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Optically controlled field effect transistors based on photochromic spiropyran and fullerene C_{60} films

Airat R. Tuktarov,*[a] Renat B. Salikhov,[b] Artur A. Khuzin,[a] Idris N. Safargalin,[b] Ilnur N. Mullagaliev,[b] Olga V. Venidiktova,[c] Tatyana M. Valova,[c] Valery A. Barachevsky[c] and Usein M. Dzhemilev[a]

[a] *Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 450075 Ufa, Russian Federation. Fax: +7 347 284 2750; e-mail: tuktarovar@gmail.com*
[b] *Bashkir State University, 450074 Ufa, Russian Federation*
[c] *Photochemistry Center, Federal Research Centre ‘Crystallography and Photonics’, Russian Academy of Sciences, 119421 Moscow, Russian Federation*

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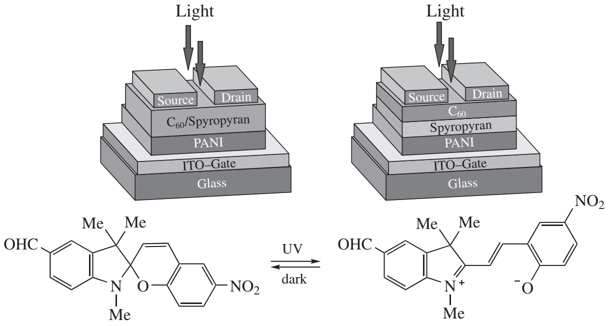
Optically controlled organic field effect transistors containing a binary mixture of fullerene C_{60} (n-semiconductor) and spiropyran (photoresponsive conductivity modulator) as the active layer were designed and fabricated. The obtained transistors demonstrated higher transfer characteristics (source-drain current), charge carrier mobility in the active layer, and response rate to an external influence than the multilayer transistor (wherein these semiconductor and photoresponsive material are in different layers), which makes them promising candidates for the design of optical memory elements.



Organic field effect transistor (OFET) is the key circuit element in modern organic electronics. Its main advantages as compared to a silicon transistor include the low cost of organic materials, low-cost and eco-friendly production of organic elements *via* printing technologies, as well as their universal qualities such as low weight, flexibility, transparency, long shelf life, and reliability.[1]

A popular trend in recent years is the design of optically controlled field effect transistors, which are promising as optical memory elements, by combining organic semiconductors with photochromic compounds,[2–4] since the latter exhibit a dual conductivity under isomerization conditions.[5–10]

Currently, there are three approaches to the design of optically controlled OFET based on photochromic molecules and organic semiconductors.[3] The first one is a multilayer approach that involves an administration of photochromes and semiconductors in different layers. The device fabrication in this case is rather costly. Furthermore, the switching efficiency decreases due to the photodegradation of photochromic molecules and the presence of a large number of layers, which hampers photons from reaching the photochromic molecule.[3] The second approach implies the utilization of binary mixture of the photochrome and organic semiconductor as the active layer. This method, unlike the first one, provides more technologically attractive devices due to the smaller number of layers, high switching rate, and cyclability. A possible alternative to the second approach is a fabrication of active layer from hybrid molecules obtained *via* covalent binding of photochromes to organic semiconductors. Unfortunately, there are currently no data on the production of transistors containing such hybrid molecules. This is somewhat surprising since this approach ensures the photochemical tuning of dynamic properties of the nanomaterials, such as conductivity or fluorescence.[11] The organic semiconductor can also contain various photochromic addends, which may give rise to multifunctional devices. Note that such hybrid molecules are more stable against photodegradation than the initial photochromes.[12]

In the creation of photocontrolled field effect transistors based on fullerenes and photochromic molecules, the OFET multilayer structure method is mainly applied.[13–16] However, there is an exception,[17] wherein a transistor based on a binary mixture of fullerene derivatives and dihetarylethenes as the active layer is reported, but no comparison between its characteristics and those of multilayer transistor is given. Thus, it is impossible to evaluate the advantages of one or another approach to OFET manufacturing. Nevertheless, despite existing gaps in the literature, some researchers have already managed to get optically controlled OFETs possessing large memory windows, low operating voltages, and switching ratios exceeding 10^4, which makes them highly promising as the optical memory elements.

