RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2019, **9**, 7505

Photocontrolled organic field effect transistors based on the fullerene C_{60} and spiropyran hybrid molecule†

A. R. Tuktarov, *[a] R. B. Salikhov,[b] A. A. Khuzin,[a] N. R. Popod'ko,[a] I. N. Safargalin,[b] I. N. Mullagaliev[b] and U. M. Dzhemilev[a]

Received 4th February 2019
Accepted 1st March 2019

DOI: 10.1039/c9ra00939f

rsc.li/rsc-advances

Photocontrolled organic field-effect transistors (OFETs) containing a hybrid compound of fullerene C_{60} (n-semiconductor) with spiropyran (electrical conductivity photocontroller) as the active layer were fabricated for the first time. It was found that an OFET based on the hybrid compound, unlike the multilayer transistor (a device based on unmodified fullerene C_{60} and spiropyran in different layers), has higher transfer characteristics (source-to-drain current), charge carrier mobility in the active layer, and response rate to external influence, which makes them promising materials for the manufacture of optical memory elements.

Introduction

The development of organic electronics may bring a broad range of new devices (displays, integrated circuits, sensors, *etc.*) in the near future. These devices will be ultrathin, lightweight, flexible, and transparent, which will open up new applications inaccessible to traditional silicon-based electronics. One of the promising devices for organic electronics is an organic field effect transistor (OFET) with a transport layer having a thickness of not greater than ten nanometers, in which the flow of charge carriers is controlled by changing the charge density in an electric field.[1,2] In most organic materials, especially those used to create electronic devices, the hole conductivity prevails above the electronic conductivity. Therefore, searching for organic materials to create electronic conduction channels is the actual problem. Fullerenes functioning as n-dopants for organic materials occupy a special place among organic semiconductors for OFETs.[3] Combining methods for the fabrication of organic transport layers with doping of the initial material with fullerenes would substantially increase the charge carrier concentration and, hence, increase the transistor currents (power of the device). Hence, this is a quite strong possibility to increase both the carrier mobility of an organic field-effect transistor to 10^2 cm^2 V^{-1} s^{-1} (extend the frequency range with simultaneous decrease in the controlled voltage level) and to increase the controlled current density (organic transistor power).

Fullerene C_{60} and its cyclopropane derivative PC[60]BM are the most promising and in-demand n-type semiconductor materials for organic electronics.[4] The use of fullerene C_{60} as an active element of low-voltage thin film transistors gives rise to devices with high performance characteristics. This is due to the fact that C_{60} forms isotropic solids and fullerene-based films can be fabricated without special control of molecular assembly, unlike films of other organic semiconductors.[5]

Simultaneously, the introduction of a photosensitive film (*e.g.*, based on hetarylethenes, spirophotochromes, or azobenzene) at the boundary between the semiconductor (fullerene) and insulator layers may give low-voltage photocontrolled OFETs and provide a promising approach to multibit optical memory devices possessing good electrical characteristics and operation stability and reliability. This approach is currently actively used by various researchers,[6–11] but the fabrication of devices is quite costly. Furthermore, the switching efficiency decreases as a result of photodegradation of the photochromic molecule and the presence of a large number of layers, which reduces the number of photons that reach the photochromic molecule.[12]

Although great experience in the design of light-controlled OFETs and the synthesis and studies of various photochromic compounds has been accumulated in the world practice, the preparation of efficient photochromic systems promising for micro- and nanoelectronics, in particular, for the fabrication of molecular transistors and 3D optical memory elements is still an important challenge of the theoretical and practical organic chemistry and organic materials science. Meanwhile, it is unknown what characteristics will be inherent in the devices

[a]*Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, Russian Federation. E-mail: tuktarovar@gmail.com*

[b]*Department of Infocommunication Technologies and Nanoelectronics, Bashkir State University, Russian Federation*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ra00939f

with key elements represented by photochromic fullerene-based hybrid molecules, highly promising for organic electronics.

