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Electron-hole mobility in 6,12-di(2-thienyl)indolo[3,2-*b*]carbazoles

Artem V. Dmitriev,[a] Azat R. Yusupov,[a] Roman A. Irgashev,[b,c] Nikita A. Kazin,[b] Eugene I. Mal'tsev,*[a] Dmitry A. Lypenko,[a] Gennady L. Rusinov,[b,c] Anatoly V. Vannikov[a] and Valery N. Charushin[b,c]

[a] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation. Fax: +7 495 955 4032; e-mail: eugenemalt@rambler.ru*
[b] *I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 620041 Ekaterinburg, Russian Federation*
[c] *Ural Federal University, 620002 Ekaterinburg, Russian Federation*

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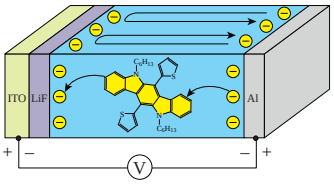
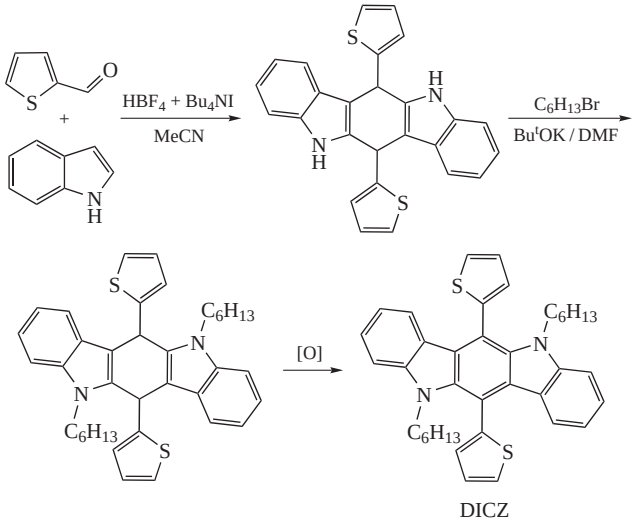
Study of electron and hole mobility for 5,11-dihexyl-6,12-di-(2-thienyl)indolo[3,2-*b*]carbazoles has shown that their hetero-aromatic cores act as electron transport centers.



The search for new organic semiconductor materials for creation of thin-film transistors (TFT), solar energy converters (SEC), light-emitting diodes (OLED), *etc*. is topical.[1] The mobility of charge carriers is the most important characteristic of such materials. The recently synthesized derivatives of 5,11-dihydroindolo-[3,2-*b*]carbazole (indolo[3,2-*b*]carbazoles, ICs) are regarded as one of the promising types of semiconducting compounds.[2–9] By now the information is available on hole mobility in ICs.[4] However, all the measurements were made not with the diode geometry structures but in field-effect transistor (FET) ones. The values obtained by these two methods can differ in orders of magnitude. Therefore, the information on FET mobilities is improper for understanding the performance of OLED- and SEC-structures. The time-of-flight (TOF) method has been used only once to measure the hole mobility in ICs based diode structures[7] providing contradictory data ranging from 4×10^{-6} to 4×10^{-5} cm^2 V^{-1} s^{-1}. The electron mobility therewith could not be determined at all because the electron transient photocurrent signals proved to be too weak.[7] In the present work, we were able to determine electron mobility in ICs for the first time using the method of charge extraction by linearly increasing voltage (CELIV) in metal–insulator–semiconductor (MIS) layered samples.[10,11] It enables to study the electron-hole transport in very thin organic layers in diode configuration samples, including opaque materials.

We used 5,11-dihexyl-6,12-di(2-thienyl)-5,11-dihydroindolo-[3,2-*b*]carbazole (DICZ) as a model compound. It was synthesized using the general procedure described previously[12] (Scheme 1). To establish the nature of the transport centers, we have deliberately introduced two different substituents such as 2-thienyl and *n*-hexyl into the heteroaromatic core of the DICZ molecule. It is well known that thiophene moieties are solely hole transporting centers,[13] whereas aliphatic *n*-hexyl groups participate neither in electron, nor in hole conductivity. DICZ has E_{HOMO} and E_{LUMO} values of –4.9 and –2.05 eV, respectively.

