Development of π-Extended Heteroacene-based Materials toward Application in Organic Field-Effect Transistors

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Chapter 1

General Introduction
1.1 Introduction

Since the discovery of the potential of organic semiconducting materials as substitutes for silicon, considerable research efforts have been devoted to the development of high-performance organic electronics devices, including organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic solar cells (OSCs). Research interests in organic electronics come from the potential to produce low-cost, large-area, lightweight and flexible devices that are able to integrate functionalities currently accomplished using expensive conventional semiconductors and components. A look at the research results and findings suggests that the performance of OFETs competes with that of amorphous silicon transistors. Therefore, OFETs can play a role in the integrated circuits used to operate RFID (Radio Frequency Identification) tags and sensors and to drive individual OLED pixels in active-matrix displays. OFETs are also especially suitable for applications requiring single or short-term use, very large-scale manufacture, low-resolution architectures, and/or plastic substrates. (Figure 1-1)
1. 2 Organic Field-Effect Transistors (OFETs)

In the most basic form, FETs are three-terminal devices that can act as electronic switches. The three terminals of a FET are the source, drain, and gate electrodes. The most important current in the FET is the current flowing from the source to the drain, $I_{DS}$. This current is partly related to the voltage applied across the source and drain electrodes, $V_{DS}$. However, $I_{DS}$ can also be controlled by the voltage applied to the gate relative to the source, $V_{GS}$. At different $V_{GS}$, the current flow from the source to the drain can be either allowed or restricted. Controlling the $I_{DS}$ by changing the $V_{GS}$ leads to the switching effect in FETs.

1. 2. 1 Device Structures

The OFETs used in this research are divided into two main classes based on geometry, top- and bottom-contact, and consist of a gate dielectric, semiconductor, and electrodes (source, drain and gate) as shown in Figures 1-2(a) and (b), respectively. To fabricate the devices, an organic semiconductor film is deposited on a dielectric/gate substrate and is contacted with metallic source and drain electrodes. In the top-contact case, the organic film is deposited first, followed by the source and drain electrodes. In the bottom-contact case, this deposition sequence is reversed. Usually, the dielectric/gate layer consists of a metal or doped-semiconductor, which serves as both the substrate and gate electrode coated with a metal oxide or polymeric insulators. The organic semiconductor film is deposited by vacuum-evaporation or solution processing. If desired, surface treatments on the dielectric layer may be used prior to deposition of the semiconductor layer to improve film structure and electrical characteristics.\textsuperscript{7,8} The metal source and drain electrodes are often vapor-deposited through a shadow mask, but conductive inks that can be printed are also being employed.

![Figure 1-2. OFET device structures: (a) Top-contact and (b) Bottom-contact](image-url)
1.2.2 Operation

The operation of an OFET can be explained as follows. The voltage applied to the gate shifts the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels with respect to the metal Fermi level ($E_F$) of the source-drain contacts, which allows for the formation of a conducting channel between the source and drain (Figure 1-3). The insulator prevents the flow of carriers from the source to the gate electrode instead of to the drain electrode. A negative gate voltage shifts the orbitals up and might result in the alignment of the HOMO with $E_F$, making it possible to have hole conduction. Otherwise, if a positive gate voltage is applied, the HOMO and LUMO will shift down, and if the LUMO becomes resonant with $E_F$, electrons will flow from the metal to the LUMO. However, one should bear in mind that the orbital shifting induces bending of the bands near the source-drain electrodes and, thus, there is an energy barrier at these contacts.

![Figure 1-3. Schematic representation of the HOMO and LUMO of the organic semiconductor with respect to the source-drain contacts.](image)

1.2.3 Electrical Characteristics and Key Parameters

Typical current-voltage characteristics of a transistor are shown in Figures 1-4(a) and (b). These curves were obtained from a device with pentacene as the semiconductor and gold as the source and drain electrodes. The key parameters in characterizing an OFET are its field-effect mobility, on/off ratio, and threshold voltage. Field-effect mobility quantifies the average drift velocity per unit electric field of charge carriers, which describes the ease with
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which charge carriers drift in an organic semiconductor. On/off ratio is defined as the drain-source current ratio between the ‘on’ and ‘off’ states. Threshold voltage can be defined as the gate voltage at which the conducting channel starts to form, usually corresponding to the voltage at which strong inversion occurs in conventional FETs. The threshold voltage \( V_{th} \) can be calculated from the x-intercept of a line drawn through the linear region of a plot of the square root of the drain-source current in saturation \( (I_{DS, sat}^{1/2}) \) vs. gate voltage \( (V_G) \) (Figure 1-4(b)).