Result and discussion

In view of the above and as a continuation of our research towards the preparation and studies of properties of hybrid molecules based on fullerenes and photochromic compounds aimed at the design of more efficient and promising organic electronic devices,[13–18] we have fabricated and investigated a photocontrolled OFET containing pyrrolidinofullerene **1** as the active layer (Fig. 1a).[13] Simultaneously, for strict and objective comparison of our results with published data, we have fabricated a multilayer transistor, in which the semiconductor (fullerene C_{60}) and the light-controlled compound (spiropyran **SpOx**) formed separate layers (Fig. 1b).

The study of the current–voltage characteristics of the fabricated transistors has shown that, in the absence of irradiation, the currents in the phototransistors are less than 1 nA or have the same order of magnitude. Under UV light irradiation (350 nm), in the field of the transistor gap the drain-to-source current increases by three orders of magnitude for both devices. Thus, the current ratio I_{on}/I_{off} is about 1000. Fig. 2 show the transfer and output characteristics of OFETs. In all cases, the currents for structures with a hybrid molecule **1** layer exceeded the values of current for structures with separate layers by several tenths of microamperes (μA). An increase in currents in the created OFETs is observed under a positive gate voltage, which corresponds to the electronic conductivity type of the OFET transport channel. Dependencies are nonlinear. The

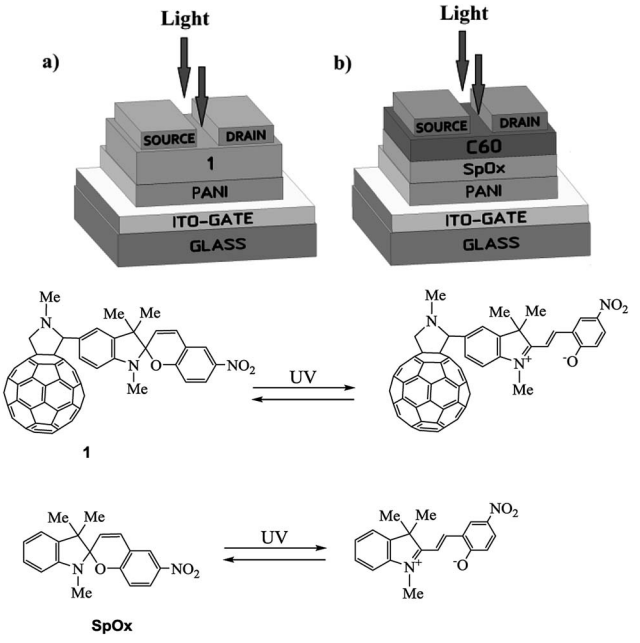

Fig. 1 Structures of photocontrolled OFETs presented in this study. The UV light-induced reversible isomerization of the spiropyran moiety to the merocyanine form within hybrid molecule **1** in OFET (a) and model spiropyran **SpOx** to merocyanine in OFET (b) is shown below.

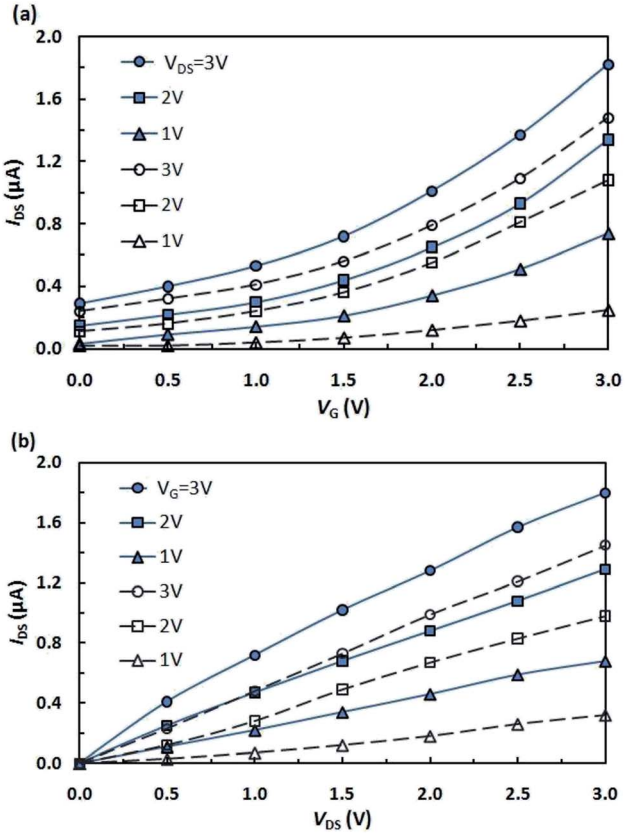

Fig. 2 (a) Transfer and (b) output characteristics of OFETs based on hybrid (solid lines) and separate (dashed lines) active layers.

output characteristics show the absence of the saturation regions. Higher voltages (V_{DS}) are most likely required to achieve them.

