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1,2,3-Triazolylfullerene-based n-type semiconductor materials for organic field-effect transistors

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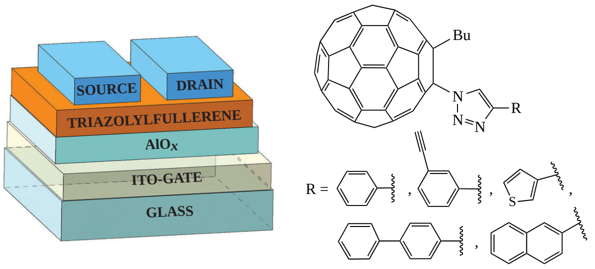
The paper describes new organic field-effect transistors with 1-(4-aryl-1,2,3-triazol-1-yl)-2-butylfullerene as a semiconductor layer. The prototype transistor having 2-naphthyl moieties have higher electron mobilities ($0.090 \pm 10\%$ cm^2 V^{-1} s^{-1}) than that with with biphenyl-4-yl moieties ($0.033 \pm 10\%$ cm^2 V^{-1} s^{-1}). The thin film surfaces of triazolylfullerenes with 3-thienyl and 2-naphthyl groups were more uniform and had a lower roughness, which is confirmed by atomic force microscopy studies.



Keywords: organic field-effect transistors, triazolylfullerenes, 1,2,3-triazoles, fullerenes, mobility of charge carriers, surface roughness.

Currently, organic microelectronics has been actively developed all over the world. The search for more economical and environmentally friendly types of materials in the form of hybrid organic compounds, especially soluble ones, remains relevant. Soluble organic compounds are used as semiconductors,[1] electronic components,[2] memory devices,[3] amplifiers,[4] integrators,[5] switches,[6] chemical sensors,[7] displays and solar batteries.[8–12] Organic electronic devices can be manufactured using deep, flexographic, offset, and stencil screen printing and laser ablation.[13] However, these techniques are not free from drawbacks such as low resolution, poor productivity, risk of polymer destruction on heating, and formation of ragged edges of printed articles.[14] These shortcomings are not typical for inkjet printing technology, and the benefits of this technique are high resolution, mechanical flexibility of the obtained devices, compatibility with almost any type of substrate, the possibility of manufacturing large area devices, and low cost.[15]

Organic semiconductor materials emit light, transfer charge, and exhibit photovoltaic and thermoelectric properties, and superconductivity.[16] Fullerenes and their cyclopropane derivatives, *e.g.*, '[6,6]-phenyl-C_{61}-butyric acid methyl ester' (PCBM), which are n-type semiconductors, occupy a special position in the development of functional materials with specified properties and improved characteristics.[17] A large number of field-effect transistors have been fabricated on the basis of fullerene derivatives[18–20] in which the mobility of charge carriers is in the range of 10^{-3}–10^{-1} cm^2 V^{-1} s^{-1}. Previously, an original method has been developed for the synthesis of previously undescribed and difficult-to-obtain styryl fullerenes by the reaction of C_{60} with aromatic terminal acetylenes in the presence of EtMgBr and $Ti(OPr^i)_4$.[21] In addition, fullerene triazole derivatives containing various aromatic and heteroaromatic substituents were obtained.[22] This type of fullerene derivatives can be very promising for the creation of organic thin-film field-effect transistors.

The purpose of this work was to fabricate organic field-effect transistors (OFETs) with triazolylfullerenes as organic semiconductors (Figure 1), to measure their current–voltage characteristics, and to evaluate the mobility of charge carriers in these semiconductors. The studied compounds were synthesized from 1-azido-2-butyl(C_{60}-I_h)[5,6]fullerene **1** by the click reaction with various terminal arylacetylenes (Scheme 1). The target triazolylfullerenes **2–6** were formed in 75–90% yields; the synthetic details and full characterization were reported previously.[22]

The current–voltage characteristics (CVCs) of OFETs (Figures 2, 3) were measured at room temperature under ambient environment. At a positive gate voltage, the current increases for all types of transistors; this corresponds to the electronic type of conductivity of the OFET transport channel. The dependences are non-linear, and no saturation regions are present in the output characteristics of the devices. The absence of saturation sections on the output characteristics can be due to the presence of leakage currents.

