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Design of optical memory elements based on n-type organic field-effect transistors comprising a light-sensitive spirooxazine layer

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The design of high-speed optical memory elements based on organic field-effect transistors comprising [60]fullerene as an n-type semiconductor and 1,3-dihydro-1,3,3-trimethylspiro(2*H*-indole-2,3′-[3*H*]naphth[2,1-*b*][1,4]oxazine) as a light-sensitive component placed at the interface with an aluminum oxide gate dielectric has been developed. The memory elements exhibit a switching coefficient of ~10^4 and a minimal programming time of 0.5–1.5 ms.

Recent publications reflect rising interest in the application of photochromic compounds to the design of advanced organic electronic devices.[1–4] Organic photochromes undergo facile photoswitching between two quasi-stable isomeric forms, which differ significantly in fundamental electronic and electrical properties such as frontier energy levels, electrical conductivity, dipole moment and dielectric constant.[5] In particular, the bistable nature of common photochromic compounds inspired their employment in the design of memory devices.[1] Diode-type memory cell configurations comprising photochromic materials in the active layer sandwiched between two electrodes were described.[6] The light-induced isomerization of photochromic components results in the formation of bipolar traps affecting charge transport through the device.[7] Alternatively, photochromic molecules arranged at the interface between a semiconductor layer and an electrode allow one to control charge injection in the diode device. This approach was used to demonstrate large-area OLEDs with optical memory capabilities.[8]

In spite of considerable progress in diode-type memory devices, the achieved photoswitching effects were not very high thus challenging their practical implementation. This might be a reason why transistor-type memory elements comprising photochromic materials have been intensively developed in the last few years.[1] While comparing the characteristics of transistor-based memory elements, a few important parameters should be considered. First, it is the switching coefficient $k_{sw} = I_{DS}(\text{state 1})/I_{DS}(\text{state 2})$, which shows how strong is hysteresis in the electrical characteristics of a transistor or how wide is the memory window. The device operating voltages, a programming speed and a long-term stability of the distinct electrical states (retention characteristics) are also crucially important.

The most popular device architecture includes a photochromic compound as a so-called dopant in the semiconductor layer of organic field-effect transistors (OFETs).[9] However, such a modification results in charge trapping in the semiconductor layer, which considerably affects the electrical characteristics of OFETs. The best devices of this type showed switching coefficients k_{sw} of 5–18, which are comparable to the characteristics achieved in diode-type memory devices.[6] Alternatively, the thin layers (or even monolayers) of photochromic molecules are placed under source and/or drain electrodes in order to control charge injection in OFETs.[10] The best switching coefficients of 2–3 were inferior compared to the results obtained using a previously described approach.[11]

It is known that the highest density of charge carriers in operating OFET flows in a few molecular layers of a semiconductor adjacent to a dielectric.[12] Therefore, the photoisomerization of a photochromic compound at the dielectric/semiconductor interface changes significantly the electrical characteristics of a conducting channel (density of traps/carriers, electrical permittivity and capacitance) and the device itself thus providing a required photoswitching effect.[13,14] This approach has been pursued by several research groups; however, the achieved switching coefficients were also not very high (k_{sw} = 0.3–10).[11–15]

Analyzing previous reports on the optical memories based on photochromic materials, one can notice their low switching coefficients, which stay typically below 10 and hardly exceed 100 for the best examples. These devices typically operate at high voltages (30–100 V), while their programming is very slow and requires light illumination within tens of seconds or even minutes. To make this type of memory more interesting for practical applications, one has to improve significantly the main device characteristics. Recently we reported memory elements based on photochromic spirooxazine **1** (Figure 1), which showed decent operating voltages (< 5 V) and reasonably high switching coefficients of ~10^3.[16] Unfortunately, the programming speeds were low mainly due to fundamental limitations of the used material and the device architecture.

