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New n-type semiconductor material based on styryl fullerene for organic field-effect transistors

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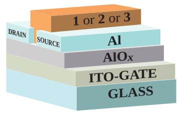
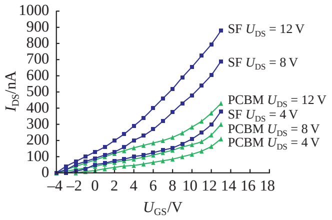
Organic field-effect transistors with styryl fullerene as a semiconductor layer applied by centrifugation are considered. Electron mobility in the transistors was 0.067 ± 10% cm^2 V^{-1} s^{-1}, whereas the mobility of electrons in these devices after the vacuum deposition of a semiconductor layer was much lower (0.023 ± 10% cm^2 V^{-1} s^{-1}).



1 (fullerene C$_{60}$)
2 (styryl fullerene)
3 (PCBM)



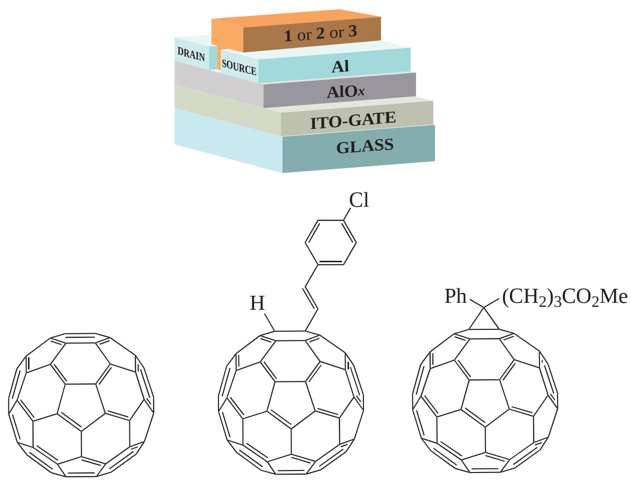
Keywords: [60]fullerene, styryl fullerene, PCBM, organic semiconductor, organic field-effect transistor, electron mobility.

Application of soluble organic compounds as semiconductors makes it possible to use inkjet printing technologies for the production of thin and flexible devices,[1,2] chemical sensors,[3] organic light-emitting diode (OLED) panels,[4] and data storage devices[5] and significantly reduces the production cost. Organic semiconductors are the main elements of electronic devices such as solar cells[6,7] and field-effect transistors.[8–10] Fullerene and its derivatives are basic materials in solar panels, thin-film organic transistors, and light-emitting diode (LED) displays.[11] Phenyl-C$_{61}$-butyric acid methyl ester (PCBM), which has enhanced acceptor properties compared to those of the original C$_{60}$, is an effective reference compound in current–voltage measurements.[12] The use of PCBM in solar cells with a hetero-volume junction orders the electron-donating polymer, which reduces the loss of open-circuit voltage energy[13] and makes these devices record-stable to radiation.[14] The power conversion efficiency (PCE) of single-junction and bulk-heterojunction (BHJ) organic solar cells based on PCBM and poly(3-hexylthiophene-2,5-diyl) (P3HT) is ~10%, while the PCE of tandem solar cells is close to 15%.[11] This system consisting of P3HT and PCBM is actively used not only in solar batteries but also in organic ambipolar field-effect transistors because the P3HT electron-donor polymer exhibits high hole mobility, and PCBM is characterized by high electron mobility.[15] The modification of donor polymers is a complex and time-consuming task, and the efficiency of energy conversion in solar batteries can be enhanced by increasing the energy of the lowest unoccupied molecular orbital (LUMO) of an acceptor fullerene derivative.[16] This can be achieved, first, by modifying PCBM by varying the length of an alkyl fragment in the original molecule, removing the carboxyl group from the cyclopropane fragment,[17] modifying the terminal ether group,[18] replacing the phenyl fragment with other aromatic substituents,[19] and using higher fullerenes (C$_{70}$, C$_{84}$, *etc.*) instead of C$_{60}$[20] or by attaching more than one fragment to the fullerene framework to form bis- and tris-adducts.[21,22]

Since most of the compounds used in organic electronics are conjugated aromatic molecules, we suggested that the introduction of C$_{60}$ fullerene derivatives linked to aromatic substituents through multiple unsaturated bonds can afford potential acceptor materials superior to PCBM in efficiency. Recently,[23] we developed the synthesis of styryl fullerenes by reacting C$_{60}$ with aromatic terminal acetylenes in the presence of EtMgBr and Ti(OPr^i)$_4$. Electrochemical studies revealed that the styryl fullerenes exhibited LUMO energy that is reasonably matched with PCBM.