![Figure 1-4](image_url)

**Figure 1-4.** OFET characteristics: (a) output curve and (b) transfer characteristics curve of a typical OFET.

Charge carrier mobility \( (\mu) \) influences the current flowing through a FET at a given set of device dimensions and applied voltages above certain threshold values and is, therefore, directly related to the switching speed of the device. Current in the linear and saturation regimes (Figure 1-4(a)) can be quantified using Eqs. (1) and (2).

\[
I_D = \frac{W}{L} \mu (V_G - V_{th} - \frac{V_D}{2}) V_D \quad \text{(Linear regime)} \tag{Eq. 1}
\]

\[
I_D = \frac{W}{2L} \mu (V_G - V_{th})^2 \quad \text{(Saturation regime)} \tag{Eq. 2}
\]

\( W \) and \( L \) are the channel width and length, respectively, \( C_i \) is the insulator capacitance per unit area, \( V_G \) and \( V_D \) are the gate and drain voltages with respect to the source voltage,
respectively, and $V_{th}$ is the threshold voltage that takes into account various potential drops through the gate insulator-semiconductor structure. In the linear regime $I_D$ increases of $V_D$ at a given $V_G$. Above a certain $V_D$, the channel is fully formed and $I_D$ saturates instead of increasing with $V_D$; this is called the saturation regime (Figure 1-4(a)).

### 1.3 Molecular Materials for Organic Field-Effect Transistors

OFETs are FETs that use organic materials for the semiconducting layer and have attracted wide spread interest since the first report in 1986.\textsuperscript{11} Their unique advantages such as light weight, low-cost, flexibility, and easy fabrication of large-areas make them highly promising for electronic paper, sensors, RFID tags, and active-matrix displays.\textsuperscript{12} The backbone of OFETs is organic semiconductors, which have experienced significant progress in mobility from the initially reported $\sim 10^{-5}$ cm$^2$/Vs for polythiophene in 1986 to $\sim 10$ cm$^2$/Vs for present organic thin films,\textsuperscript{13} and $\sim 15$–$40$ cm$^2$/Vs for organic single-crystals.\textsuperscript{14,15} A basic timeline of the best mobilities in organic semiconductors is depicted in Figure 1-5.\textsuperscript{16} The high mobility organic semiconductors (i.e., higher than amorphous silicon) have the greatest prospect for application in organic electronic devices. Certainly, it should be noted that regardless of the rapid progress, fundamental aspects such as design strategies and packing motifs for high mobility and stability in organic semiconductors are still unclear.

![Figure 1-5: Progress in mobility of high-performance organic semiconductors.](image)
1.3.1 Charge Transport in Molecular Materials

Charge transport from one molecule to another should be as efficient as possible to achieve a high mobility in organic semiconductors. This, in turn, is intimately related to the electron cloud on the molecule and the electron cloud splitting with its neighbor molecules. Two parameters, the transfer integral and the reorganization energy, are both believed to strongly affect the mobility of organic semiconductors. The transfer integral defines the splitting of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This is enhanced by a large, extended π-overlap between neighboring molecules.\(^\text{17}\)

The reorganization energy is the energy loss when a charge carrier passes between neighboring molecules and normally depends on the conjugation length, degree, and packing of the organic molecules.\(^\text{18-21}\)

In general, the larger the transfer integral and the smaller the reorganization energy, the higher the mobility.\(^\text{20,21}\) The transfer integral and reorganization energy are extremely dependent on the packing of the organic molecules. Therefore, understanding the packing mode of the organic semiconductors becomes very important for the fundamental analysis of the charge transport between molecules.

1.3.2 Small-Molecule Semiconductor Materials

Small molecule semiconductors have been widely studied because they are easy to purify and easily form crystalline films, which can be desirable for fabrication of high performance devices. Indeed, until now, the π-conjugated systems that are reported to have the highest mobility are small molecules such as pentacene,\(^\text{23}\) rubrene,\(^\text{14}\) and C\(_8\)-BTBT.\(^\text{24}\)

1.3.2.1 Semiconducting π–Extended Acenes

Pentacene (2 in Figure 1-6) OFETs have received particular attention since they have shown hole mobilities of up to 5 cm\(^2\)/Vs with on/off current ratios as high as 10\(^8\). However, pentacene is only moderately stable in oxygen as a dense solid and is unstable under illumination. Pentacene also has a very high melting point and is virtually insoluble, even in hot aromatic solvents. Hexacene (3) has received some attention and appears, in the solid state, to follow a homologous series with tetracene (1) and pentacene (2).\(^\text{25}\) However, like pentacene, this molecule has been proven to be unstable, being highly reactive in the 6- and
15-positions due to p electron localization.

