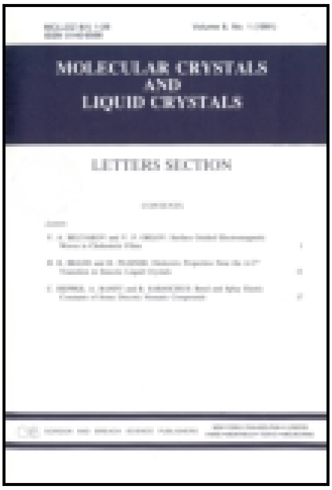

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Electro-Acoustic Effect in Organic Structure Based on Star-Shaped Carbazole Derivatives

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We have found that the structures based on ITO/tri(9-hexylcarbazol-3-yl)amine/Ca/Al fabricated by means of vacuum deposition generate acoustic oscillations when pulse voltage is applied. Impedance spectroscopy study indicates the presence of significant inductive response, which is the result of significant energy barriers at the semiconductor-metal interface. We assume that a very heterogeneous spatial distribution of the electric field at the organic/metal interface and the noncoplanarity of the molecules cause the electrostriction effect in the structures.

Keywords Electromechanical transducers; electrostriction effect; inductive response

Introduction

Progress of organic electronics is directly related to the search for new highly functional organic materials and to the development of new generation devices based on these new organic materials [1]. Along widely investigated devices such as organic electroluminescent diodes (OLED) [2], organic field effect transistors (OFET) [3] and organic solar cells [4], the research of electromechanical transducers, actuators based on organic materials [5] is also carried out. These devices can be integrated into optoelectronics and integrated circuits. It is shown that certain organic semiconductor materials can have different functional applications, e.g., P3HT can be used as light emitting active material and nanoscale electromechanical transducer [5]. An increase in the realization of such systems is due to the growing interest in nanoactuators in electronics and biomedicine [6].

In the process of establishing the optimum pulse power supply in the OLEDs based on star-shaped carbazole derivatives (THCA) [7] (Fig. 1), in order to slow the process of device aging in the operation we discovered the electroacoustic response. Obviously, the acoustic response is due to the modulation of the geometrical dimensions of the structure, but the nature of this modulation can vary [8]. To determine the nature of the electromechanical response high-precision interferometric optical methods are usually used [5].

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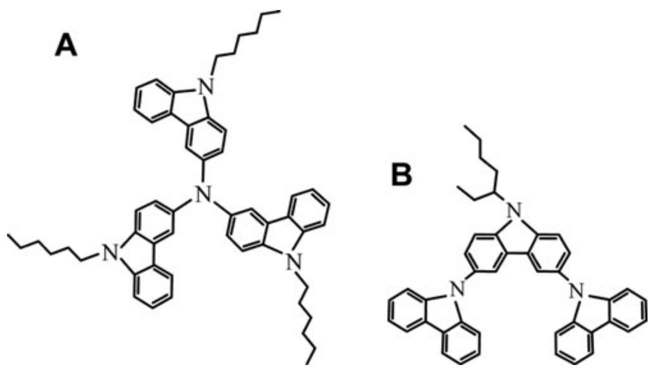

Figure 1. Chemical formulas of THCA (a) and TCz1 (b).

In this paper we propose a new approach for the study of nature of electromechanical response of electro-organic structures based on the developed acousto-electric registration system and impedance spectroscopy method.

Experimental Details

Materials

As basic organic semiconductor materials we used hole-transporting star-shaped carbazole derivative tri(9-hexylcarbazol-3-yl)amine (THCA) (Fig. 1a) and electron-transporting compound 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole (TCz1) (Fig. 1b) that were recently successfully used as for efficient blue and white OLEDs [7, 9].

Device Fabrication

Devices were fabricated by means of vacuum deposition of organic semiconductor (Fig. 2) layers and metal electrodes onto ITO coated glass substrate under vacuum of 10^{-5} Torr. The structures of the devices were as follows:

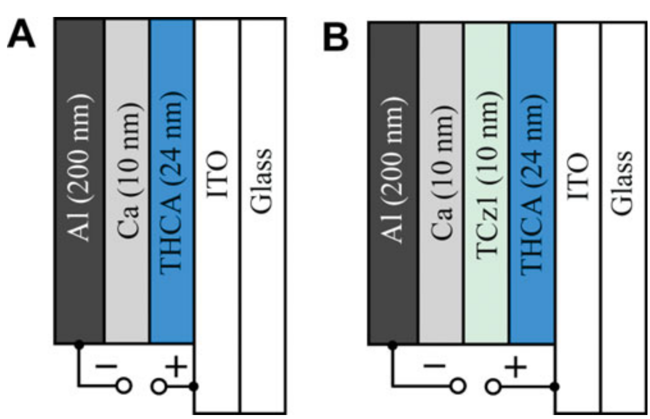

Figure 2. Schematic representation of devices A (a) and B (b).