As a continuation, we developed organic field-effect transistors (OFET) with unmodified fullerene C$_{60}$ **1**, styryl fullerene **2**, and reference PCBM **3** as organic semiconductors (Figure 1) and compared their physicochemical properties.

At the first stage, we developed an OFET with a transport layer containing a semiconductor material (C$_{60}$, styryl fullerene, or PCBM), which was vacuum deposited on a glass substrate containing indium tin oxide (ITO) layers (gate), 400 nm thick AlO$_x$ acting as a gate dielectric, two aluminum electrodes, a



1 (fullerene C$_{60}$) **2** (styryl fullerene) **3** (PCBM)

Figure 1 Structures of the experimental field-effect transistors and semiconductor layers based on fullerenes **1**–**3**.

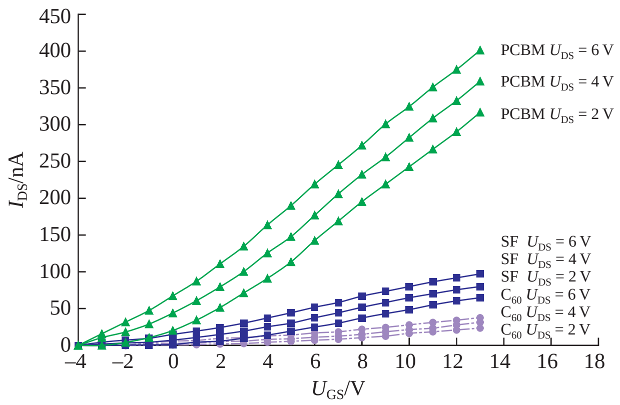


Figure 2 Transfer properties of a field-effect transistor with a conductive layer of C_{60}, styryl fullerene (SF), and PCBM.

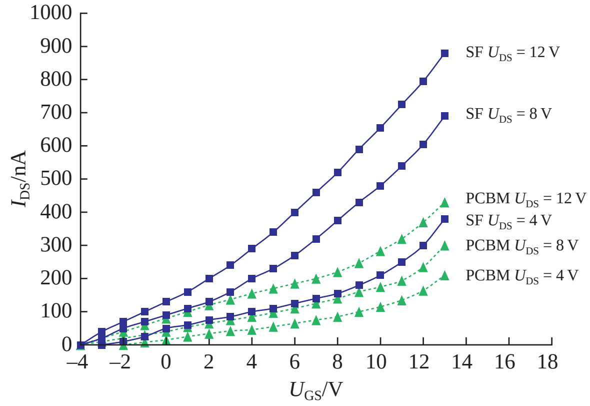


Figure 4 Transfer properties of a field-effect transistor with a conducting layer of styryl fullerene (SF) and PCBM prepared by the wet method.

drain, and a 500 nm thick source. The temperature regime of evaporation was maintained in such a way that the thermal destruction of PCBM did not occur.[24–26] The gap between the drain and source contacts was 50 μm, and the gap width was 4 mm. The thickness of the semiconductor material was ~150 nm.

Figures 2 and 3 show the transfer and output properties of the transistors prepared by a dry method (vacuum deposition of organic semiconductor materials).

A positive gate voltage increased the currents of all the three types of transistors; this behaviour corresponds to the electronic conductivity type of the OFET transport channel. Moreover, the resulting dependences are nonlinear. The absence of saturation sections from the output characteristics of the devices (see Figure 3) can be due to the presence of leakage currents.

A transistor with a semiconductor layer based on unmodified C_{60} fullerene was characterized by the smallest currents of 40 nA. The best results were achieved for a device with an n-type semiconductor layer based on PCBM: the output currents were higher than the currents of transistors based on styryl fullerene and unmodified fullerene by factors of 3 and 9, respectively.

The mobility μ of charge carriers in the active layer of OFETs was calculated by the equation

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

where W is the channel width, L is the channel length, C is the capacitance per square area of the AlO_x gate insulator (for a thickness of 400 nm, C = 8.9 nF cm^{-2}), V_G is the gate voltage, V_{DS} is the voltage between the drain and source, and V_{th} is the threshold voltage.

The calculated carrier mobilities were 0.002, 0.017 and 0.070 cm^2 V^{-1} s^{-1} for n-semiconductor structures based on unmodified C_{60} fullerene, styryl fullerene, and PCBM, respectively. These values are comparable with published data[27,28] for fullerene-based transistors. Since the carrier mobility depends on the ordering of film molecules on the surface,[29] we studied the morphology of the films formed by vacuum deposition of PCBM and styryl fullerene on a glass substrate in order to find reasons for such a strong difference between the output and transfer characteristics of the devices (Figure S1). The surface of the films was analyzed on a scanning probe microscope in the atomic force microscopy mode.

