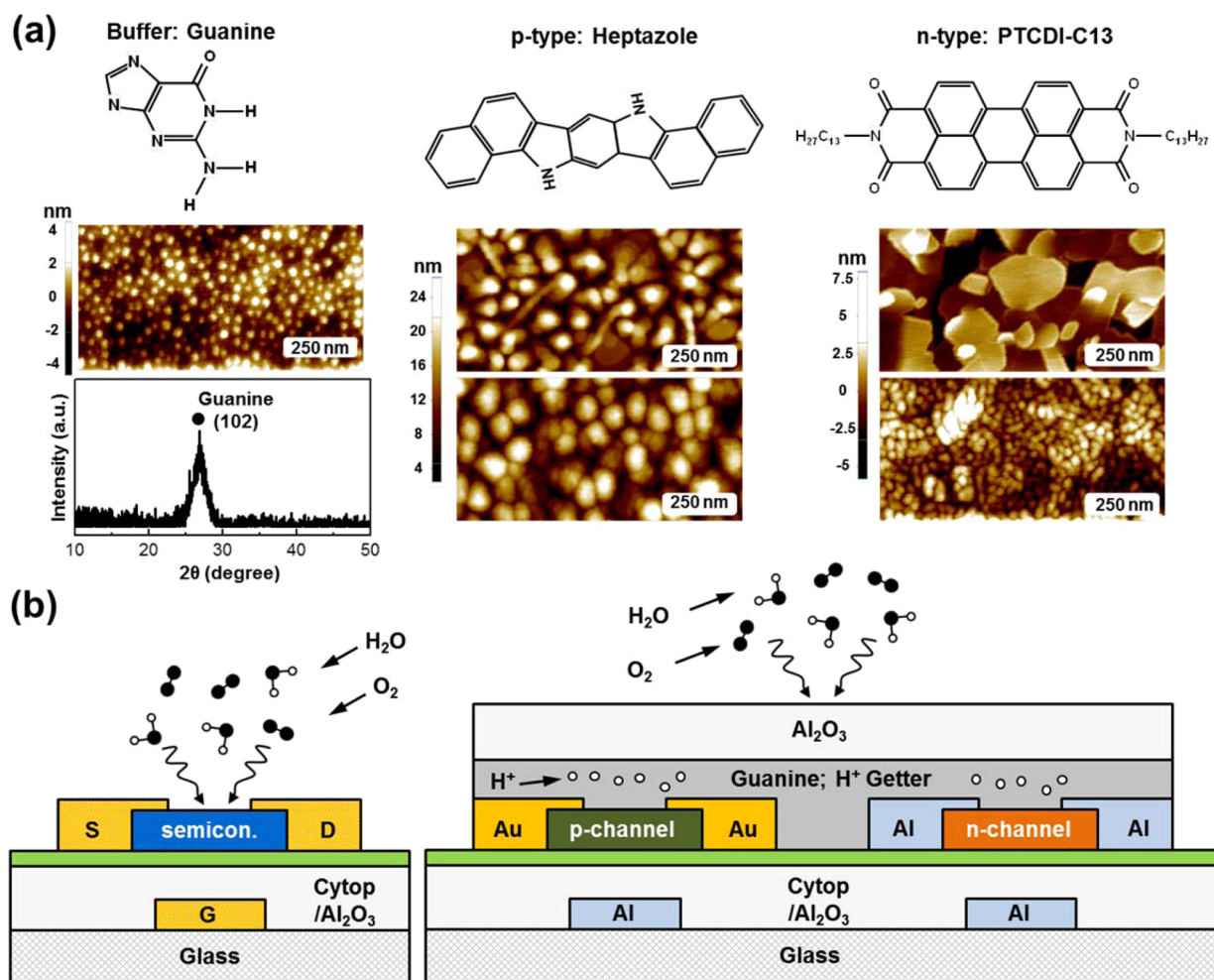


Figure 1. (a) Chemical structures of organic materials; Guanine (buffer passivation), Heptazole (p-type semiconductor), and PTCDI-C13 (n-type semiconductor). Guanine layer shows monoclinic crystalline structure with (102) orientation in XRD analysis. Atomic force microscopy (AFM) image of guanine layer is also displayed containing very small domains. Above half AFM images for p- and n-type organics are those before guanine deposition while the other half images down below are with guanine layer. (b) Schematic cross-section of bottom-gate top-contact architecture OFETs. The guanine/ Al_2O_3 passivation layer is protecting our OFETs from the penetration of oxygen and water molecules.