A possible explanation for the pronounced increase in the current through the transistor is the zwitter-ion effect, which leads to a sharp increase in the dipole moment of the spiropyran molecule (from 6.4 D to 13.9 D)[19] upon UV irradiation. Voltage application to the transistor gate induces predominant orientation of polarized molecules, which in turn sharply increases the field effect in the transistor.

The charge carrier mobilities of the OFET active layer μ were found from eqn (1):

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

where W is the channel width, L is the channel length, C is the capacitance per squared area of the gate insulator PANI (for thickness of 500 nm, $C = 0.7$ nF cm^{-2}), V_G is the gate voltage, V_{DS} is the drain-to-source voltage, V_{th} is the threshold voltage.

The calculated carrier mobilities were 1.8 cm^2 V^{-1} s^{-1} and 2.3 cm^2 V^{-1} s^{-1} for the "separately deposited" active layer and for the hybrid active layer, respectively. The obtained values are comparable with data[3,20] determined recently for films of fullerenes and fullerene derivatives used in organic electronics.

A typical I_{DS} relaxation kinetics for OFETs upon light switching on and off (with a power of ~150 W cm^{-2}) with V_{DS} =

3 V and $V_g = 3$ V is shown in Fig. 3. It can be seen that the output current depends on the irradiation time of the conducting channel, with the maximum values being attained within 12 s after the light is switched on. The initial state of transistors is attained within 1–2 s after the activating light is switched off.

It can be seen in Fig. 3 that the current is higher in the OFET based on the hybrid compound than in the multilayer device, which is attributable to the fact that in the latter case, fewer photons reach the photochromic layer as a result of absorption in the organic semiconductor film.

The response of the transistors to external influence was evaluated using characteristics such as photosensitivity (P) and responsivity (R). The photosensitivity P is defined as the photogenerated to dark current ratio and can be found as

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

where I_{ph} is the photocurrent, I_{illum} is the channel current on irradiation, and I_{dark} is the drain current in the dark and located at 610 nm.

On the other hand, the R value can be defined as the ratio of the generated photocurrent to the incident optical power (P_{opt}); hence, the responsivity R can be calculated by the following equation:

$$R = I_{ph}/P_{opt} = (I_{illum} - I_{dark})/E_{opt}a \quad (3)$$

where E_{opt} is the incident radiation power density, a is the device area accessible to the incident radiation.

The photosensitivities estimated by relation (3) were 1800 and 1400 for the phototransistor based on fullerene C_{60} and spiropyran hybrid film and the phototransistor fabricated with separate film deposition, respectively. The responsivity calculation yielded the values of 180 μA W^{-1} for the hybrid transistor and 140 μA W^{-1} for the separate-layer transistor. The calculations assumed that the area of the device accessible to the incident light was not more than 5×10^{-3} cm^2. Then, considering the emitter characteristics which provide the incident power density of approximately 2 W cm^{-2}, we obtain the overall radiation power on the phototransistor to be about 10 mW.

Experiment and the literature data show that the best results are achieved in transistors with a multilayer structure (Fig. 1b) having layers thickness (semiconductor (C_{60}) and photochromic) of 200 nm each. Upon fabrication of the device based on hybrid compound **1** (Fig. 1a), the thickness of the combined semiconductor and photochromic layers was done 300 nm (see ESI†). At the same time, it was found that the increase in the thickness of the photochromic layer in the device (Fig. 1b) leads to a decrease in the output current due to a decrease in the influence of the gate field on the carrier concentration in the transport layer. A decrease in the thickness of this layer leads to a weakening of the zwitterion effect and, as a consequence, a weakening of the output current.

In view of the potential applications of these transistors as memory cells, special attention in the development of these devices is paid to their stability and reliability. It is shown in Fig. 4 that the transistors that we fabricated can repeatedly switch between on- and off-states with their electrical characteristics being retained.