![Figure 1-6. Chemical structures of acenes and thienoacenes](image)

### 1. 3. 2. 2 Semiconducting Thienoacenes

Sulfur-rich annulated oligomers and polymers have attracted growing interest owing to their desirable characteristics (electronic, optical, and magnetic properties) for fabricating electronic and optic devices. In particular, thiophene-based conjugated oligomers and polymers have been shown to be environmentally stable and robust in nature. Oligothienoacenes (nTA: fully fused oligothiophenes; 4-6 in Figure 1-6) and thiophene-based acenes are among the most frequently studied organic semiconducting materials. The advantages of these molecules have been attributed to their unique structural features: all of the sulfur atoms are positioned at the molecular periphery, facilitating multiple short intermolecular S···S contacts which increase the effective dimensionality of the electronic structure. These interactions may lead to enhanced transport properties.

Condensed derivatives of thiophenes have attracted considerable interest as building blocks for electrically conducting polymers. Their low oxidation potential, high degree of conjugation achieved using fused aromatic rings and high degree of rigidity favor an enhanced π···π overlap in the solid state, leading to efficient intra- and interchain charge transport, and high charge carrier mobilities. Ring fusion can also induce changes in molecular packing, for instance, from a less favorable herringbone packing to the desired π-stacking.

Pentathienoacene (5), the thiophene equivalent of pentacene (2), is one of the latest
additions to the family of organic crystal semiconductors with great potential for use in OFETs. Recently, an improved synthesis of tetrathienoacene (4) and extension of the series to make heptathienoacene (6) has been reported by Zhang and co-workers. These thienoacenes show molecular packing in the desired face-to-face π-stacking motif, rather than the herringbone packing typical of non-fused oligothiophenes and pentacene. Tetrathienoacene (4) was successfully used as an active semiconducting material in OFETs and achieved a mobility of 0.045 cm²/Vs when deposited on a heated substrate at a temperature of 80 °C. Hexathienoacene (6) and octathienoacene, consisting of an even number of thiophene rings, have also been synthesized, although somewhat later than tetrathienoacene (4) and heptathienoacene, mainly due to their limited solubility during the synthetic steps.

By using density functional theory and gas-phase ultraviolet photoelectron spectroscopy, Kim et al. investigated the microscopic charge transport parameters of pentathienoacene crystals. They found that the valence band exhibited a stronger dispersion than those in pentacene and rubrene single crystals, with marked uniaxial characteristics within the molecular layer due to the presence of one-dimensional π-stacks; a small hole effective mass was also found along the direction perpendicular to the molecular layers. In the conduction band, strong intermolecular S···S interactions gave rise to a significant inter-stack electronic coupling, where as the intra-stack dispersion was greatly reduced. The intra-molecular reorganization energy was found to be stronger than that in pentacene but comparable to that in sexithiophene (which contains six non-fused thiophene moieties); it was also found to be larger for holes than for electrons, as a result of low-frequency modes induced by the sulfur atoms.

1.3.2.3 Semiconducting Sulfur-Containing Heteroacene Systems

Incorporating fused thiophenes into oligoacene frameworks is a promising strategy in the development of novel air stable organic semiconductors, since fused thiophene moieties can improve the extent of intermolecular π···π overlap in the solid state, a feature that is closely related to charge carrier mobility. Takimiya et al. have focused their attention on the thieno-[3,2-b]thiophene (7 in Figure 1-7) derivative 2,7-diphenyl[1]-benzothieno[3,2-b][1]-benzothiophene (DPh-BTBT; 8 in Figure 1-7) and have successfully developed a series of excellent organic semiconductors for OFETs. The HOMO energy level of DPh-BTBT (-
5.41 eV) is lower than that of pentacene and is comparable to that of anthracene. The best devices afforded impressive mobilities as high as 2.0 cm²/Vs and an on/off ratio of 10⁸.