The size of deposited particles in the film formed by the deposition of PCBM was significantly smaller than that in the styryl fullerene film (see Figure S1). This can result from styryl fullerene polymerization under vacuum deposition at high temperatures. In this case, PCBM films were characterized by a lower roughness. Thus, we prepared PCBM and styryl fullerene films using a wet (spin-coating) method (Figure S2).

Indeed, the wet method in the case of styryl fullerene afforded the formation of a film with smaller particles compared to those under vacuum deposition. The PCBM films made from a solution by centrifugation were significantly inferior to the PCBM film obtained by the dry method. Furthermore, the roughness of the PCBM and styryl fullerene films prepared by the wet method significantly exceeded that of similar films formed under vacuum deposition (Figure S3). The atomic force microscopic analysis of the film surfaces showed that transport layers of high carrier mobility had lower surface roughness in the cases of both vacuum deposition and centrifugation.

Next, we studied the influence of the wet method for producing films based on PCBM and styryl fullerene on the output and transfer properties of organic field-effect transistors. Figures 4 and 5 show that the output and transfer properties of the devices with styryl fullerene increased by a factor of 2.5 as a result of applying

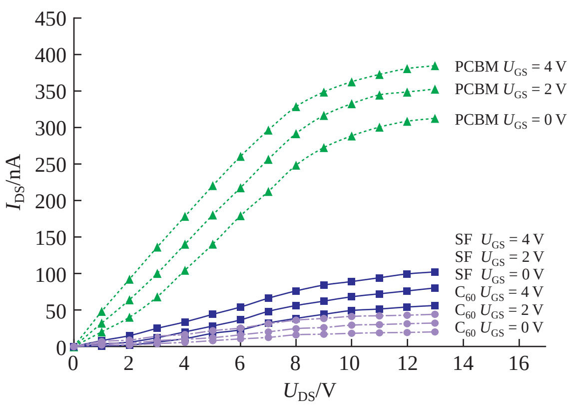


Figure 3 Output properties of a field-effect transistor with a conductive layer of C_{60}, styryl fullerene (SF), and PCBM.

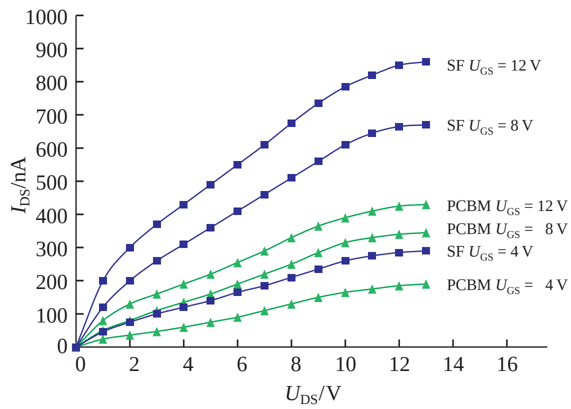


Figure 5 Output properties of a field-effect transistor with a conductive layer of styryl fullerene (SF) and PCBM prepared by the wet method.

Table 1 Calculated carrier mobilities ($cm^2\ V^{-1}\ s^{-1}$) of field-effect transistor with a conductive layer of C_{60}, PCBM, and styryl fullerene.

Compound	Vacuum deposition	Spin coating
[60]Fullerene **1**	0.002	–
Styryl fullerene **2**	0.017	0.035
PCBM **3**	0.070	0.021

gentle manufacturing conditions, and the mobility of charge carriers increased by an order of magnitude (Table 1).

Based on the given values of the mobility of charge carriers, the maximum switching frequency for the developed transistor structures can be calculated from the equation[30]

$$f = \mu V_{DS}/(2\pi L^2), \quad (2)$$

where L is the transport channel length, V_{DS} is the drain–source voltage, and μ is the carrier mobility.

The values of 432 and 1.7 kHz were obtained for styryl fullerene and PCBM, respectively, prepared by the dry method. In the case of the wet method, the switching frequencies of 891 and 534 Hz were found for the transistors based on styryl fullerene and PCBM, respectively. Note that these values are not very large resulting from a large transport channel length of 50 μm. According to equation (2), a 100-fold decrease in this parameter increases the switching frequency by four orders of magnitude.

Thus, we developed an innovative organic field-effect transistor containing styryl fullerene as a semiconductor layer and compared its performance with that of the transistors based on unmodified fullerene C_{60} and PCBM.

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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.2021.09.016.

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