It should be noted that structures fabricated from pyrrolidinofullerene **1** proved to be stable to UV radiation. The films of separately deposited C_{60} and **SpOx** degraded during operation thus destroying contact Al films. The studies of transistors described above indicate that transistors based on the hybrid molecule were superior in all of the measured characteristics; furthermore, their fabrication is more feasible.

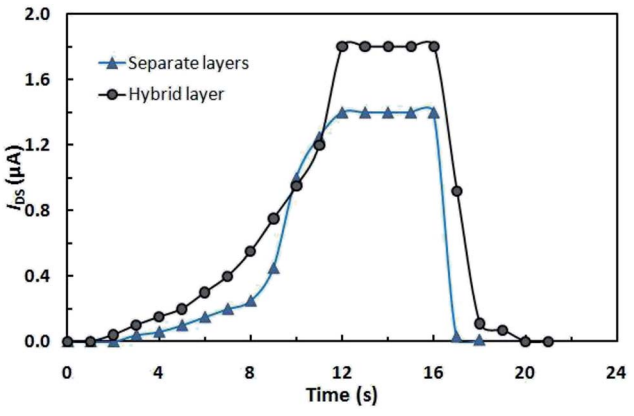

Fig. 3 Kinetics of the increase and decrease in the currents I_{DS} for OFETs based on double layers and hybrid layer **1** on switching on and off of ultraviolet light (150 W, 350 nm) for $V_{DS} = 3$ V and $V_G = 3$ V.

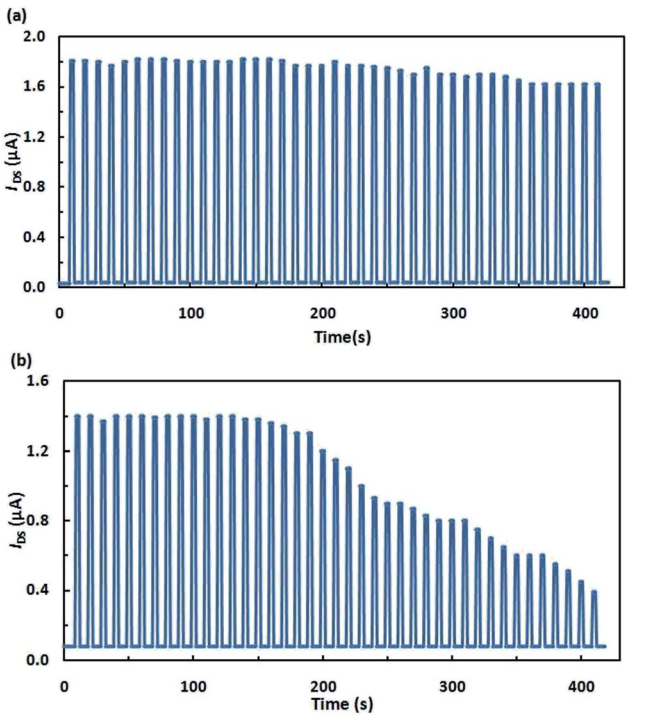

Fig. 4 Cycling stability of the devices switched 40 times between two arbitrarily selected electrical states: (a) hybrid layer; (b) separate layers.

Conclusions

Thus, OFETs with active layers based on the fullerene C_{60} and spiropyran hybrid molecule studied in this work possess high carrier mobility in the channel and relatively high responsivity and photosensitivity. The main advantage of such hybrid structures is their high stability, which was confirmed during high-speed tests with multiple switching (ON and OFF) that reflect the performance of a device. The results of the studies are of practical value for the design of memory cells with optical recording, optrons, and photosensors. An advantage of these devices is that their fabrication technique is compatible with the modern organic printed electronic techniques. All measurements were carried out under normal conditions – in the air, which is the advantage of the transistor structures studied, as compared with most experimental structures based on other compounds, when you have to work in inert gas or dry nitrogen using glove box. Further studies of the transport, generation, and relaxation of photoinduced charge carriers in these structures are required for optimization of their performance characteristics.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (N 18-33-20027) and Grants of the RF President (MK-3058.2018.3 and Sci. Sh.-5240.2018.3). The structural studies were performed at the Center for Collective Use "Agidel" at the Institute of Petrochemistry and Catalysis of the RAS.