damage because the deposition process contains several chemical impurities from precursor and water. (Figure S1 in Supporting Information shows degraded drain current and ON/OFF current ratio in heptazole OFETs as the examples of damages caused by the direct Al_2O_3 layer passivation.) So we adopted an organic layer to buffer/or minimize the damaging effects; a 40 nm thick layer of guanine, one of the DNA-base small molecules as extracted from DNA polymer, was deposited on n- and p-channel OFETs before atomic layer deposition (ALD) of a thin Al_2O_3 layer, because unintentional doping of hydrogen from the ALD process is efficiently prohibited or getterred by guanine.³⁷ Using the guanine/ Al_2O_3 passivation layer, both p-type (heptazole) and n-type (PTCDI-C13) OFETs demonstrated dramatic endurance under gate-bias stress and 30 days-long aging, showing little threshold and mobility change. As a result, a highly stable complementary-type logic inverter was even accomplished by combining p-type and n-type FETs, successfully operating at 5 V as a minimum low voltage with a high voltage gain over ~ 30 .

EXPERIMENTAL SECTION

Device Fabrication. The p-type heptazole and n-type PTCDI-C13 OFETs are designed as bottom-gate top-contact architecture on a

precleaned corning glass substrate. At first, a 50 nm Al bottom gate was deposited by thermal evaporator system. Then 50 nm Al_2O_3 gate insulator layer was deposited by atomic layer deposition (ALD) process at 100 °C, followed by spin-coating of 1 wt % dilute CYTOP (Ashai glass. Co.) and postannealing process in oven at 180 °C for 2 h. The C_{ox} value of our Al_2O_3 /CYTOP bilayer dielectric layer is precisely measured to be 36.8 nF/cm² by LCR parameter analyzer (HP 4284A, Agilent Technologies). After that, each organic semiconductor layer was thermally evaporated by organic molecule beam deposition (OMBD) at room temperature with growth rate ~ 0.1 nm/s. In case of n-type PTCDI-C13, the postannealing process was conducted in oven at 80 °C for 1 h. Source/drain electrodes of 50 nm Au were deposited on p-type heptazole and 50 nm Al were deposited on n-type PTCDI-C13, respectively. As a final step, the passivation layer of 40 nm-guanine (Sigma-Aldrich Co.) was deposited by OMBD at room temperature with growth rate ~ 0.05 nm/s, followed by 40 nm Al_2O_3 deposited by the same ALD process as for the gate dielectric. In general, a sufficient density of OH⁻ group is a requirement for Al_2O_3 growth on inorganic substrate, however, organic substrate such as guanine layer meets the situation in a different way; TMA diffuses into organic guanine layer first, and water molecules follow after to meet TMA molecules in guanine. Then, this process forms sufficient amount of Al(OH) compounds in guanine and on the surface of guanine. Therefore, ALD deposition of oxide is possibly carried out on organic guanine.³⁸ Every electrode and organic layer in our device was