The same group later found that thin films prepared from 2,7-dialkyl[1]benzothieno[3,2-b][1]benzothiophenes (Cₙ-BTBT; 9 in Figure 1-7) are stable to oxidation and exhibit hole mobilities up to 2.75 cm²/Vs.²⁹ The crystal assumes a “layer-by-layer” structure consisting of alternately stacked aliphatic layers. In the BTBT core layer, the molecules adopt a herringbone packing which facilitates 2-D carrier transport properties, as discussed in more in Section 1.4.1. In addition, a network of intermolecular interactions through short S···S contacts (3.54 and 3.63 Å) exists. The high mobilities of Cₙ-BTBT-based FET devices can be attributed to these structural aspects, since the existence of 2-D semiconducting layers with strong intermolecular overlap is considered to be one of the prerequisites to realizing high performance OFET devices. Expansion of the π-framework has the potential to provide even more durable high-performance organic semiconductors. An additional compound that Takimiya et al. designed with this idea in mind is dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT; 10 in Figure 1-7) with six fused aromatic rings.³² The calculated HOMO and LUMO levels for this compound are -5.19 and -1.81 eV, respectively. The molecules are almost planar with a small standard deviation of 0.058 Å and form a layer-by-layer structure in crystals. In a preliminary examination, a device fabricated with DNTT operated in air and showed a very high hole mobility of 2.9 cm²/Vs, close to the record level for thin film pentacene, and the on/off ratio of 10⁷ was also excellent.

Figure 7. Chemical structures of thieno[3,2-b]thiophene derivatives.

1.4 Single-Crystal OFETs (SCFETs)

The successful realization of FETs on the surface of organic molecular crystals (OMC) was an important milestone in the research of electronic transport in organic semiconductors.
Single crystals of organic semiconductors are preferable candidates for achieving high field-effect performance since single crystals can show intrinsic charge-transport properties and high mobility because of the perfect order of molecules, the absence of grain boundaries, and the minimized concentration of charge traps in single crystals. Single-crystal OFETs\textsuperscript{33} can also be regarded as model systems to carry out correlation studies between microscopic molecular packing and macroscopic charge transport, since in such devices parameters such as grain boundaries, alignment, film morphology, and crystallinity can be ruled out.

Moreover, the study of organic single crystals is also crucial for the design of new organic semiconductors and the fabrication of high-performance devices. In this section, the study of molecular packing motifs and growth methods of single crystals OFETs, and the fabrication methods of single-crystal OFETs are discussed.

\textbf{1.4.1 Molecular Packing Motifs in Single Crystals}

In organic semiconductors, charge carriers transport along molecular \(\pi\)-orbitals. Therefore, the degree of overlap between the orbitals of neighboring molecular significantly affects the mobility of charges. Molecular packing with strong intermolecular overlap is favorable for efficient charge carrier transport and high field-effect mobility.

There are four different kinds of packing motifs as shown in Figure 1-8\textsuperscript{34-36} (a) herringbone packing (face-to-edge) without \(\pi\)-\(\pi\) overlap between adjacent molecules; (b) herringbone packing with \(\pi\cdots\pi\) overlap between adjacent molecules, also called slipped \(\pi\)-stacking in some literature reports; (c) lamellar packing with one-dimension (1-D) \(\pi\)-stacking; and (d) lamellar packing with two-dimension (2-D) \(\pi\)-stacking. Of the four kinds of packing motifs, that of lamellar packing is believed to the most efficient for charge transport\textsuperscript{35} because it can maximize the transfer integrals and transport the charge carriers through an almost straight line (i.e., the shortest route). Much research has focused on molecular design and crystal engineering in order to obtain lamellar packing.
Figure 1-8. Different possible molecular packing motifs existing in single crystals: (a) herringbone without π···π overlap packing motifs (example: pentacene\textsuperscript{37}); (b) herringbone packing motifs with π···π overlap packing motifs (example: rubrene\textsuperscript{38}); (c) lamellar stacking motifs with one-dimensional (1D) π–stacking (example: hexyl substituted naphthalene diimide\textsuperscript{39}); (d) lamellar stacking motifs with two-dimensional (2D) π–stacking (example: TIPS-PEN\textsuperscript{40})

1.4.2 Growth Methods of Single Crystals

The techniques for the growth of organic crystals mainly focus on solution and vapor processes. Vapor growth is a dry process usually performed at reduced pressure using a carrier gas to transport molecules in the vapor phase. On the other hand, methods based on solution processing, including recrystallization,\textsuperscript{41} solvent-exchange\textsuperscript{42} and drop-casting assembly,\textsuperscript{43,44} are usually suitable for organic materials with good solubility but require the use of a solvent, which can easily lead to solvent molecules being doped into the organic single crystals during the crystallization process. While this residual solvent may cause reduced performance, the solution-based methods have attracted extensive attention, because they provide facile and low-cost routes for preparing large-area single crystals. Some of these growth methods are discussed in more detail in the section.
1.4.2.1 Physical Vapor Transport (PVT)