Transistors with semiconductor layers based on triazolylfullerenes **4** and **6** show the highest currents that reach

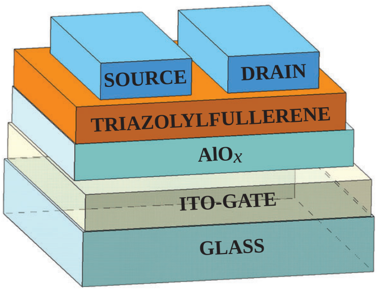
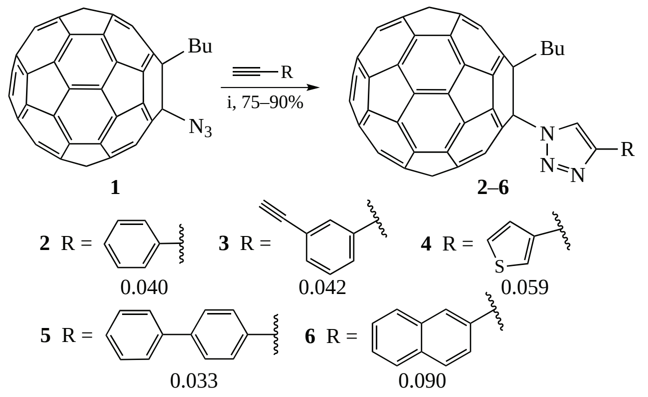


Figure 1 Structure of the experimental field-effect transistor based on triazolylfullerenes.



Values below are the charge carrier mobilities in cm^2 V^{-1} s^{-1}

Scheme 1 *Reagents and conditions*: i, Cu(OAc)$_2$ (10 mol%), Na-ascorbate (20 mol%), PhCl, room temperature, 12 h (see ref. 22).

700–800 nA at a voltage of 10 V. This may be attributable to the structure of the obtained triazolylfullerenes. Compound **4** containing thiophen-3-yl group has a smaller band gap due to the presence of sulfur than other five-membered oxygen- and nitrogen-containing heterocycles. Owing to the narrow band gap, the sulfur-containing molecule can more efficiently transfer charges between donor and acceptor molecules. The presence of heterocyclic units is needed to design organic semiconductors with a broad range of electronic properties. Without heterocyclic units, organic semiconductors would have been restricted to conjugated chains consisting only of carbon, which emit only blue light. Heterocyclic units are reliable building blocks for the development of molecular and polymer organic semiconductors with specified properties. Sulfur has a larger atomic size and enhances the polarizability of heterocycles. Thiophene rings experience a number of interactions such as intramolecular and intermolecular interactions, π–π stacking, and van der Waals forces.[23] These interactions make thiophene derivatives more appropriate for organic thin films.[24] Regarding compound **6**, it can be stated that naphthalene as a part of bulky triazolylfullerene molecule is widely used as a building block in the synthesis of organic photoelectron materials owing to its stable structure.[21,25,26] Naphthalene derivatives perform electron transfer due to their electron-deficient nature, as indicated by high electron affinity determined by electrochemical methods and by the lowest LUMO level. Owing to these characteristics, the organic semiconductors in question are stable under operating conditions and against electron capture, which facilitates the charge transport in thin solid layers.

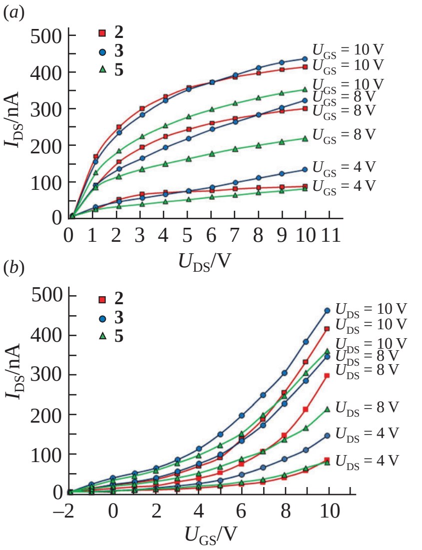


Figure 2 Output and transfer characteristics of OFETs based on triazolylfullerenes **2**, **3** and **5**.