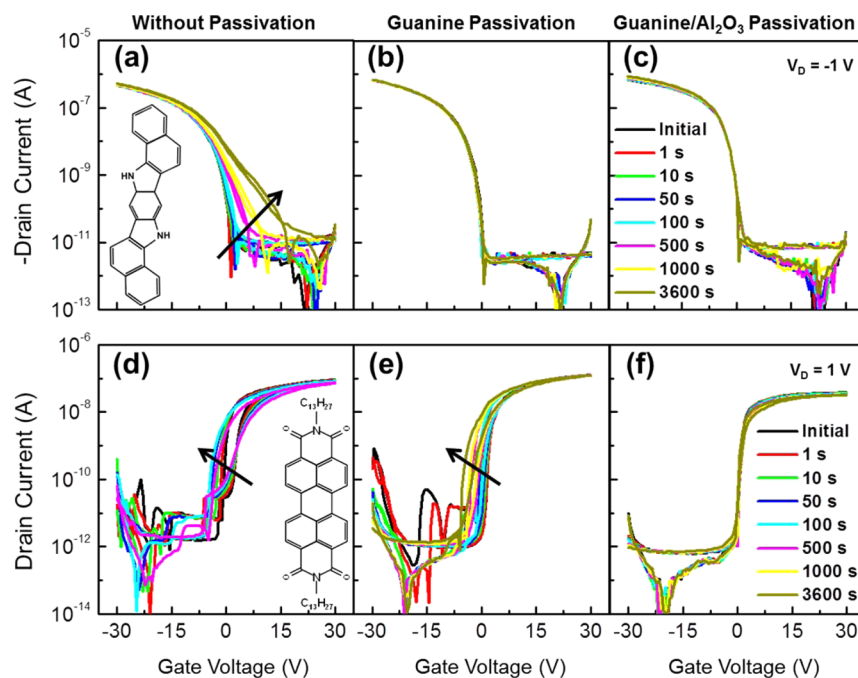


Figure 2. Time-dependent transfer characteristics of our OFETs under OFF-state bias stress condition: ($V_G = +30$ V, $V_D = -1$ V) for p-type heptazole-based OFETs (a) without passivation, (b) with guanine passivation, (c) with guanine/ Al_2O_3 passivation, and ($V_G = -30$ V, $V_D = +1$ V) for n-type PTCDI-C13 based OFETs (d) without passivation, (e) with guanine passivation, (f) with guanine/ Al_2O_3 passivation.

patterned through shadow mask, and width/length ratio was prepared to be $500 \mu\text{m}/70 \mu\text{m}$.

Electrical Measurements. The device current–voltage (I – V) and capacitance characterizations were carried out by a semiconductor parameter analyzer (HP 4155C and HP 4284A, Agilent Technologies). Electrical dynamics measurements were investigated with a function generator (AFG 310, Sony/Tektronix) and an oscilloscope (TDS210, Tektronix).

■ RESULT AND DISCUSSION

A. Surface Morphologies of DNA-Base Guanine, Heptazole, and PTCDI-C13 Layers. Figure 1a introduces three important small molecules which were adopted in the present study: guanine as buffer molecule layer for protecting n- and p-type channels, heptazole ($\text{C}_{26}\text{H}_{16}\text{N}_2$) as hole transporting p-type semiconductor, and PTCDI-C13 as well-known n-type molecule. The guanine small molecule is one of DNA-base materials which construct the DNA double helix structure by hydrogen bonding. Since ALD Al_2O_3 deposition needs a precursor of trimethylaluminum (TMA) and reactant of water vapor (these species usually act as chemical impurity), adopting such guanine small molecule for buffer layer would be a promising strategy to prevent the damage from direct ALD processes. In addition, the guanine layer is expected to prevent unintentional hydrogen doping because it plays as H atom/ H^+ ion getter during ALD process attributed to natural basicity of guanine molecules and to their strong tendency to compensate their unpaired dipoles with H atoms.³⁷ The guanine layer was crystalline (monoclinic; (102) texture orientation) and the crystalline domain size was as small as ~ 10 nm when deposited on hydrophobic CYTOP layer, as observed by $\text{Cu-K}\alpha$ X-ray diffraction (XRD) and atomic force microscopy (AFM). Heptazole has been a recently synthesized indolocarbazole-type small molecule, 8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole.^{39,40} The indolocarbazole-type small molecules usually provide high ambient and photo stability due to their

large highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap.²⁷ The HOMO–LUMO gap for our heptazole layer was measured as ~ 2.95 eV with deep HOMO level of ~ 4.95 eV, and in our previous work, the heptazole-based OFET actually displays better photostability than typical small molecule, pentacene-based OFET.³⁹ On the one hand, the electron transporting n-type small molecule, *N,N'*-ditridecyl-perylene-3,4:9,10-tetracarboxylic diimide–C13 (PTCDI–C13) layer has its HOMO–LUMO gap as ~ 2.0 eV with a quite deep LUMO level of ~ 3.4 eV.⁴¹ According to the AFM images of p-type heptazole and n-type PTCDI-C13 layers, the latter (n-type) shows much larger domains (~ 150 nm) than those of former (average ~ 30 nm). After guanine deposition, PTCDI-C13 layer surface appeared totally different from without guanine, since guanine small domains cover the large domain of PTCDI-C13 layer. However, the guanine domains could not much change the surface morphology of heptazole layer except that the heptazole domains look a little larger with guanine molecules on them. It is conjectured that heptazole domain was not large enough to well-accommodate many of the small guanine domains on its surface. Figure 1b displays the bottom-gate top-contact architecture OFETs on glass substrate with and without guanine/ Al_2O_3 passivation layer, which is designed to prevent the channels from oxygen and water molecule diffusion. A thin fluoropolymer CYTOP was also coated on Al_2O_3 dielectric layer to control the interface between semiconductor and dielectric layers,^{13–15} and the C_{ox} value of following dielectric was $36.8 \text{ nF}/\text{cm}^2$ as directly measured from our OFETs in the ON state (charge accumulation) and from the capacitor itself.

