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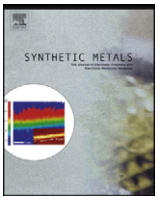

Organic single crystalline micro- and nanowires field-effect transistors of a tetrathiafulvalene (TTF) derivative with strong π–π orbits and S···S interactions

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ABSTRACT

Tetrathiafulvalene (TTF) was one of the most widely studied heterocyclic systems. However, TTF itself was easily oxidized, which induced the low stability and limited its potential applications. Here, a TTF derivative, 2,3,6,7-tetrakis(2-cyanoethylthio)tetrathiafulvalene (TCE-TTF), was synthesized. It was found that single crystalline micro- and nanowires of TCE-TTF were easily obtained by simple casting due to the enhanced π–π overlapping and S···S interaction. The thermal and vacuum stability analyses revealed TCE-TTF was much better than TTF. Single crystalline micro- and nanowires field-effect transistors were also fabricated by in situ dropping method. The typical mobility and on/off ratio were ~0.02 $cm^2/V\,s$ and ~10^3, which predicted great potential applications of organic nanowires electronics.

1. Introduction

Since tetrathiafulvalene (TTF) was discovered in 1971 by Wudl and co-workers [1], TTF and its derivatives have been the most widely studied heterocyclic systems [2–6], whose advantages were well displayed in different applications including electrochemical switches [7], photosensitive switches [8,9], sensors and catalysts etc. [10,11]. Moreover, it is found that these compounds including TTF [12] and its derivatives [13–18] showed high mobility because of good overlapping of π–π orbits [19,20] as well as S···S and C–H···S interactions [21–23]. Both theoretical and experimental results revealed that solution self-assembly via strong π–π overlapping and interaction can be easy to form low dimensional nanostructures, such as micro- and nanowires and nanoribbons, which was an ideal model to investigate intrinsic property of organic semiconductor since the charge transfer preferable direction can be easily obtained [24,25]. Actually including TTF and many derivatives [12–14] were belonged to this category. We also reported that the high performance of TTF derivatives was mainly attributed to TTF itself [12]. The excellent performance of TTF families has made them one of the most promising materials for organic electronics. However, as the famous electron donor, unsubstituted TTF itself could be easily oxidized to the cation radical and dication sequentially at rather low oxidation potential [5]. Instead, the purposive modifications for the side chains of TTF were proved to increase the oxidation potential and stability [26,27], for example, the theoretical research indicated that one of the TTF derivatives, bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), was more stable, mainly because the combination of attractive S···S interaction with the formation of C–H···S interaction at each end of the molecules [21]. And this enhanced S···S interaction was also proved to play a very important role in the charge transfer process and result in high mobility [28,29]. It is a tendency to design a molecule with strong π–π overlapping as well S···S interaction. The reconstruction task for TTF was mainly focused on the side chains modifications.

Rovira and co-workers [30] analyzed the molecular structures and the corresponding field-effect mobility based on many similar TTF derivatives and drew the conclusion that symmetrical structures could afford better performance than unsymmetrical ones, such as dithiophene-tetrathiafulvalene (DT-TTF) and dibenzo-tetrathiafulvalene (DB-TTF) [13,14]. More and more results showed that side chains substituent can improve face-

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to-face π–π interaction of the main building block and increase the charge transfer efficiency. Actually, many single crystal structures of this kind of molecules were commonly formed into low dimensional nanostructures [29]. One of the TTF derivatives, tetrakis-(octadecylthio)-tetrathiafulvalene (TTF-4SC18) [28] was a good example to show the easy formation process of regular nanofibers with some kinds of crystallization. However, single crystal structure of this molecule was not obtained. It was maybe attributed to the introduction of overlong alkyl side chains. So moderate side chains substitution was also a good solution for single crystal growth as well nanostructures.

In this study, we have taken TTF as the main building block to reconstruct the side chains of TTF, especially to replace the instable positions by the stable groups, improve the interaction of π–π orbits and S···S interactions. A TTF derivative, single crystal of 2,3,6,7-tetrakis(2-cyanoethylthio)tetrathiafulvalene (TCE-TTF) was demonstrated to achieve this gain. In fact, TCE-TTF was a good donor and had many potential applications. It had symmetrical molecular structures and can be used as a precursor [31], building block of macrocyclic compounds [32], radical salts [33], etc. Recently the magnetic properties of TCE-TTF were also studied [34]. In this paper we mainly studied the neutral TCE-TTF itself for potential application of micro- and nanowire electronics.

2. Experimental

2.1. Synthesis and characterization

TCE-TTF was synthesized by the previous methods [35,36]. The original material was purified several times by re-crystallization in the dichloromethane saturated solution. The achievable purity was greater than 99.9%. The desirable crystals were cast from solution. The saturated solution was directly poured onto the substrate and then the substrate was sealed in the chamber for slow evaporation. Different solvents including dichloromethane, chloroform, tetrahydrofuran and acetonitrile were used to obtain wire-like crystals. TTF was purchased from Alfa Aesar and also purified by re-crystallization. TTF and TCE-TTF were investigated by CHI660C electrochemistry workstation and Hitachi U-3010 ultraviolet spectroscopic instruments. These crystals were characterized by Hitachi S-4300 scanning electron microscopy (SEM), Hitachi JEOL-2010 transmission electron microscopy (TEM) and powder X-ray diffraction (XRD, D/max 2500).

