

# Growth of conjugated semiconductor monocrystals based on benzothienobenzothiophenes from solutions

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**Abstract.** Organic semiconductors are actively used for numerous applications, their use in flexible electronics technologies is especially promising. The mobility of current carriers is a determining parameter whose value is strongly influenced by the crystallinity and arrangement of molecules in the crystal lattice of the synthesized semiconductor materials. The goal of this work was to obtain thin monocrystal films of conjugated oligothiophene-phenylenes (OTP) structures from solutions and their characterization. In this work, the solvent vapor annealing method was adapted to obtain conjugated structures based on dihexyl- and dioctylbenzothienobenzothiophene (C6-BTBT and C8-BTBT) from dichlorobenzene and toluene solutions with a concentration of 0.06 to 0.80 g / l. Solutions of various concentrations were applied to silicon substrates by centrifugation and droplet method. According to microscopic studies, C8-BTBT single crystals of the required geometry and size of about 1 mm were grown from solutions in toluene with a concentration of less than 0.06 g / l by centrifugation at a speed of 800 rpm. Electrophysical measurements showed that the obtained crystals have hole conductivity with a fairly high carrier mobility up to  $0.047 \text{ cm}^2 / \text{V} \cdot \text{s}$  (average  $0.03 \text{ cm}^2 / \text{V} \cdot \text{s}$ ), which makes it possible to use these materials for the manufacture of field effect transistors and other electronic devices based on them.

## 1. Introduction

Electronic devices based on organic crystals cause a need for developing simple methods for applying organic compounds to various very cheap substrates: glass, polymers, metal foil, etc. Very bright and colorful thin displays based on organic light emitting devices (OLEDs) are already in commercial production [1, 2]. Significant progress has been made also in the production of thin-film transistors [3] (OTT) and thin-film organic photocells [4, 5] for the cheap production of solar energy. Despite this, the final implementation of such technologies is not so much in the reliability and performance of organic components, which in some cases have already approached or even exceeded the requirements of a particular application, but rather in the possibility of manufacturing the product at a very low price [6]. Although the cost of organic materials used in most thin-film devices is low, the successful use of this group of materials will depend on the efficiency of using their low cost in the manufacture of devices on inexpensive substrates with a large area [7].

The contemporary approach is not to completely replace existing application niches with organic semiconductors, but to effectively use the inexpensive and unique technological capabilities inherent in organic systems that are not available in inorganic materials. The success of creating very cheap electronics is almost entirely dependent on the ability to produce organic electronic devices using methods that differ from the labor-intensive and expensive methods commonly used in today's high-



performance electronics industry. Thus, a large number of modern studies are focused on obtaining films of a large area with the necessary parameters, excluding traditional labor-intensive methods, such as photolithography.

The structural features of organic semiconductor materials open up the possibility of their use for flexible electronics. In addition, the nature of the materials allows them to be applied by inkjet printing or by methods of applying from solutions [8, 9], which is not only convenient for large-scale implementation, but also inexpensive and distinguishes these materials from inorganic semiconductors. Certain technological advantages, as well as unique electronic and optical properties, open up obvious prospects for the production of inexpensive and reliable devices based on them that can fill the niches occupied by silicon-based electronics.

Conjugated oligomers can serve as the basis for the creation of semiconductor organic crystals. Lamellar crystals are obtained from such materials [10]. During crystallization,  $\pi$ -orbitals overlap between co-oligomer molecules, which ensures high carrier mobility. Active crystalline layers of conjugated structures obtained using solution and vapor-phase methods will greatly simplify and reduce the cost of manufacturing devices based on them [8, 9].

The goal of this work was to obtain thin monocrystal films of conjugated oligothiophene-phenylenes (OTP) structures from solutions and their characterization.

## 2. Formulation of the problem

Semiconductor molecular single crystals are the most promising material for organic electronics due to their high ordering and low number of defects. The best charge mobilities in organic field effect transistors (OPTs) were obtained precisely on single crystals and exceed the mobilities in inorganic transistors on amorphous active layers [11]. Organic crystals are associates of molecules connected by relatively weak intermolecular bonds (Van-der-Waals,  $\pi$ - $\pi$ , etc.), in contrast to inorganic crystals, the structure of which is based on much stronger covalent bonds. Also, specifically directed atom – atom contacts, for example, hydrogen bonds, play a special role in an organic crystal [12].

The optoelectronic characteristics of the final device also strongly depend on the chemical structure of the oligomer. Thiophene-based materials are used to develop effective OPT, while compounds containing phenyl groups are used to create light-emitting devices. The C6-BTBT and C8-BTBT studied in the research belong to the class of oligothiophene-phenylenes (OTP) and are promising organic materials whose crystals allow combining high charge mobility with effective electroluminescence [13]. Their molecules consist of a thiophene-phenylene core with terminal hexyl and octyl substituents. The conjugated molecular structures of these oligomers impart rigidity to the molecules, so that they can be considered as stiff rods. The molecular packing of oligothiophene-phenylenes is called “Christmas tree” and provides dense packing of molecules with overlapping  $\pi$ -orbitals, which is a decisive factor for the efficiency of OPTs based on such crystals [14]. Varying the terminal substituents of OTP affects the solubility and degree of ordering of OTP molecules. As a rule, the low mobility of carriers observed in synthesized films is caused by their polycrystalline nature [15].