B. Protection of Organic p- and n-Channel Layers against Bias-Stress Test. Figure 2a–c displays the drain current–gate voltage (I_D – V_G) transfer characteristics as respectively obtained from our p-channel heptazole OFETs without passivation, with guanine, and with guanine/ Al_2O_3 passivation, while the three devices went through OFF-state

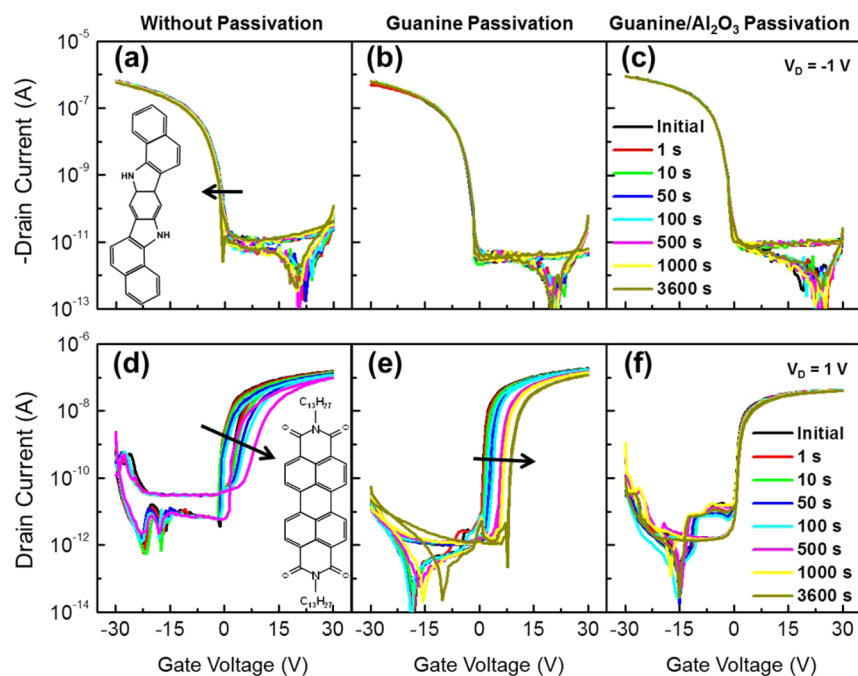


Figure 3. Time-dependent transfer characteristics of our OFETs under ON-state bias stress condition: ($V_G = -30$ V, $V_D = -1$ V) for p-type heptazole based OFETs (a) without passivation, (b) with guanine passivation, (c) with guanine/ Al_2O_3 passivation, and ($V_G = +30$ V, $V_D = +1$ V) for n-type PTCDI-C13 based OFETs (d) without passivation, (e) with guanine passivation, (f) with guanine/ Al_2O_3 passivation.

gate bias stress at +30 V for maximum 3600 s in air ambient (relative humidity $\sim 40\%$) at room temperature (25°C). Without any passivation (Figure 2a), the p-channel OFET shows large increase of off-current along with noticeable threshold voltage shift due to the ambient molecule-induced current, which might be the back channel current⁴² attributed to dipole-containing ambient molecules. Because the organic back channel surface is depleted but also has E-field (electrically active) under OFF-state gate bias, ambient molecules are more easily adsorbed on the surface, making back channel charges/current. Noteworthy is the case of guanine-only passivation in Figure 2b, which indicates that thin guanine layer is quite enough to protect the heptazole surface and film itself from molecules under bias stress. Figure 2d–f show the similar transfer curves but obtained from n-type channel OFETs after the same ways of passivation and OFF-state gate bias stress (-30 V for n-type). Because the n-channel organic PTCDI-C13 molecules are very unstable in general, it seems that only the OFET with guanine/ Al_2O_3 double-layer passivation survives the serious gate stress. Without Al_2O_3 , some of ambient molecules penetrate the guanine by diffusion to react with the surface or interface of n-channel PTCDI-C13 layer, which is much more reactive than those of p-type heptazole because of its lower reduction potential; the radical anions in oxygen/water molecules easily trap mobile charges in n-channel organics, disturbing any charge transport to degrade intrinsic device performance. (Arrows in Figure 2a, d, and e indicate the direction of threshold voltage shift, which is a sign of OFET degradation.)