Considering the enormous practical interest in photo controlled OFETs as well as the above-mentioned technological disadvantages of multilayer transistors, in this work we aimed at the fabrication and evaluation of mixed-type optically controlled OFET containing a binary mixture of fullerene C_{60} and spiropyran **1** as the active layer [Figure 1(*a*)].[†] For more objective and rigorous comparison of our results with published data, we have also manufactured a

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[†] A glass covered with a conducting indium tin oxide (ITO) layer as the gate was used as the substrate. A film of polyaniline (PANI) occurring in the non-conducting state (~10^{-12} Sm), which acted as the gate dielectric, was applied by thermal vacuum deposition from a Knudsen cell.[18] The same method was used to deposit either a mixed spiropyran (10 mg) and fullerene C_{60} (10 mg) layer or separate layers of them at the Knudsen cell temperature of 300 °C. The distance between the cell and the substrate was 3 cm. Then two aluminum electrodes (drain and source) at a distance of 50 μm between them were deposited by thermal sputtering

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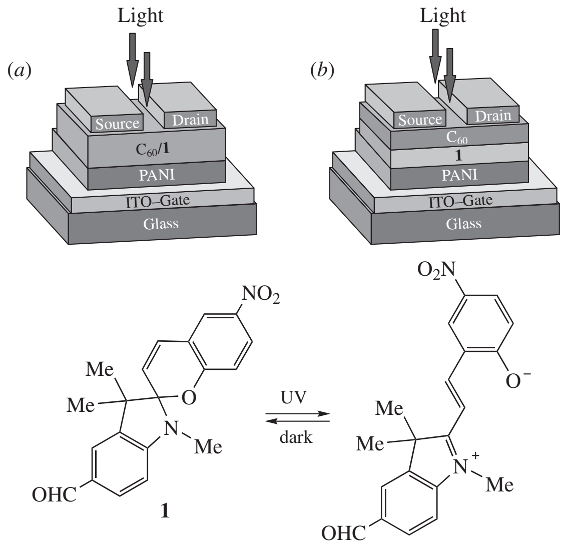

Figure 1 Structures of optically controlled (*a*) mixed-type and (*b*) multilayer OFETs and the reversible UV light-induced isomerization of spiropyran **1** into its merocyanine form.

multilayer transistor, where fullerene C_{60} and spiropyran **1** are located in the separate layers [Figure 1(*b*)].

UV irradiation of spiropyrans in solution is known to induce as their reversible isomerization into the electrically conducing merocyanine form. In the absence of light, the unstable zwitterion is converted back to the stable spiropyran form within several minutes. The similar transformations of spiropyran **1** occur both in solutions and in films (Figure S1, see Online Supplementary Materials). The generation of zwitter-ion form of photochromic compound **1** was confirmed by the new absorption band appearing at 580–620 (in a chloroform solution) and 560 nm (in an amorphous film).

It is noteworthy that these light-induced reversible transformations occur more efficiently in solution than in amorphous film, although this causes virtually no effect on the performance of designed OFETs.

Measurement of the current–voltage characteristics of designed transistors (Figure S2) revealed that in the absence of irradiation, the current through the phototransistors was about or lower than 1 nA. Upon UV irradiation (350 nm) of the transistor channel, the source–drain current was increased by three orders of magnitude for a multilayer device and tenfold more for the phototransistor based on the film made of binary mixture of fullerene C_{60} and spiropyran **1**. An increased current in the OFET was observed in the case of positive gate voltage, which corresponds to the electronic conduction of OFET transport channel. The characteristics imply a normally open field effect transistor, *i.e.*, the conducting channel is formed during the sample fabrication and, consequently, no current saturation region is present. The dependences are non-linear. The sharp increase in the current may be explained by the zwitterionic effect leading to the pronounced increase in the dipole moment of spiropyran (from 6.4 to 13.9 D)[21] under UV light. Upon the application of voltage onto the gate of transistor, the presumable orientation of polarized molecules occurs, which in turn significantly enhances the field effect inside the transistor.