Since most organic semiconductors are not very soluble, most of their single crystals have been prepared by sublimation of the organic material in a variety of vacuum deposition systems (Figure 1-9). The most common technique used to obtain organic single crystals is physical vapor transport (PVT).\(^{45,46}\) PVT is a general method that has been used to produce crystals with high-quality\(^ {47,48}\) such as plate-like rubrene and pentacene single crystals,\(^ {37,38}\) and micro/nanometer-sized single crystals of copper phthalocyanines (CuPc).\(^ {49}\) PVT involves heating the source organic material placed at the hottest end of a glass or quartz tube submitted to a gradient of temperatures with an inert gas flowing along it. As the organic material is sublimed, it is carried down the tube by the gas and solidifies at its solidification temperature. Typically, the use of vapor phases allows for higher purity materials to be obtained, and hence, higher OFET mobilities have been achieved this way.

**Figure 1-9.** Physical vapor transport method for growth of single crystals. Purified semiconductor is placed in a glass or quartz tube, heated by a resistive heating element to its sublimation temperature, and carried down a temperature gradient by a stream of inert carrier gas, such as Ar, N\(_2\), or He. The material resublimes in the cooler zone of the furnace to form crystals, while impurities are deposited up- and downstream, providing a degree of in situ purification. The crystals are collected from glass or quartz sleeves for fabrication of SCFETs.
1.4.2.2 Solvent Vapor Annealing (SVA)

Solvent vapor annealing (SVA) has been increasingly deemed as an appealing option in the last few years,\textsuperscript{50-52} and involves exposing the deposited samples to an environment saturated with solvent vapor. The SVA treatment (Figure 1-10(a)) can lead to an improvement of the crystalline character of molecular assemblies, when a solvent with the appropriate polarity in relation to the chemical nature of the deposited species is chosen.\textsuperscript{53,54}

Before SVA, the film is usually fabricated by spin-coating a solution of poly(methyl methacrylate) (PMMA) mixed with the semiconductors because films with PMMA shows domains while films not containing PMMA are usually polycrystalline (Figure 1-10(b)). Subsequently, the samples are annealed at room temperature for about 12 hours in chloroform vapor, as chloroform is a good solvent for many materials and has a low boiling point to give a high vapor pressure. After annealing, single crystals can be observed (Figure 1-10(c, d)).

![Spin-coating and SVA process](image)

**Figure 1-10.** SVA treatment process and optical microscopy images. a) spin-coated film from mixed solution (semiconducting material and PMMA). b) a microscopy image of Spin-coated film and c) after SVA for 12h. d) a polarizing microscopy image. (scale bar : 500μm)
1.4.2.3 Drop Casting

Among the many processing methods for OFETs, the most often discussed advantages of drop-casting are simplicity and low-cost fabrication of large-area transistors. However, drop-casting suffers from some limitations. For example, organic semiconductors with poor solubility limit the growth of organic crystals on the prefabricated electrodes. Moreover, during the drop-casting process for crystal growth (Figure 1-11), molecules of solvent or impurities may be easily trapped in the crystals or trapped at the semiconductor interface, especially during the drop-casting of suspensions. It is also very sensitive to the parameters of the process, such as concentration, solvent purities, temperature, and evaporation rate, which play a crucial role in the size and quality of the crystals.

Figure 1-11. A supersaturated solution of organic semiconductor is applied to a substrate, either by immersing and removing the substrate into the solution or by dropping the solution onto the surface.

1.4.3 Single-Crystal OFET Fabrication

The shadow mask technique is a general method for the fabrication of organic thin-film field-effect transistors. In 1996, Horowitz et al. fabricated top-contact and bottom-gate organic single-crystal OFETs with gold electrodes through a shadow mask deposition. Decades of study suggest that this approach works well for most crystals with sizes of hundreds of micrometers. However, it is challenging to apply this general mask technique to single crystals only several micrometers in size, and growing large crystals of most organic semiconductors is difficult.

In this study, the shadow mask technique was used. The details of the method are described by Figure 1-12. The OFETs devices were fabricated with single crystals prepared by PVT
processing.

The single crystals were picked up and placed onto the substrate using hair static. A shadow mask was then aligned on top of the single under an optical microscope. After that, electrodes for source/drain were vacuum deposited on to the structure through the mask.