Figure 3a–c displays the drain current–gate voltage (I_D – V_G) transfer characteristics as respectively obtained under ON-state bias stress (-30 V) from our p-channel heptazole OFETs without passivation, with guanine, and with guanine/ Al_2O_3 passivation. Unlike the case of OFF-state stress in Figure 2a, our heptazole OFET appears to have no problem even without any passivation layer (Figure 3a). The heptazole layer surface

must have then been less active to air molecules in the ON-state than in the OFF-state, because the ON-state has hole accumulation at the dielectric/channel interface and any electric field (E-field) can hardly propagate to the surface.⁴² However, in contrast to p-channel organics, intrinsically unstable n-channel PTCDI-C13 FETs still display a high degree of instability even under ON-state bias. According to the transfer curves of Figure 3d–f, only the device with guanine/ Al_2O_3 double-layer passivation survives the ON-state bias stress. (It is noted in Figure 3d–f that n-channel OFET with double-layer passivation shows slightly lower ON-current than the device without passivation. It is because ALD Al_2O_3 passivation is carried out at 100°C , which is higher than an optimum postannealing temperature of $\sim 80^\circ\text{C}$ for n-channel organic, PTCDI-C13.¹⁵ Also see Figure S2 in the Supporting Information for more details.)

Regarding the bias stress results from Figures 2 and 3, a guanine/ Al_2O_3 double layer is quite necessary for perfect protection of both n- and p-channels against long-term gate bias stress, although p-channel heptazole appeared relatively stable even with a guanine layer only. For more details on device degradation by ON-state stress,¹¹ ON current vs bias time plots are prepared in the Supporting Information, Figure S3a, b, where guanine-only condition is certainly less effective than the case of guanine/ Al_2O_3 double layer. According to the degradation kinetics curves of Figure S3a, b in the Supporting Information, the p-channel OFET without passivation shows rapid degradation in time scale although it appeared unaffected by ambient molecules in transfer curve sweeps of Figure 3a. Our double-layer encapsulated devices are incomparably superior to the others without double layer treatment, demonstrating surprisingly good characteristic time, τ and dispersion parameter, β of $\sim 1 \times 10^{14}$ s ($\sim 1 \times 10^9$ s) and 0.15 (0.18), respectively, for p-channel (n-channel) (see Table S1 in the Supporting Information for the values). Such characteristic numbers are in fact so amazing compared to other results

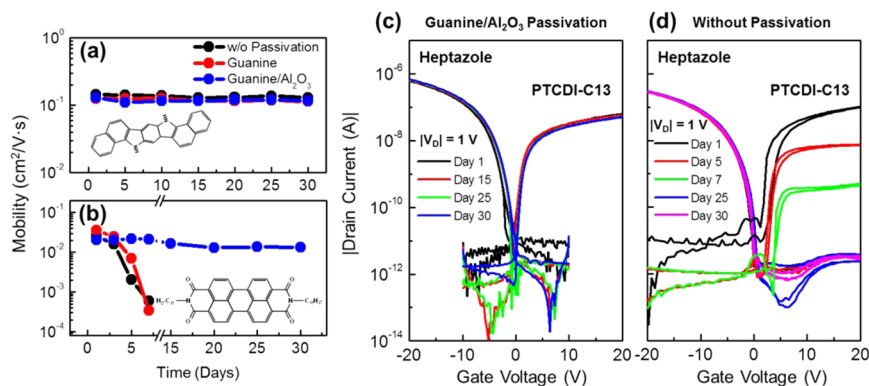


Figure 4. Linear mobility degradation in air ambient for (a) p-channel heptazole and (b) n-channel PTCDI-C13 based OFET with respective passivation layers: without passivation, guanine passivation, guanine/Al₂O₃ passivation. Detail degradation of transfer characteristics are also shown for (c) guanine/Al₂O₃ passivation and (d) without passivation.

