

C_{10} - and C_{12} -BTBT Single Crystalline Organic Field Effect Transistor

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Introduction:

An organic field-effect transistor (OFET) is the key component in realizing flexible organic electronics, and an OFET is cheaper and more energy-efficient for production than its inorganic counterpart [1]. In particular, single crystalline OFETs have been shown to exhibit higher carrier mobility than thin film OFETs made of polycrystalline or amorphous semiconductors [1].

Recently, materials based on a [1]benzothieno[3,2-*b*] [1]-benzothiophene (BTBT) core structure with 2,7-dialkyl derivatives (C_n -BTBT) have been found to be air-stable and solution-processible organic semiconductors [2]. C_8 -BTBT has been demonstrated to form single crystals of hundreds of microns in length on polymer dielectric surface [3]. Single-crystal C_8 -BTBT OFETs exhibit average mobility of $3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is higher than conventional thin-film OFETs and comparable to some inorganic FETs [1, 3]. Until this work, none of the other C_n -BTBT materials have been explored for single-crystal OFETs applications.

Here we report the fabrication and characterization of C_{10} -BTBT and C_{12} -BTBT single crystal OFETs.

Experimental Technique:

To fabricate single-crystal OFETs, we followed the procedures previously reported by Liu, et al. [3], which involved spin-coating, solvent vapor annealing (SVA) and thermal evaporation of metal electrodes.

Results and Discussion:

Figure 1 compares the crystal size of C_8 -BTBT, C_{10} -BTBT and C_{12} -BTBT. C_8 -BTBT crystals are typically several 100 microns long. On the other hand, a large crystal on a C_{10} -BTBT sample could be longer than $50 \mu\text{m}$, but shorter than $100 \mu\text{m}$. Most C_{12} -BTBT crystals do not exceed $50 \mu\text{m}$.

We suspect this is due to the different solubility of the three functional materials in chloroform. For solubility in chloroform, we have the following relationship: C_8 -BTBT > C_{10} -BTBT > C_{12} -BTBT.

Since C_8 -BTBT is most soluble, more C_8 -BTBT molecules become mobilized during SVA than C_{10} - and C_{12} -BTBT molecules. Therefore, C_8 -BTBT molecules form the largest crystal.

Large crystals are more desirable for OFET fabrication. Treossi, et al. have demonstrated that lowering the temperature of the samples with respect to that of the solvent by $1\sim 2^\circ\text{C}$ will increase the amount of vapor absorbed on the sample surface, which in turn enhances the molecules' functional long-range mobility [4]. Hence, larger crystals can be obtained.

We conducted two temperature-enhanced solvent vapor annealing (TESVA) experiments using C_{10} -BTBT molecules only. First, we put a glass of cool water on top of the sample during SVA. Since there was no external cooling device to

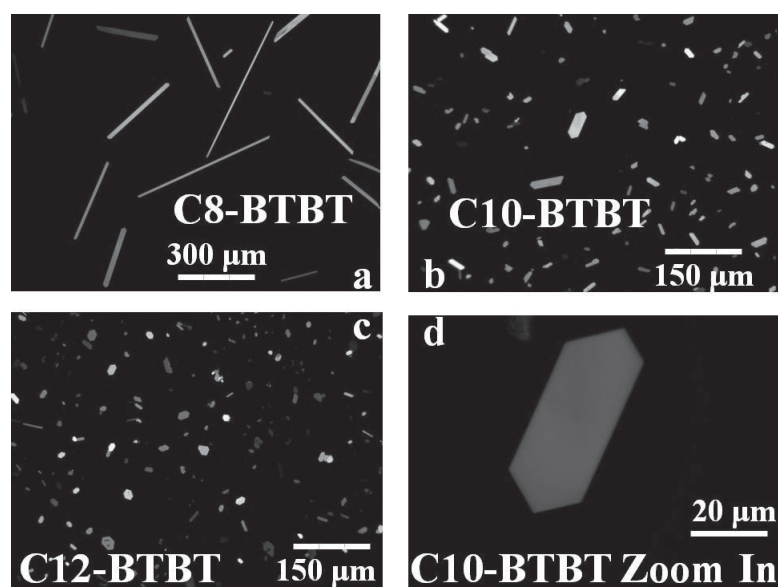


Figure 1: C_8 - (reproduced from Liu, et al. [3]), C_{10} - and C_{12} -BTBT crystals.