![Figure 1-12. Schematic of device fabrication by using shadow mask technique.](image)

**1. 5 Motivation and Research**

It is believed that organic electronics will be able to successfully compete with inorganic electronics for applications that require mechanical flexibility, large area coverage and inexpensive mass production. Principally, the mobility of the organic semiconductor should be as high as possible to achieve high-performance, competitive devices. There is no doubt that the semiconducting $\pi$-conjugated system incorporated into OFETs is one of the most important factors determining the ultimate performance of the device, and two parameters dependent on the orbital interaction and molecular structure, the transfer integral and the reorganization energy, are both believed to strongly affect the mobility of organic semiconductors.

In general, the larger the transfer integral and the smaller the reorganization energy are the higher the mobility. The transfer integral and reorganization energy are extremely dependent on the packing of the organic molecules. Therefore, understanding the packing mode of the organic semiconductors becomes very important for the fundamental analysis of the charge transport between molecules. Among the four kinds of packing motifs, lamellar packing is believed to the most efficient for charge transport because it can maximize the transfer integrals.\(^{61}\) Much research has focused on molecular design and crystal engineering in order
to form lamellar packing.

The rapid development of sulfur-containing heterocyclic semiconductors can be explained by the following reasons. First, the thiophene ring has six $\pi$ electrons \((4n+2)\) and hence high aromaticity owing to its similarity to the benzene ring. Second of all, compared to the corresponding benzene-ring-based materials, those containing thiophene units benefit from the fact that the molecules can pack in planar structures.\(^6^2\) Third, the fused-thiophene-ring materials exhibit much higher ability for antioxidation due to the absence of a Diels-Alder cyclization active center.\(^6^3\) Even higher thienoacenes with six or seven fused aromatic rings exhibit excellent OFETs performance and high stability because of the introduction of heteroatoms. Finally, S atoms are able to introduce $S \cdots S$, $S \cdots H$, and $S \cdots \pi$ intermolecular interactions which enhance intermolecular interactions. This not only facilitates charge transport but also could change the packing motifs of the organic semiconductors. As a result, sulfur-containing materials have become one of the most important semiconductors for OFET applications.

This research focuses on the design and synthesis of new materials for high-performance organic semiconductors, with high mobility and stability by considering the important factors discussed above. The new materials are then applied them to single-crystal field-effect transistors in order to verify their characterizations.

In Chapter 2, new seven-ring-fused heteroacenesing hetero atom (C, S, and O) for better stability and high mobility are designed, synthesized, and characterized in OFETs. In general, $\pi$-extended molecular shows high mobility due to the enhancement of intermolecular $\pi \cdots \pi$ interaction but low stability. These new molecules are expected to have enhanced stability because of the replacement of benzene rings with thiophene (or furan) can increase the benzenoid character of the ladder $\pi$-conjugated architecture.

Next, the synthesis and design of derivatives utilizing a dithieno[3,2-b:2',3'-d]thiophene core are discussed in Chapter 3. This core is chosen because of the recent understanding that both intermolecular $\pi \cdots \pi$ interaction and intermolecular $S \cdots S$ interaction can play important roles in determining molecular packing and mobility. The characterization of these single crystals with both intermolecular $S \cdots S$ interactions and van der Waals intermolecular interactions between the alkyl groups are studied, and FET devices are fabricated and analyzed.
1.6 Reference


Chapter 1. General Introduction

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Chapter 2

Organic Single-Crystal Transistors Based on \( \pi \)-Extended Heteroheptacene Microribbons
2. 1 Introduction

Due to the rapid progress in organic electronics, the development of high-performance organic semiconductors continues to be a crucial area of research.\textsuperscript{1,2} Organic field-effect transistors (OFETs) have attracted great interest,\textsuperscript{2,3} as a low-cost alternative to traditional silicon transistors for their use in electronics applications, including active-matrix displays, circuits, and radio-frequency identification (RFID) devices.\textsuperscript{4} The design and synthesis of novel $\pi$-conjugated materials with comprehensively excellent properties and sophisticated self-organized structures are major challenges to enhance the OFET performance.

Compared with OFETs based on organic thin films, those using organic single crystals (e.g., pentacene and rubrene) can produce significantly enhanced carrier transport functionality on account of their near-perfect molecular order and defect-free morphologies.\textsuperscript{5} Recently, high-performance OFETs have successfully been demonstrated using one-dimensional (1D) nano- or micro-sized organic crystalline materials.\textsuperscript{6} One can expect that the construction of linearly $\pi$-extended oligoacene structures leads to further enhancement of intermolecular $\pi$-orbital overlap (or transfer integrals) and carrier transport properties of the materials. Nevertheless, so far, there are only a few reports on stable $\pi$-conjugated oligoacenes with more than six fused rings as organic semiconductors.\textsuperscript{7} Moreover, most of these materials still suffer from a complicated synthesis and bothersome purification processes.