One of the promising methods for the growth of single-crystal structures is the annealing method in solvent vapor. This method was first published in 2013 and was presented for the case of a cyanine dye that does not have semiconductor properties [14]. In the above work, a solution of the compound was applied by centrifugation (spincoating) on a substrate, with or without hydrophobic patterns. The substrate was then placed in a closed atmosphere, where molecules were reorganized in solvent vapor to achieve a more energetically favorable configuration. The growth result was single crystals with lateral sizes up to 40  $\mu\text{m}$  and a thickness of 100 to 1000 nm. The adaptation of this method to obtain C6-BTBT and C8-BTBT single crystals on substrates will simplify the process of creating devices

based on them, and an increase in single-crystal regions will ensure the achievement of better electrical characteristics.

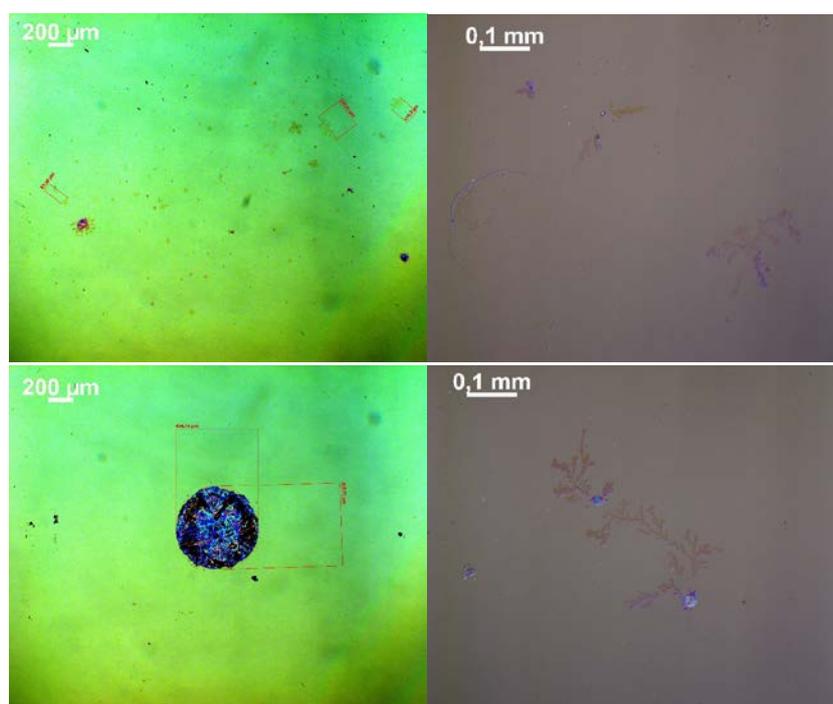
### 3. Experimental

Thin-film samples of organic semiconductors were obtained from solutions by annealing in solvent vapors, which was first described in [14]. In the work, the method was adapted for the studied organic materials. Solutions of C6-BTBT and C8-BTBT in toluene and dichlorobenzene with concentrations from 0.03 g / l to 0.8 g / l were used to obtain single-crystal films. For uniform application of solutions, spincoating and drop casting of solutions on a silicon substrate were used.

Preparation of solutions, preparation of substrates, modes and methods of applying solutions to substrates, characterization of the obtained samples by microscopy and their electrophysical studies were carried out by standard methods [16].

### 4. Results and considerations

Microscopic studies showed that under annealing in a solvent, dichlorobenzene by the spincoating method in the case of substrate rotation speeds of 400 rpm and 800 rpm in the entire concentration range of C8-BTBT oligomer solutions grow thin-layer dendrites. In the case of C6-BTBT under the same conditions, thick concentric single crystals were obtained whose size correlates with the concentration of the oligomer solution (Fig. 1). The observed absence of a crystalline structure in the C8-BTBT oligomer samples is explained by the polarity of the dichlorobenzene selected as a solvent.

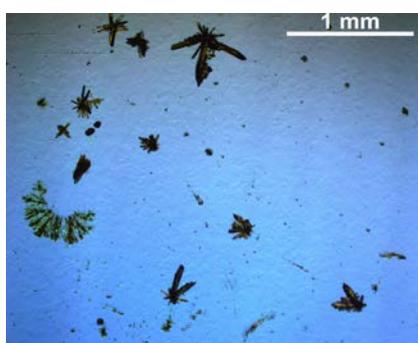


**Figure 1.** The results of the single crystals C6-BTBT growth (left) and C8-BTBT (right) from solutions in dichlorobenzene with an oligomer concentration of 0.12 g / l (top) and 0.25 g / l (bottom), deposited by centrifugation with a substrate rotation speed of 800 rpm.