A) ITO/THCA(50 nm)/Ca(10 nm)/Al(200 nm)
B) ITO/THCA(50 nm)/TCz1(10nm)/Ca(10 nm)/Al(200 nm)

The layer of TCz1 was used as electron transporting layer in the device B [10]. Devices A and B were fabricated by step-by-step deposition of the different organic layers. On the top of the structure the Ca/Al electrode was deposited (Fig. 2). The deposition rate was 1 nm/s. Since Ca is highly reactive and corrodes quickly in the ambient atmosphere, Ca layer topped with 200 nm aluminum (Al) layer was used as the cathode. The thickness of the obtained films was estimated by Mikropack Nanocalc 2000 reflectometer. The active area of the obtained device was 3×6 mm^2.

Characterization of the Devices

Impedance spectroscopy was used for the investigation of bulk and interface parameters of the fabricated devices. The impedance measurements were done in the frequency range of 10–10^6 Hz at constant bias voltages of 0, 1.0, 3.0 V, using instrument "AUTOLAB" (Eco Chemie, the Netherlands) with FRA-2 and GPES software. Frequency dependencies of complex resistivity Z were analyzed by graphic-analytical method using ZView 2.3 (Scribner Associates) software. The approximation inaccuracy did not exceed 6%.

In the study of electroacoustic response we used oscillator of U-shaped signals with frequency of 2 kHz and pulse duration of 0.3 ms. The registration of acoustic signals, generated by device A, was carried out by developed electromechanical acoustic system (Fig. 3). This system is realized on the base of low-noise, high-speed operational amplifier TI (Texas Instruments) RC4558. The application of this microcircuit allows using source voltage of 5 V from USB port. Registration of acoustic vibrations is conducted through electret microphone, operating current on microphone is set by resistor R1. The generated electrical signal through a capacitor C1 goes to inverting input of operational amplifier. Resistor R3 is included in the feedback circuits and it sets the required gain (amplification factor). The operation point of the op-amp is set by resistive divider R2 R4. Amplified signal through capacitor C4 goes to the audio input of the personal computer, which performs its registration and further processing using Spectrum Analysis software.

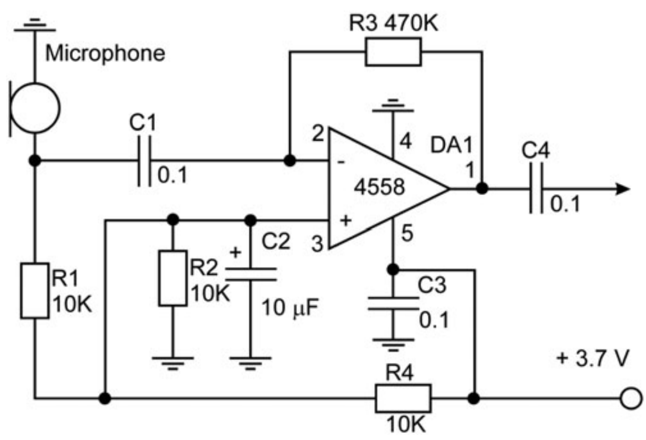

Figure 3. Developed high sensitive electro-mechanical acoustic system.

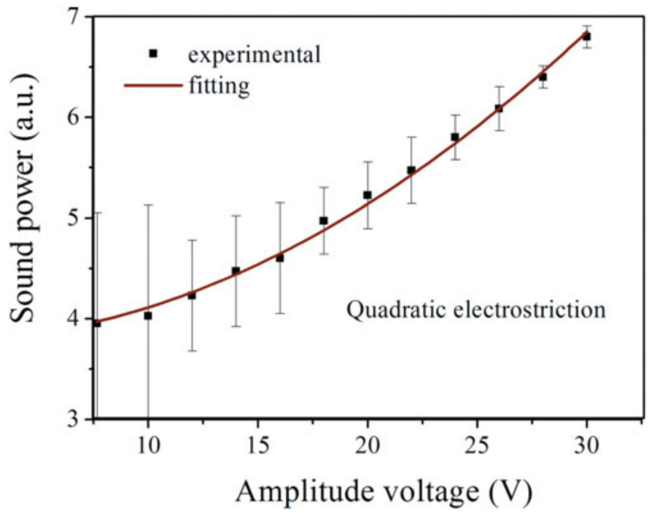

Figure 4. Sound power recorded using developed electro-mechanical acoustic system on a device A for forward applied voltages.

It should be noted that the proposed method does not provide quantitative information on the magnitude of the modulation bias, but only the change of the acoustic signal amplitude.