![Chemical structures of new seven-ring fused thienoacenes developed in this study.](image)

We herein disclose the facile synthesis, photophysical properties, self-organization, and OFET properties of seven-ring fused $\pi$-extended thienoacenes (Figure 2-1), bisbenzo[$d,d'$]thieno[2,3-$d$;2',3'-$d'$]benzo[1,2-$b$;4,5-$b'$]dithiophene (BTBDT), bisthieno[2',3':4,5]thieno[2,3-$d$;2',3'-$d'$]benzo[1,2-$b$;4,5-$b'$]dithiophene (TTBDT), and
bisbenzo\([d,d']\)furo\([2,3-d;2',3'-d']\)benzo\([1,2-b;4,5-b']\)dithiophene (BFBDT) as a novel series of \(p\)-type organic semiconductors. BTBDT and TTBDT can be regarded as a tetrathieno and hexathieno analogue of phenanthro\([1,2-b]\)chrysene, respectively.

2.2 Synthesis of \(\pi\)-Extended Heteroheptacene

The synthetic procedures used to prepare new thienoacenes are outlined in Scheme 2-1 (see Experimental for details). The Suzuki–Miyaura cross-coupling reactions between 1,4-dibromo-2,5-bis(methylsulfinyl)benzene (1) and the corresponding boronic acids with \(\text{Pd(PPh}_3\text{)}_4\) as a catalyst afforded key precursors (2–4) in 73–80% yields.

Compounds 2–4 having methylsulfinyl groups were subsequently converted into TTBDT, BTBDT, and BFBDT, respectively, in 67–95% yields, via the intramolecular double cyclization reaction\(^8\) with an excess of trifluoromethanesulfonic acid. This synthetic method is applicable for constructing a variety of \(\pi\)-extended heteroacenes including the benzodithiophene core, without producing any structural isomers. The target materials were all insoluble in common organic solvents, and were purified by temperature-gradient sublimation under vacuum to give yellow crystalline solids.

2.3 Experiments

2.3.1 Synthesis

\[\text{Scheme 2-1. Synthesis of TTBDT, BTBDT, and BFBDT.}\]
The synthetic routes for TTBDT, BTBDT, and BFBDT are outlined in scheme 3-1. All reagents and solvents were purchased from Aldrich, Tokyo Kasei, or Wako, and used as received unless otherwise noted. All reactions were performed under an N₂ atmosphere in dry solvents using standard Schlenk techniques. The synthetic procedures used to prepare TTBDT, BTBDT, and BFBDT are outlined in Scheme 1. 1,4-Dibromo-2,5-bis(methylsulfinyl)benzene (1)\textsuperscript{14} was prepared according to the literature.

2. 3. 1. 1 Synthesis of 1,4-Bis(thieno[3,2-b]thiophen-2-yl)-2,5-bis(methylsulfinyl)benzene (2)

To a solution of 1 (0.89 g, 2.47 mmol) and thieno[3,2-b]thiophene-2-boronic acid (1.00 g, 5.43 mmol) in dry THF (60 mL) were added Pd(PPh₃)₄ (0.17 g, 0.15 mmol) and aqueous Na₂CO₃ (2.0 M, 30 mL; Ar bubbled before use). The mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into water. The formed precipitate was collected by filtration, and washed with water and methanol in this order. The product was purified by silica gel column chromatography (eluent: CH₂Cl₂) and dried under vacuum to afford 2 as a yellow solid (yield = 0.94 g, 80%). M.p. 320 °C (concurrent thermal decomposition). \(^1\)H NMR (500 MHz, CDCl₃): \(\delta\) 8.27 (s, 2H), 7.52 (s, 2H), 7.49 (d, \(J = 5.5\) Hz, 2H), 7.32 (d, \(J = 5.5\) Hz, 2H), 2.61 (s, 6H). \(^13\)C\(^{\langle1}\)H) NMR (125 MHz, CDCl₃): \(\delta\) 147.69, 140.88, 139.78, 138.73, 132.78, 128.85, 126.45, 120.68, 119.50, 41.96. MS (MALDI): \(m/z\) 478.85 [M+H]+; calcd 478.94.