Here, we investigated a commercially available photochromic material, 1,3-dihydro-1,3,3-trimethylspiro(2*H*-indole-2,3′-[3*H*]-

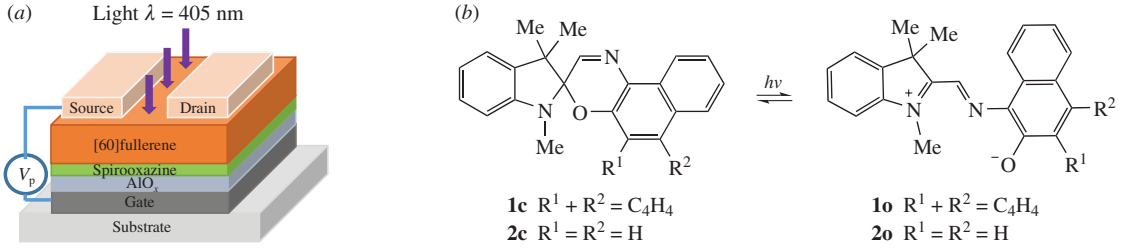

Figure 1 (*a*) OFET-based memory elements and (*b*) reversible photoisomerization of spirooxazines.

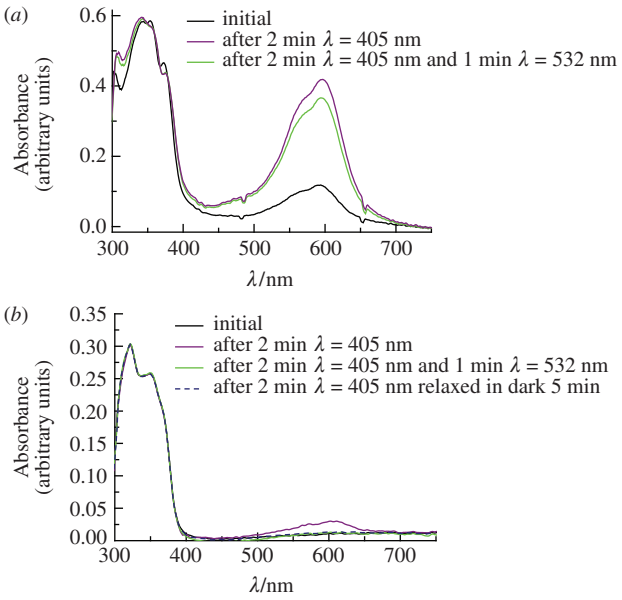

Figure 2 Absorption spectra of the thin films of spirooxazines (*a*) **1** and (*b*) **2** in different states: pristine (initial), illuminated with violet light for 2 min and then with green light for 1 min.

naphth[2,1-*b*][1,4]oxazine) **2**, as a light-sensitive component of OFET-based memory elements (Figure 1). The application of this material allowed us to improve the operation speed of the memory elements by more than one order of magnitude.

It is known that the closed forms of spirooxazines [**2c**, Figure 1(*b*)] undergo reversible photoisomerization to quasi-stable open zwitterionic forms [**2o**, Figure 1(*b*)] under illumination in solution with UV or violet light. Back isomerization occurs when the system is illuminated with visible light or stored at elevated temperatures.

Note that the freshly prepared films of spirooxazine **1** contain both closed and open isomers as it follows from their absorption spectra. The absorption band at 520–660 nm corresponding to zwitterionic form **1o** starts to increase considerably under illumination of the films with violet light (λ = 405 nm) from a 20 mW diode laser [Figure 2(*a*)]. Illumination of the films with green light (λ = 532 nm, 20 mW) reverses the process, as follows from the decreased intensity of an absorption band at 520–660 nm. However, even continuous illumination with green light does not allow one to achieve the complete conversion of zwitter-ionic form **1o** to neutral isomer **1c** in the thin films.

It should be emphasized that the thin films of spirooxazine **2** demonstrated a drastically different photochemical behavior. First, freshly prepared films showed very week absorptions at long wavelengths, which can be attributed to zwitter-ionic form **2o** [Figure 2(*b*)]. This result proves that, in contrast to spirooxazine **1**, compound **2** forms the films comprising almost entirely the neutral molecules of **2c**. Illumination of the films with violet light (λ = 405 nm) induces the conversion of **2c** to **2o**. However, the observed relatively small increase in the intensity of the absorption band at 520–660 nm suggests the presence of just a minor amount of the photoinduced zwitterionic molecules of **2o** in the films. Moreover, they undergo spontaneous backward isomerization. The vast majority of **2o** is converted into **2c** just in 5 min after switching off the violet laser [Figure 2(*b*)]. It seems that illumination with green light (λ = 532 nm, 20 mW) accelerates the cyclization of **2o**.