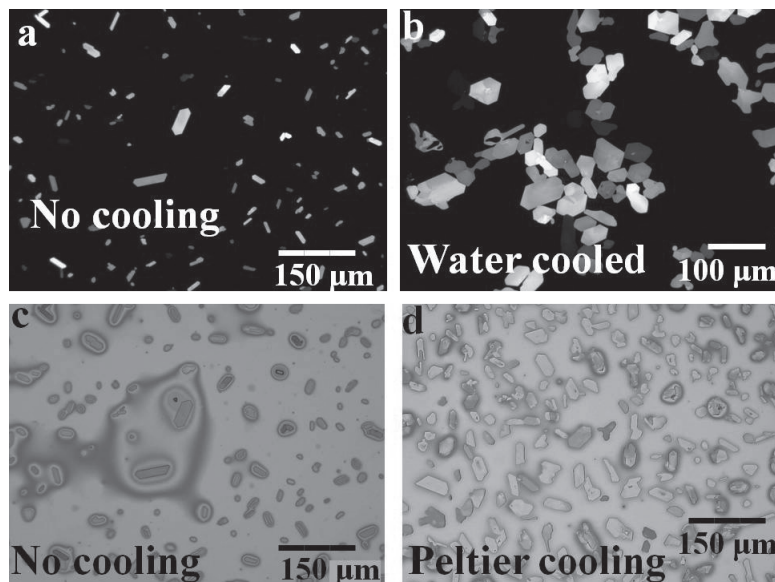


Figure 2: Comparison between cooled and non-cooled C_{10} -BTBT samples.

keep the water temperature constant, the cooling is only effective during the first hour.

Figure 2a and 2b compares a water-cooled sample with a non-cooled sample. The crystal size of a water-cooled sample is relatively larger and aggregation of these crystals is observed. We believe this result shows that cooling effect help the crystal growth.

In order to better control the cooling effect, we employed a Peltier cooler to set the sample temperature to be $1\sim 2^{\circ}\text{C}$ lower than room temperature (T_{room}). However, since T_{room} fluctuates, the temperature difference between the sample and the solvent is often more than 2°C . As Treossi, et al. have explained, when the temperature difference between sample and solvent is too large, macroscopic droplets will form on the surface of the sample [4]. Hence, the functional materials will be completely dissolved and become amorphous once again.

Since it is difficult to control T_{room} , we carried out the Peltier cooling experiment discontinuously, stopping it every two hours to adjust the sample temperature. At the end, only one cooled sample was successfully made (Figure 2d).

Comparing Figure 2c and 2d, we observe little difference in crystal size between the two samples. However, since only one sample was successfully made and the experiment was carried out discontinuously, we cannot conclusively determine whether the cooling effect is promoting the crystal growth or not. More samples and better control of the solvent temperature is needed before we can obtain any conclusive results.

It is relatively difficult to fabricate OFETs with C_{10} -BTBT or C_{12} -BTBT since the channel between two electrodes is usually longer than the crystals. Nonetheless, after many trials, we successfully obtained four devices. The mobilities and threshold voltages of these OFETs are listed in Table 1. Notice devices a and b exhibit very different mobilities from devices c and d. The electrodes of devices a and b were evaporated together. Devices c and d were also fabricated together, but on a different day and with a different evaporator from devices a and b. It is very likely that the electrodes of devices a and b were not well made, leading to large contact resistance and lower mobilities. The mobilities of devices c and d are among the highest ones of single-crystalline OFETs.

At this point, we cannot compare the electronic properties of C_8 -BTBT and C_{10} -BTBT due to the limited sample size (i.e., four) obtained for C_{10} -BTBT. However, these results once again demonstrate that our fabrication method has high potential of producing inexpensive high performance single-crystal OFETs on polymer substrate.

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OFET Device	Mobility ($\text{cm V}^{-1}\text{s}^{-1}$)	Threshold Voltage (V)
a	0.03	-19.98
b	0.03	-19.64
c	6.00	-11.67
d	5.18	-15.28

Table 1: Characteristics of four C_{10} -BTBT single-crystal OFETs.