Results and Discussion

The plot of amplitude of acoustic wave (I_{ac}) versus the amplitude of the applied voltage (V_{app}) of rectangular pulse shows power law dependence $I_{ac} \sim V_{app}^2$ (Fig. 4). This pattern of dependency is referred to quadratic electrostriction [11], that is usually observed in dielectric materials, when the voltage V is applied, and leads to the changes of sample dimension.

We believe that in this case the appearance of electrostriction effect is due to several reasons. It was shown that star-shaped molecules with three sidearms owing to the non-coplanarity can be viewed as 3D systems which provide interesting electrical, optical, and morphological properties [7, 12].

It is well-known that such materials provide easily electromechanical effects due to their softness [13]. The heterogeneity of the electric field on the THCA/Ca interface, which is associated with the presence of a significant energy barrier of 0.65 eV for injection of electrons from Ca into LUMO level of THCA (Fig. 5a), leads to the spatial distribution of the carriers at the interface. It should be noted that at the construction of the energy band structure diagram (Fig. 5) we have taken into account the condition of vacuum leveling at the interface, which ideally should be subject to the rules of classical Mott-Schottky rules for weakly interacting interfaces [14].

To determine the actual vacuum level shift and modification of energy barriers at the interface there is a need for experimental studies, e.g. by ultraviolet photoelectron spectroscopy [14].

To test the hypothesis of the impact of the energy barrier value on the presence of the effect of electrostriction, we formed structure B, where electron-transport layer TCz1 was

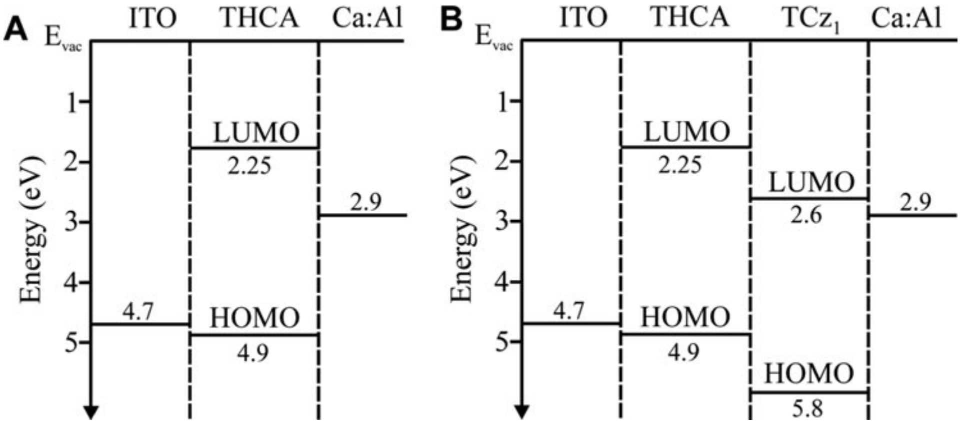

Figure 5. Energy-band diagram of the A (a) and B (b) devices [7, 9].

icorporated to lower the potential barrier for electrons (Fig. 5b). Functional characteristic feature of this structure is the absence of electrostriction when U-shaped signals are applied.

The more detailed analysis of the behavior of the developed structures in alternating current can be obtained from the impedance spectroscopy data [15].

The impedance characteristics of devices A and B and electrical equivalent circuit and calculated parameters for the devices are shown on Fig. 6 and Table 1. The Nyquist diagrams and equivalent circuit for the device B (Fig. 6c, e), that consist of a series connection of two serial RC circuits (Fig. 6e), is characteristic of most light-emitting and photovoltaic structures based on organic heterostructures and of Schottky diodes [16].

However, on the Nyquist diagrams for the device A, at the higher voltage (3 V) greater than the threshold voltage (Fig. 6a), in the fourth quadrant of the complex impedance plane inductive response was observed (Fig. 6b) and the equivalent circuit of such structures

Table 1. Calculated parameters of equivalent circuits shown in Fig. 6a and c.

	Applied bias		
Elements	0V	1V	3V
	Device A (Fig. 6a)		
R1 [Ω]	112.7	105.3	102.9
C1 [nF]	0.18	0.35	0.4
R2 [Ω]	1080	599.1	365.5
C2 [nF]	2.1	2.02	1.9
L1 [H]	—	—	30.82
R3 [Ω]	—	—	14039
	Device B (Fig. 6c)		
R1 [Ω]	193.6	197.8	95.96
C1 [F]	$6.1241 \cdot 10^{-11}$	$9.2425 \cdot 10^{-11}$	$4.9669 \cdot 10^{-8}$
R2 [Ω]	$1.008 \cdot 10^{5}$	20245	197.8
C2 [F]	$1.0129 \cdot 10^{-8}$	$1.0841 \cdot 10^{-8}$	$6.2801 \cdot 10^{-11}$