The absorption spectra of **1**/C_{60} and **2**/C_{60} bilayer films revealed interesting results (Figure S1, Online Supplementary Materials). It is remarkable that bilayer **2**/C_{60} films were completely non-sensitive to the violet (405 nm) or green (532 nm) light thus implying the fact that **2** does not undergo photochemical isomerization under the specified conditions. These findings suggest that the application of spirooxazine **2** as a light-sensitive component for designing memory elements should reveal different results, as compared to the previously studied system comprising spirooxazine **1**.

The architecture of the fabricated memory devices is schematically shown in Figure 1(*a*). To construct such devices, the aluminum gate electrodes are initially subjected to electrochemical passivation in order to grow a thin AlO_x dielectric layer. Afterwards, the photoactive spirooxazine layer is deposited by spin coating from a solution in toluene. Fullerene C_{60} used as an n-type semiconductor in this work was deposited by sublimation *in vacuo* (~10^{-6} mbar). Finally, silver source and drain electrodes were evaporated through a shadow mask forming a transistor channel with W = 1 mm and l = 60 μm (for details, see Online Supplementary Materials).

While programming the memory elements, we applied the electrical bias between the source and gate electrodes of the transistor (programming voltage V_p) and illuminated the channel of the device with violet light (λ = 405 nm, 20 mW diode laser), as shown in Figure 1(*a*). The length of the single laser pulses was changed between 0.5 and 1000 ms in a controlled fashion in order to reveal the actual operation speed of the memory elements. The transfer characteristics of the devices were measured after each programming step. Note that only the simultaneous action of electrical bias and light induces programming effects reflected by considerable changes in the transistor threshold voltage V_{TH} (see below).

Figure 3(*a*) shows that the threshold voltage of the devices shifts towards values that are more negative when the devices are programmed under negative V_p potentials. The backward transition can be accomplished using positive V_p voltages [Figure 3(*b*)].

The test devices demonstrated remarkably high programming speeds. Thus, applying V_p = –10 V for just 1.0 ms changes the drain current of the device by a factor of 1500 (V_{GS} = –1.25 V). An increase in the programming time to 3.0 ms gives a switching coefficient of ~15000. Maximum switching coefficient of ~90000 is reached at the programming time of 20 ms. This represents one

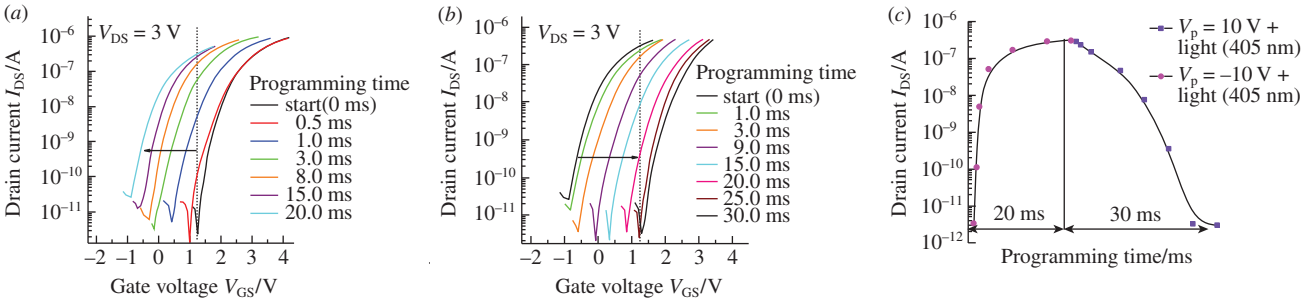

Figure 3 Transfer characteristics of the OFETs programmed at (*a*) V_p = –10 V and (*b*) V_p = +10 V using different lengths of the light pulses (λ = 405 nm, 20 mW diode laser); (*c*) dependence of the device drain current at V_{GS} = 1.25 V on the programming time.