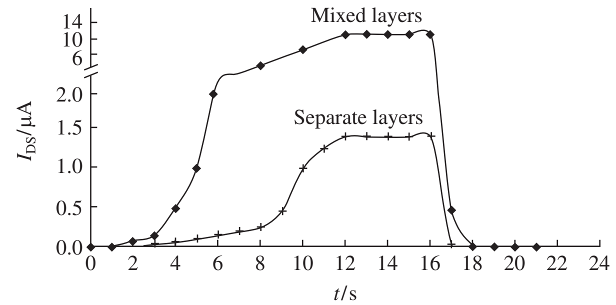

Figure 2 Kinetics of I_{DS} increase and decrease for OFETs based on separate and mixed active layers upon switching on and off the UV light (2–3 W cm^{-2}, 350 nm) for V_{DS} = 3 V and V_G = 3 V.

The charge carrier mobility in the OFET active layer μ was estimated from equation (1) for the low field mode:

$$I_{DS} = (W/L)\mu C(V_G - V_{th})V_{DS}, \qquad (1)$$

where W is the channel width, L is the channel length, C is the capacity per area of gate dielectric PANI (for 500 nm thickness, C = 0.7 nF cm^{-2}), V_G is the gate voltage, V_{DS} is the drain-source voltage, and V_{th} is the threshold voltage. The estimated values for the carrier mobility are 1 and 10 cm^2 V^{-1} s^{-1} in order of magnitude for the structures containing the active layer deposited separately and mixed manually, respectively. This is several times greater than the values obtained earlier for the transistors produced using a vacuum deposition of C_{60} and polymer dielectric.[22]

Figure 2 shows a typical kinetics of I_{DS} current relaxation for OFETs upon switching on and off the light (2–3 W cm^{-2}) for V_{DS} = 3 V and V_G = 3 V. The output current depends on the irradiation time of conducting channel, while the maximum value is attained within 12 s after switching on the light. The initial state of transistors is restored within 1–2 s after the activating radiation has been switched off. One can see from Figure 2 that the current in mixed-layer transistor begins to increase after 3 s, while the multilayer device starts to operate within 6–8 s after switching on the light. This is apparently caused by a lower number of photons reaching the photochromic layer in the latter transistor due to the absorption in the organic semiconductor film.

The response of fabricated transistors to external influence was evaluated using the photosensitivity (P) and responsivity (R) characteristics. The P value is defined as the photocurrent to dark current ratio:

$$P = I_{ph}/I_{dark} = (I_{illum} - I_{dark})/I_{dark}, \qquad (2)$$

where I_{ph} is the photocurrent, I_{illum} is the channel current under illumination, and I_{dark} is the drain current in the dark.

The R value was defined as the ratio between the generated photocurrent and the incident optical power (P_{opt}); hence, the responsivity R can be calculated as

$$R = I_{ph}P_{opt} = (I_{illum} - I_{dark})/aE_{opt}, \qquad (3)$$

where E_{opt} is the incident radiation power density and a is the area accessible for incident radiation.

The photosensitivity estimation from equation (3) gave values of 14000 and 1400 for the phototransistor based on the film made of binary mixture and for separately deposited films, respectively. The calculated responsivity values were 1.4 to 3 mA W^{-1} for the transistor made of binary mixture and 10 times less for that containing the separate layers. During the calculations, it was taken into account that the device area exposed to the light was not more than 5×10^{-3} cm^2. Thus proceeding from the emitter characteristics, which provided an incident power density of approximately 2–3 W cm^{-2}, the overall radiation density on the phototransistor was about 10 mW.

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in a vacuum chamber of the VUP-5 (vacuum universal post) setup. This method of manufacturing multilayer thin-film devices based on organic compounds was described in more detail.[19,20] The film thickness and structure were determined using a NanoScan 3D atomic force microscope. The fabricated devices had the channel width and channel length of 10 and 0.5 mm, respectively.

In the light of potential utilization of these transistors as the memory cells, the particular attention was paid to the stability and reliability of these devices (Figure S3). Therefore, it was shown that the developed transistors could be repeatedly switched between the two on–off states, while their electrical characteristics were being maintained.

In summary, the designed OFETs containing the active layers based on fullerenes and spiropyran possess the high mobility of charge carriers in the channel and demonstrated the fairly high photosensitivity and responsivity. These results are of practical interest for the design of optical memory cells, optrons, and photosensors. An essential benefit of these devices is their manufacturing process that is compatible with the modern printed organic electronics technology. Further investigations into the transport, generation, and relaxation of photoinduced charge carriers in these structures are required in order to optimize their performance.

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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.2019.03.014.

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