The extraction current transients were studied in the following two structures fabricated in a vacuum chamber (10^{-6} mbar) for electron-only (structure 1) and hole-only (structure 2) mobility



Scheme 1

measurements: glass/ITO/LiF(20 nm)/DICZ(100 nm)/Al (structure 1), glass/ITO/DICZ(100 nm)/LiF(20 nm)/Al (structure 2).

At applying a forward bias voltage to structure 1, the electrons injected from the Al cathode drifted across the DICZ layer and accumulated at the LiF/DICZ interface. In structure 2, conversely, holes were injected into the DICZ layer from the ITO electrode, drifted across DICZ layer and accumulated at the DICZ/LiF interface. The mobility of electrons and holes was further determined due to a procedure of their subsequent extraction under a linearly increasing reverse bias voltage. Transient currents for these two structures are shown in Figure 1.

The charge carrier mobility μ is given by equation

$$\mu = \frac{2d_s^2}{At_{tr}^2}\left(1+\frac{\varepsilon_s d_i}{\varepsilon_i d_s}\right), \quad (1)$$

where $t_{tr} = ct_{2j0}$ is the carrier transit time to opposite electrode ($c = 4/\pi$ is a parameter that considered the charge carrier diffusion in the material under study), d_s is the thickness of the DICZ layer,

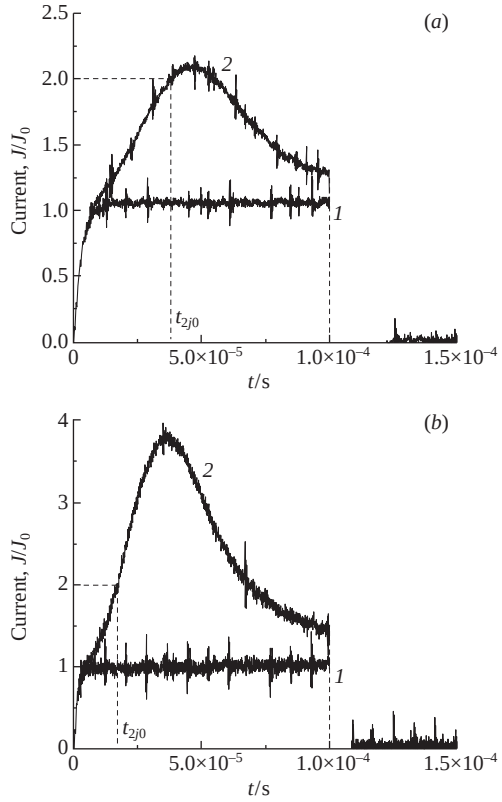


Figure 1 Extraction current transients for determining (*a*) electron and (*b*) hole mobility in multilayered diode structures 1 and 2, respectively. (*1*) Bias voltage is off and (*2*) on.

d_i is the thickness of the LiF layer, ε_s and ε_i are dielectric constants of the semiconductor and insulator, respectively (since we did not determine the value of ε_s, it was assumed that $\varepsilon_s/\varepsilon_i \approx 1$), A is the rate of voltage increase. The obtained results (Table 1) show that the respective hole and electron mobility values are 2.55×10^{-5} and 5.21×10^{-6} cm^2 V^{-1} s^{-1}, respectively.

The results provide convincing evidence that the indolo[3,2-*b*]-carbazoles are not only hole conducting, but also efficient electron conducting materials, although their hole mobility is higher by a factor of five. Considering the molecular structure of DICZ and transport properties of the substituents, one can conclude that the electron transport center in the molecule is a polycyclic aromatic core. Apparently, this conclusion is valid for all other representatives of this type of compounds.

Table 1 Electron and hole transport characteristics of DICZ layers.

Structure	t_{tr}/s	A/V s^{-1}	μ/cm^2 V^{-1} s^{-1}
Structure 1 (electrons)	4.8×10^{-5}	20000	5.21×10^{-6}
Structure 2 (holes)	2.17×10^{-5}	20000	2.55×10^{-5}

Thus, we measured the carrier mobility in newly synthesized substituted indolo[3,2-*b*]carbazoles for samples having a diode configuration. It has been shown that the electron conductivity in DICZ is accounted for by the presence of a polycyclic aromatic core in its molecule.

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