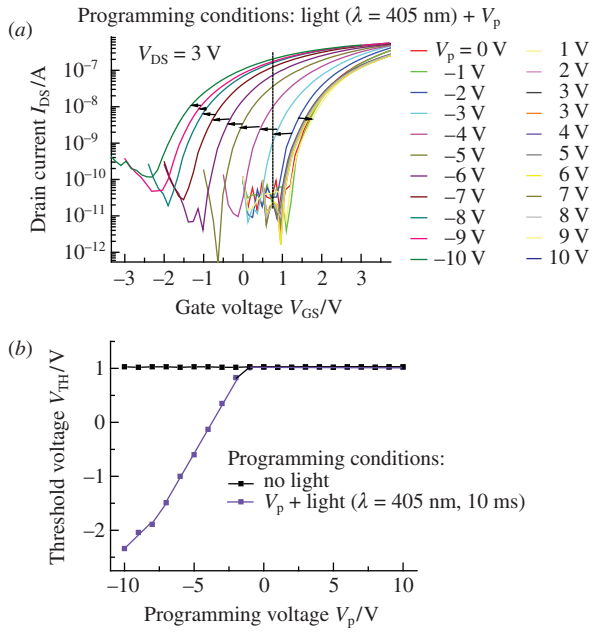

Figure 4 (*a*) Transfer characteristics of the photoswitchable OFETs programmed at different bias voltages for 10 ms at each consecutive step. (*b*) The dependences of the device threshold voltage V_{TH} on the programming voltage V_p.

of the highest values reported for OFET-based optical memory elements comprising photochromic molecules. Backward transition occurs with a lower rate and it is necessary to apply V_p = +10 V for 30 ms. Nevertheless, the operation speed of the memory elements based on spirooxazine **2** is improved by one (positive V_p) or two (negative V_p) orders of magnitude compared to the devices based on spirooxazine **1**.[16] This result proves that the transient and electrical characteristics of OFET-based optical memory elements can be tuned using different spirooxazines as materials for constructing a light-sensitive layer of the devices.

Applying different programming voltages for 10 ms allows one to induce multiple discrete electrical states in a single device [Figure 4(*a*)]. The threshold voltage of the devices can be changed between –2.3 and +1.0 V thus providing a reasonably wide memory window.

Note that only the negative V_p biases induce significant programming effects. Applying positive V_p voltages can be used for the quick erasing of states induced by negative potentials. However, positive programming voltages cannot be used for creating new discrete states characterized by V_{TH} > +1.0 V. On the contrary, a previously reported system comprising spirooxazine **1** operated in the V_{TH} range between –3 and +3 V.[16] The observed differences in the electrical behavior of the memory elements comprising spirooxazines **1** and **2** should be closely related to the optoelectronic and physical properties of these photochromic materials.

Considering the potential multibit memory applications of the designed devices, special attention should be paid to their stability and reliability and to the achievable current ratios for 'on' and 'off' states. Figure S2(*a*) (Online Supplementary Materials) shows that the devices can be switched many times between any two arbitrary selected states with a high accuracy. Figure S2(*b*) exhibits ten manually recorded write-read-erase cycles, which demonstrate the appreciable reproducibility and cycling stability of the devices. Retention characteristics presented in Figure S2(*c*) also prove the capability of applying the designed photoswitchable OFETs as memory elements.

In conclusion, we found that a relatively small change in the molecular structure of photosensitive spirooxazine strongly affects the electrical behavior of the photoswitchable OFETs. In particular, the replacement of spirooxazine **1** with spirooxazine **2** changed the memory window of the devices [shifted the positive edge from ~+3.0 V (**1**) to +1.0 V (**2**)] and improved their programming speeds by one or two orders of magnitude. These results suggest that different organic photochromic materials can be used for tuning the electrical parameters of the OFETs and designing multibit optical memory elements with advanced operational characteristics, good stability and reliability.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.01.011.

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