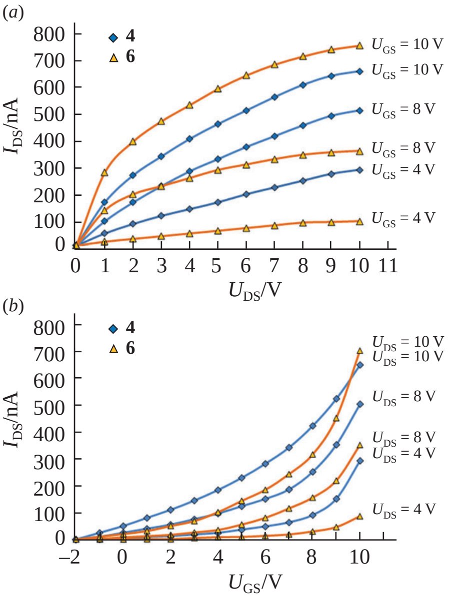


Figure 3 Output and transfer characteristics of OFETs based on triazolylfullerenes **4** and **6**.

For transistors based on layers made of triazolylfullerenes **5**, **2**, and **3**, the currents reach 300–400 nA at the same voltage of 10 V.

The charge carrier mobilities for the *μ* OFET active layers were calculated by the formula[27]

$$I_{DS} = (W/L)\mu C(V_G - V_{th} - V_{DS}/2)U_{DS}, \tag{1}$$

where *W* is the channel width, *L* is the channel length, *μ* is the mobility, *C* is the capacitance per unit area of the gate insulator AlOx (for the 400 nm thickness, $C = 8.9$ nF cm^{-2}), U_G is the gate voltage, and U_{DS} is the drain–source voltage, U_{th} is the threshold voltage. The threshold voltage U_{th} is found from the plots of the current root $I_D^{1/2}$ *versus* the voltage U_{DS} at U_G = const.[28] The mobility values *μ* for structures with triazolylfullerene-based n-semiconductor layers calculated in this way are presented in Scheme 1. The values are comparable with analogous data[29,30] for fullerene C$_{60}$-based transistors and PCBM.[21] The ON/OFF current ratios were calculated based on the maximum and minimum values of the transistor output current in the on and off states of the transistor. The values of these ratios are in the range 1800–3700.

In view of the fact that the charge mobility depends on the ordering of film molecules on the surface[31] and in order to explain the differences between the output and transfer characteristics of the obtained devices, we studied the film morphology. The film surfaces were explored using a scanning probe microscope in the atomic force microscopy mode. The morphology of the surfaces of the films was also studied. Atomic force microscopy (AFM) images (see Online Supplementary Materials, Figure S1) were obtained using a Nanoeducator II NT-MDT instrument; the scan size was 20 by 20 μm. As can be seen from Figure S1, the films formed from compounds **4** and **6** have a smoother surface that the films based on compounds **2**, **3** and **5** and have a lower mean roughness.

The parameter values characterizing the surface of fullerene derivatives were determined: average roughness Ra, root-mean-square roughness Rq and maximum peak height Rz, using the Gwyddion program with an error of 10% (Figure 4). The consideration of thin films based on compounds **4** and **6** is associated with insignificant roughness values, that is, they are the most uniform and ordered. In field-effect transistors based on

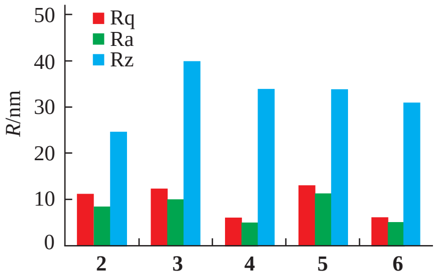


Figure 4 Surface roughness for triazolylfullerenes **2**–**6**.

these compounds, the electron mobilities have higher values compared to the rest.

In conclusion, thin films based on triazolylfullerenes **2–6** were tested as transport layers for organic field-effect transistors. Measurements of the output and transfer current–voltage characteristics for these transistors demonstrated that the output currents reach rather high values of 700–800 nA. Using these results, charge carrier mobilities were calculated. The resulting values for the triazolylfullerene films were comparable with the charge carrier mobilities for fullerene C_{60} and PCBM thin films. The charge carrier mobilities for prototype transistors based on triazolylfullerenes **4** and **6** have a high mobility, which is explained by the nature of these compounds. In addition, AFM examination of the film morphology showed that film surfaces of these compounds were more uniform and had a lower roughness. The studies showed that the compounds of these triazolylfullerenes are quite applicable for manufacturing field-effect transistors.

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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.2023.04.007.

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