The polarity of this solvent provides poorer solubility of the C8-BTBT oligomer compared to the C6-BTBT, which is caused by the longer length of the octyl terminal substituents. This fact prevents the ordered arrangement of molecules and leads to the growth of dendrites from solutions of the C8-

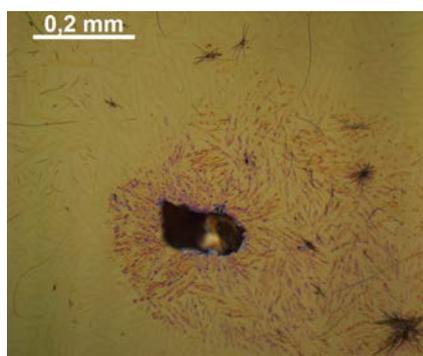
BTBT oligomer in dichlorobenzene. The shorter length of hexyl radicals contributes to their better dissolution compared to octyl- radicals and does not cause steric difficulties in ordering molecules, which leads to the growth of crystal structures from solutions of C6-BTBT in dichlorobenzene under the same conditions.

Using the “drop casting” method from solutions in dichlorobenzene, star-formed crystals with value of the order of 1 mm are obtained, and the size and shape of the crystals are practically independent of the concentration of the oligomer solution (Fig. 2). This method of applying a solution is characterized by a decrease in the time of evaporation of the solvent, which as a result does not allow oligomer molecules to create dense regular packing and does not lead to directed growth of single crystals. As a result, by a drop method of applying a solution to a substrate, single crystals with the required lateral sizes were not to obtain.



**Figure 2.** C8-BTBT single crystals grown from solutions in dichlorobenzene deposited by the drop casting method

Monocrystal structures of C8-BTBT with the required geometric parameters were obtained from oligomer solutions in toluene by centrifugation at a speed of 800 rpm from solutions with a low oligomer concentration of 0.03 to 0.06 g / l (Fig. 3). The solubility in nonpolar toluene increases as the terminal groups of the oligomers elongate, which leads to an increase in the ordering of C8-BTBT molecules in solution and, as a result, to an orderly growth of crystals on the substrate.



**Figure 3.** C8-BTBT single crystals grown from oligomer solutions in toluene by centrifugation at a speed of 800 rpm from solutions with an oligomer concentration of 0.06 g / l.

As a result, C8-BTBT single crystals of the required geometry were obtained from oligomer solutions in toluene with a concentration below 0.06 g / l by centrifugation at a substrate rotation speed

of 800 rpm. For C6-BTBT, the best crystals were obtained from solutions in dichlorobenzene by centrifugation in the entire concentration range studied and for all substrate rotation speeds used in this work. Moreover, the obtained C6-BTBT crystals have a concentric shape and size, increasing with increasing concentration of the oligomer in the solution.

Toluene and dichlorobenzene are characterized by a slight difference in boiling points (110.6 and 131 °C, respectively); therefore, the evaporation rate of these solvents does not differ significantly. This fact lead to the conclusion that the evaporation rate of the solvent does not determine the geometry of the crystals synthesized in the work. Presumably, the geometry of the synthesized C6-BTBT and C8-BTBT crystals is affected by the polarity of the solvent used and the effect of increasing the solubility of oligomer molecules with an increase in the length of the terminal group of organic molecules, leading to an ordered distribution of oligomer molecules.

As a result of electrophysical studies [16], it was established that the obtained crystals have hole conductivity with a fairly high carrier mobility up to  $0.047 \text{ cm}^2 / \text{V} \cdot \text{s}$  (on average  $0.03 \text{ cm}^2 / \text{V} \cdot \text{s}$ ), which makes it possible to use these materials for the manufacture of field effect transistors and other electronic devices based on them.

A correlation between the nature of the solvent, the solubility of the oligothiophene-phenylenes molecules, related to the length of the terminal substituent, and the lateral parameters of single crystals were revealed. Further studies will allow us to establish patterns related to the nature of the solvent, the structure of the oligomer, and the parameters of the synthesized single-crystal structures, which will lead to the development of a method for selecting a solvent in accordance with the nature, composition and structure of organic semiconductors molecules and will provide a basis for developing a technology for producing organic semiconductors crystalline structures with specified properties.

## 5. Summary

As a result, the solvent vapor annealing method was adapted to obtain conjugated structures based on dihexyl- and dioctylbenzothienobenzothiophene (C6-BTBT and C8-BTBT) from dichlorobenzene and toluene solutions with a concentration of from 0.06 to 0.80 g / l. C8-BTBT monocrystals of the required geometry were obtained from oligomer solutions in toluene with a concentration from 0.03 to 0.06 g / l by centrifugation at a substrate rotation frequency of 800 rpm. For C6-BTBT, the best crystals were obtained from solutions in dichlorobenzene by centrifugation in the entire range of concentration and substrate rotation frequencies studied in this work.

The obtained crystals had hole conductivity with a fairly high carrier mobility up to  $0.047 \text{ cm}^2 / \text{V} \cdot \text{s}$  (average  $0.03 \text{ cm}^2 / \text{V} \cdot \text{s}$ ), which makes it possible to use these materials for the manufacture of field effect transistors and other electronic devices.

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