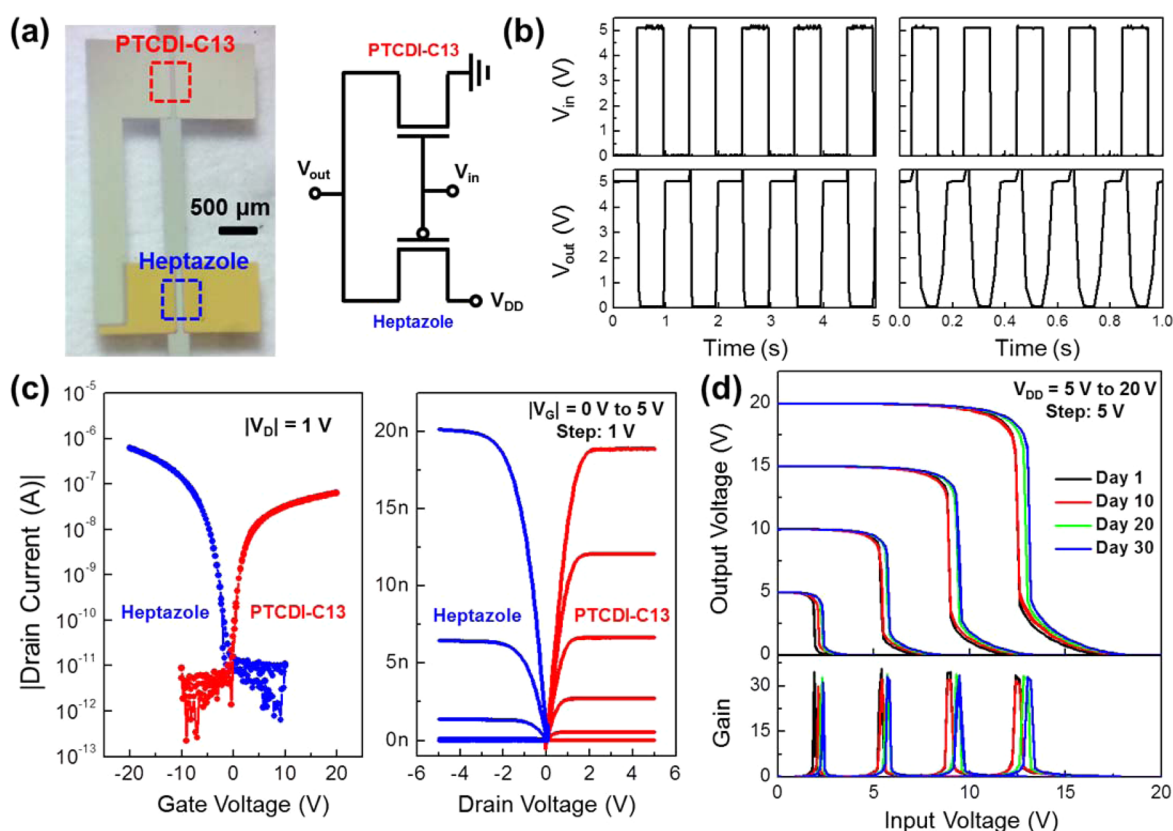


Figure 5. Complementary type inverter with guanine/Al₂O₃ passivation layer on glass. (a) Optical image of our heptazole and PTCDI-C13 OFETs. Blue and red dashed rectangles indicate patterned heptazole and PTCDI-C13 organic semiconductor layer, respectively. Schematic circuit diagram is also illustrated. (b) Dynamic complementary inverter behavior under V_{DD} = 5 V, 1 Hz (left column) and 5 Hz (right) operation. (c) Transfer and output characteristics of our heptazole and PTCDI-C13 OFETs. (d) Static voltage transfer characteristics (VTC) and gain of our inverter measured up to day 30.

reported so far,^{11,28} (Here, we used a severe bias stress condition of 30 and 1 V respectively for gate bias and drain-source bias, which is more stressful than those of previous works.^{30,39})