Notes and references

1 M. E. Gemayel, K. Borjesson, M. Herder, D. T. Duong, J. A. Hutchison, C. Ruzie, G. Schweicher, A. Salleo, Y. Geerts, S. Hecht, E. Orgiu and P. Samori, *Nat. Commun*, 2015, **1**, 6330.

2 L.-N. Fu, B. Leng, Y.-S. Li and X.-K. Gao, *Chin. Chem. Lett.*, 2016, **27**, 1319.

3 Y. Zhang, I. Murtaza and H. Meng, *J. Mater. Chem. C*, 2018, **6**, 3514.

4 A. Pivrikas, N. S. Sariciftci, G. Juska and R. Osterbacka, *Prog. Photovoltaics*, 2007, **15**, 677.

5 F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries and P. Alnot, *J. Am. Chem. Soc.*, 1993, **115**, 8716.

6 A. R. Tuktarov, A. A. Khuzin and U. M. Dzhemilev, *Russ. Chem. Rev.*, 2017, **86**, 474.

7 K. Borjesson, M. Herder, L. Grubert, D. T. Duong, A. Salleo, S. Hecht, E. Orgiu and P. Samori, *J. Mater. Chem. C*, 2015, **3**, 4156.

8 L. A. Frolova, A. A. Rezvanova, B. S. Lukyanov, N. A. Sanina, P. A. Troshin and S. M. Aldoshin, *J. Mater. Chem. C*, 2015, **3**, 11675.

9 L. A. Frolova, P. A. Troshin, D. K. Susarova, A. V. Kulikov, N. A. Sanina and S. M. Aldoshin, *Chem. Commun.*, 2015, **51**, 6130.

10 L. A. Frolova, A. A. Rezvanova, V. Z. Shirinian, A. G. Lvov, A. V. Kulikov, M. M. Krayushkin and P. A. Troshin, *Adv. Electron. Mater.*, 2016, **2**, 1500219.

11 A. A. Rezvanova, L. A. Frolova and P. A. Troshin, *Mendeleev Commun.*, 2016, **26**, 26.

12 E. Orgiu and P. Samori, *Adv. Mater.*, 2014, **26**, 1827.

13 A. R. Tuktarov, A. A. Khuzin, A. R. Tulyabaev, O. V. Venidictova, T. M. Valova, V. A. Barachevsky, L. M. Khalilov and U. M. Dzhemilev, *RSC Adv.*, 2016, **6**, 71151.

14 V. A. Pomogaev, V. A. Barachevsky, A. R. Tuktarov, P. V. Avramov and V. Ya. Artyukhov, *J. Phys. Chem. A*, 2018, **122**, 505.

15 A. R. Tuktarov, A. A. Khuzin, L. M. Khalilov, A. R. Tulyabaev, A. R. Akhmetov and U. M. Dzhemilev, *Mendeleev Commun.*, 2015, **25**, 470.

16 A. R. Tuktarov, A. A. Khuzin, A. R. Akhmetov, V. A. Barachevsky, O. V. Venidiktova and U. M. Dzhemilev, *Tetrahedron Lett.*, 2015, **56**, 7154.

17 A. R. Tuktarov, A. A. Khuzin, A. R. Akhmetov, L. M. Khalilov, A. R. Tulyabaev, V. A. Barachevsky, O. V. Venidiktova and U. M. Dzhemilev, *Mendeleev Commun.*, 2016, **26**, 143.

18 A. R. Tuktarov, A. R. Akhmetov, A. A. Khuzin, O. V. Venidiktova, V. A. Barachevskii and U. M. Dzhemilev, *Russ. J. Org. Chem.*, 2017, **53**, 891.

19 Y. Ishiguro, R. Hayakawa, T. Chikyow and Y. Wakayama, *J. Mater. Chem. C*, 2013, **1**, 3012.

20 J. M. Ball, R. K. M. Bouwer, F. B. Kooistra, J. M. Frost, Y. Qi, E. B. Domingo, J. Smith, D. M. de Leeuw, J. C. Hummelen, J. Nelson, A. Kahn and N. Stin, *J. Appl. Phys.*, 2011, **110**, 014506.