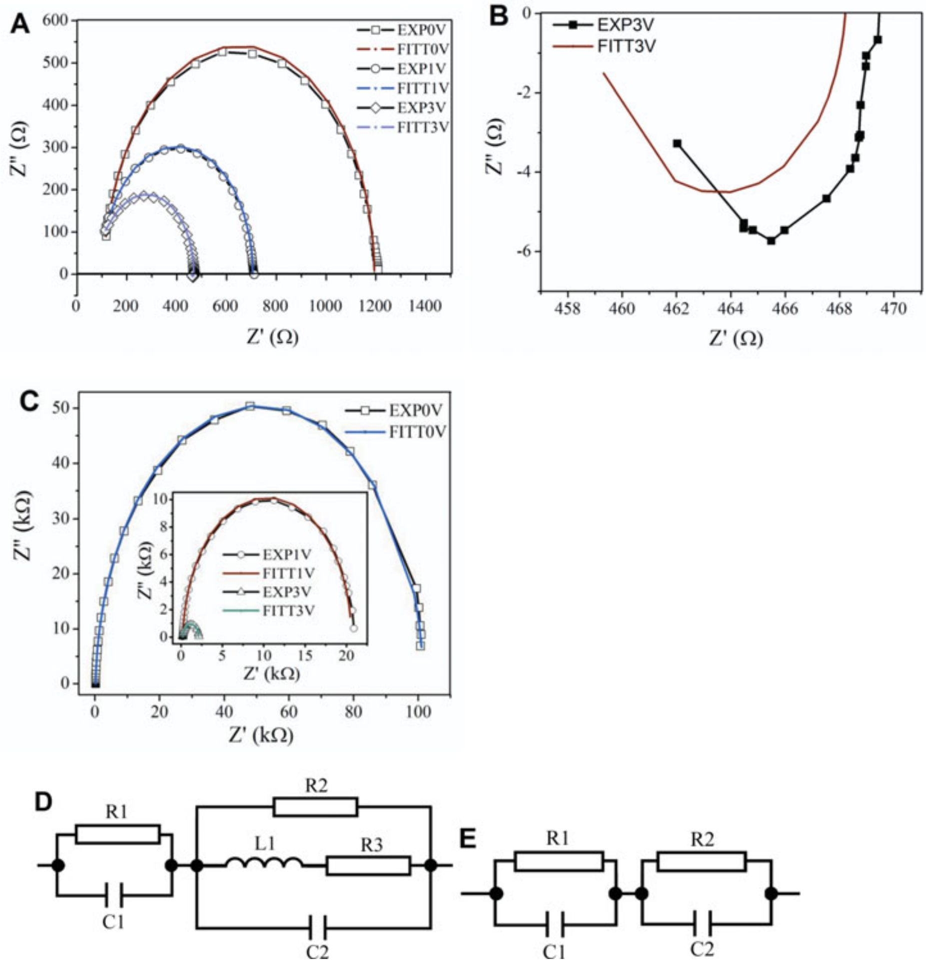

Figure 6. Impedance spectra of device A (a, b) and B (c), and corresponding equivalent circuits (d) and (e).

transforms into the form shown in (Fig. 6d). The appearance of an inductive response in our case probably is the result of significant energy barriers at interfaces, giving rise to the capture of charges at the interface THCA/Ca (Fig. 5a) that leads to the accumulation of carriers at the interface. As results the time dependent recombination current leads to a negative contribution to the low frequency capacitance [17]. A higher total resistance of device B in comparison with device A is due to the resistance of the additional organic layer TCz1.

However, it should be noted that the presence of an inductive response is a necessary but not sufficient condition for the appearance of electromechanical responses in the structure [18]. Better understanding of the nature of occurrence of such an effect in organic structures requires further research.

Conclusions

We have found acoustic oscillations generated by organic structure ITO/THCA/Ca/Al based on low-molecular-weight organic semiconductor under applied pulse voltage. We have shown that such acoustic oscillations are due to electrostrictive responses of the structure where the electric stimulus is provided by an applied voltage. The nature of such effect can be explained by the non-uniform spatial electric field distribution across the sample. Investigation of interface properties of the structure by methods of impedance spectroscopy showed the presence of an inductive response, which is probably the result of significant energy barriers at interfaces, giving rise to the capture of charges at the interface THCA/Ca. It is shown that the introduction of the electron-transporting layer (TCz1) at the interface THCA/Ca leads to the decrease of the potential barrier between the metal and the organic semiconductor, to the disappearance of the induction response and of electromechanical response of the structure. We have shown the way to overcome the “negative electroacoustic effect” in terms of the practical use of organic structures in display technology. However this effect may be useful in design of nanoactuators, microphones, etc.

Acknowledgments

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