2.2. Device fabrication and characterization

Organic single crystalline field-effect transistor (OFET) was fabricated on a 500 nm SiO_2 substrate. The substrate was thermally grown on a heavily doped n-type silicon wafer, which was used as a gate electrode. The substrate was firstly immerged into hot sulfuric acid (98%):hydrogen peroxide = 2:1 for half an hour to get rid of organic compounds physically absorbed on the substrate, and successively cleaned with pure water, alcohol, and hot acetone by ultrasonic cleaner for about 15 min, then dried in N_2 ambient. Poly(vinyl alcohol) (PVA) was introduced to improve the interface compatibility and form one thin buffer layer. PVA (dissolved into water, the selected preferred concentration was 2.5 mg/ml) was spun at 2500 rpm/min on top of the substrate. The thin films were annealed in the vacuum chamber at 100 °C for about 1 h, and then dried at 60 °C for about 12 h to make sure all the solvent was removed. Octadecyltrichlorosilane (OTS) modification was carried out for about 10 h, and the thin films were cooled slowly to the room temperature.

Bottom contact geometry was adopted to avoid the heat influence in the process of electrode evaporation. The source and drain electrodes were fabricated by deposition of 8–10 nm gold film through shadow masks.

Single crystalline TCE-TTF transistor was fabricated by the solution cast. *I–V* characteristics of OFETs were recorded by a Keithley 4200 SCS and a micromanipulator 6150 probe station in a clean and shielded box at room temperature.

3. Results and discussion

3.1. Single crystalline micro- and nanowires synthesis of TCE-TTF

Low dimensional single crystalline micro- and nanowire do help research the preferential growth direction of single crystal, verify the efficient molecular packing, understand structure–property relationships, elucidate transport mechanisms and simplify the fabrication process of single crystalline device [12,37–40]. Strong π–π overlapping can easily result in one-dimensional nanostructure, and this face-to-face interaction was proved to be reinforced by the side chains substituent [29]. For TCE-TTF molecule, firstly we reconstructed four sulfur atoms at the four ends of TTF by single bond connection, which was regarded as improvements of S···S interaction [28]. Appropriate alkyls can reinforce the π–π overlapping. Rear-end connection of nitrile group also increased the stability and keep good planar configuration of the molecule.

Single crystals of TCE-TTF were very easily achieved. TCE-TTF micro- and nanowires single crystals were presented in Fig. 1. Direct drop casting was used to obtain various single crystalline micro- and nanowires using different solvents, such as acetonitrile (Fig. 1(a–e)), dichloromethane (Fig. 1(f)), chloroform (Fig. 1(g)) and tetrahydrofuran (Fig. 1(h)). The size control was mainly dependent on the solvent evaporation rate, surface treatments such as octadecyltrichlorosilane (OTS) modification. For example, acetonitrile was a good solvent to realize desirable single crystalline micro- and nanowires. The dimension of micro- and nanowires was precisely controlled by combining the parameters of substrate selection (such as silicon dioxide), surface modification (such as OTS) and evaporation speed (high or slow) as shown in Fig. 1(a–e). A large number of crystals could be simply cast on the silicon dioxide (Fig. 1(a)), and the corresponding crystal length could be greater than several hundred micrometers (Fig. 1(b)) and the diameters could range from several hundred nanometers to several tens micrometers (Fig. 1(c–e)). Other solvent like tetrahydrofuran resulted in more thinner and longer nanowires (Fig. 1(h)) while chloroform tended to form bigger and shorter microwires (Fig. 1(g)).

3.2. Single crystal confirmation and structure analysis

TCE-TTF molecules can easily self-assemble into desirable micro- and nanowires. The selected area electron diffraction (SAED) was adopted to confirm whether the wire-like structure was single crystal or not. The results revealed that the wire-like structure (Fig. 2(b)) was single crystal and all of them could be indexed quite well with the lattice parameters obtained from XRD data (Fig. 2(a)), the SAED pattern (Fig. 2(c)) was indexed with lattice constants $a = 5.1016$ Å, $b = 26.753$ Å, $c = 8.8805$ Å, and $\beta = 96.031°$ [36].

Classical organic semiconductors, TTF (α phase, α-TTF) [1], DB-TTF [41], DT-TTF [27], BEDT-TTF [26] and TCE-TTF [36] were selected to analyze structural difference. The above five typical molecules were the same monoclinic systems and had strong π–π interaction. Here two main parameters was adopted, the spacing between two π–π packing planes ($d_{\pi-\pi}$), and the minimum intra-stack S···S contact distance between two π–π packing planes