C. Protection of Organic p- and n-Channel Layers against Aging Test. Equivalent to the bias stress resistance, aging stability in air ambient is also important as a measure of device stability in organic FETs. Figures 4a-b show the linear mobility change (or degradation), respectively for p- and n-channel OFETs. (The maximum initial linear mobility was estimated as 1.7×10^{-1} and 2.0×10^{-2} cm²/(V s) for heptazole

and PTCDI-C13, respectively.) According to Figure 4a, b, the mobility of p-channel heptazole OFET is quite stably maintained in air ambient for 30 days whether the device is passivated or not, whereas that of n-channel OFET quickly drops within few days if without guanine/Al₂O₃ double layer passivation. In respect of time-dependent stability, these results are similar to those we have observed from the bias stressed p-channel and n-channel OFETs. Details on the aging stability are shown in the transfer curves of both p- and n-channel OFETs as seen in Figure 4c, d. Passivated by guanine/Al₂O₃ double layer, the p- and n-channel OFETs hardly show I_D current

decrease or hysteresis; however, if without passivation, the I_D of n-channel PTCDI-C13 OFET particularly decreases down to few pA from initial 100 nA after only few days pass.

D. Stable Organic Complementary Inverter Using Guanine/ Al_2O_3 Double Passivation Layer. Because both p- and n-channel OFETs are superiorly protected by guanine/ Al_2O_3 passivation, we fabricated complementary type inverters with our heptazole and PTCDI-C13 OFETs to simultaneously protect the both as shown in Figure 5a. The optical image shows our OFETs where the red and blue dashed rectangles indicate PTCDI-C13 and heptazole semiconductors fabricated on glass, respectively, and the equivalent circuit is also illustrated. Figure 5c is the transfer and output characteristics of our OFETs, obtained before they are connected for complementary inverter. The both output (I_D-V_D) characteristics for p- and n-channel OFETs apparently divide the linear and saturation regimes depending on the drain voltage, indicating a pinch-off phenomenon (output curves also show the signs of good ohmic contacts). The maximum linear mobility was calculated here as 2.1×10^{-1} and 2.0×10^{-2} cm^2/Vs for heptazole and PTCDI-C13, respectively. The voltage transfer characteristic (VTC) curve of our inverter is well demonstrated in Figure 5d, and it shows clear voltage switching with a high voltage gain of more than 30 and negligible hysteresis up to supply voltage (V_{DD}) of 20 V. Because of the guanine/ Al_2O_3 layer passivation against ambient aging, our inverter did hardly show any significant change in voltage gain and transition voltage until at least 30 days (except slight positive shift of transition voltage from 12.4 to 13 V for $V_{DD} = 20$ V). Such a negligible shift seems to stem from the slight threshold voltage shift on transfer characteristics in Figure 4c. Finally, we measured dynamic switching behavior of our inverter under the condition of fixed $V_{DD} = 5$ V and switching input voltage $V_{in} = 5$ and 0 V. As a result, we found that our organic complementary inverter was normally working with a minimum switching time of ~ 30 ms induced by RC delay, as shown in Figure 5b which was acquired from 1 and 5 Hz operations.

CONCLUSION

In summary, we adopted one of the DNA-base small molecules, guanine, as a buffer passivation layer between organic semiconductor channels and ALD-deposited Al_2O_3 . Because direct deposition of Al_2O_3 on organic semiconductor usually provokes serious degradation of electrical performance, the buffer is essentially necessary and the guanine is thought to be a promising candidate as the buffer because of its H ion getter capacity. Both of p-type heptazole and n-type PTCDI-C13-based OFETs with guanine/ Al_2O_3 passivation layer show superior gate-bias and ambient aging stabilities, so that the complementary type inverter with the p- and n-channel OFETs might well demonstrate its electrostatic and dynamic performances, enduring more than 30 days in air ambient without performance degradation. We conclude that our DNA-base guanine/ Al_2O_3 passivation approach is novel and essential to simultaneously cover the both p- and n-type organic channel materials in OFETs.

ASSOCIATED CONTENT

Supporting Information

Transfer characteristics of our p-type heptazole-based OFETs with Al_2O_3 passivation layer only; $I_D^{1/2}$ vs gate voltage plot; normalized drain current [$I_D(t)/I_D(0)$] vs ON gate bias time

plots for heptazole and PTCDI-C13 based OFETs; Characteristic time (τ) and dispersion parameter (β) calculated with stretched-exponential formula. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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