2. 3. 1. 2 Synthesis of 1,4-Bis(benzo[b]thiophen-2-yl)-2,5-bis(methylsulfinyl)benzene (3)

This compound was synthesized from 1 (1.20 g, 3.33 mmol), benzo[b]thiophene-2-boronic acid (1.30 g, 7.32 mmol), and Pd(PPh₃)₄ (0.23 g, 0.20 mmol) by adopting the procedure used for 2. The product was obtained as a yellow solid (yield = 1.20 g, 77%). M.p. 318 °C (concurrent thermal decomposition). \(^1\)H NMR (500 MHz, CDCl₃): \(\delta\) 8.35 (s, 2H), 7.91-7.85 (m, 4H), 7.58 (s, 2H), 7.47-7.41 (m, 4H), 2.60 (s, 6H). \(^13\)C\(^{\langle1}\)H) NMR (125 MHz, CDCl₃): \(\delta\) 147.99, 140.67, 139.66, 137.34, 132.93, 126.66, 125.58, 125.43, 125.17, 124.37, 122.36, 42.08. MS (MALDI): \(m/z\) 466.92 [M+H]+; calcd 467.03.
2. 3. 1. 3 Synthesis of 1,4-Bis(benzo[b]thiophen-2-yl)-2,5-bis(methylsulfanyl)benzene (4)

This compound was synthesized from 1 (0.80 g, 2.22 mmol), benzofuran-2-boronic acid (0.79 g, 4.88 mmol), and Pd(PPh₃)₄ (0.15 g, 0.13 mmol) by adopting the procedure used for 2. The product was obtained as a yellow solid (yield = 0.70 g, 73%). M.p. 347 °C (concurrent thermal decomposition). ¹H NMR (500 MHz, CDCl₃): δ 8.73 (s, 2H), 7.69 (d, J = 7.5 Hz, 2H), 7.59 (dd, J = 8.0, 1.0 Hz, 2H), 7.41 (td, J = 7.5, 1.0 Hz, 2H), 7.35-7.31 (m, 4H), 2.87 (s, 6H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 155.13, 151.85, 147.02, 128.29, 127.57, 125.99, 123.90, 123.62, 121.88, 111.51, 107.54, 43.39. MS (MALDI): m/z 434.93 [M+H]+; calcd 435.07.

2. 3. 1. 4 Synthesis of Bisthieno[2',3':4,5]thieno[2,3-d;2',3'-d']benzo[1,2-b;4,5-b']dithiophene (TTBDT)

The mixture of 2 (0.90 g, 1.88 mmol), phosphorus pentoxide (0.10 g, 0.70 mmol), and trifluoromethanesulfonic acid (15 mL) was stirred for 72 h at room temperature, which was then poured into ice-water. The formed yellow precipitate was collected by filtration and dried under vacuum. This material was added into pyridine (80 mL), and the suspension was heated under reflux for 12 h. After cooling to room temperature, the reaction mixture was added into a large volume of acetone. The product was collected by filtration, washed with methanol and acetone, and then dried under vacuum (yield = 0.72 g, 92%). Yellow crystals of pure TTBDT were obtained by repetitive temperature-gradient sublimation. T_decomp. >360 °C. MS (MALDI): m/z 413.71 [M]+; calcd 413.88. Anal. calcd for C₁₈H₆S₆: C, 52.14; H, 1.46%. Found: C, 52.28; H, 1.40%.

2. 3. 1. 5 Synthesis of Bisbenzo[d,d']thieno[2,3-d;2',3'-d']benzo[1,2-b;4,5-b']dithiophene (BTBDT)

This compound was synthesized from 3 (0.75 g, 1.60 mmol) under the same conditions used for TTBDT. The product was obtained as yellow crystals (yield = 0.61 g, 95%), and further purified by repetitive temperature-gradient sublimation. T_decomp. >380 °C. MS (MALDI): m/z 401.77 [M]+; calcd 401.97. Anal. calcd for C₂₂H₁₀S₄: C, 65.64; H, 2.50%. Found: C, 65.62; H 2.42%.
2. 3. 1. 6 Synthesis of Bisbenzo[\textit{d,d'}]furo[2,3-\textit{d};2',3'-\textit{d'}]benzo[1,2-b;4,5-b']dithiophene (BFBDT)

This compound was synthesized from 4 (0.60 g, 1.38 mmol) under the same conditions used for TTBDT. The product was obtained as yellow crystals (yield = 0.34 g, 67%), and further purified by repetitive temperature-gradient sublimation. $T_{\text{decomp.}} > 340 \, ^\circ\text{C}$. MS (MALDI): $m/z$ 369.76 [$M^+$]; calcd 370.01. Anal. calcd for C$_{22}$H$_{10}$O$_2$S$_2$: C, 71.33; H, 2.72%. Found: C, 71.14; H, 2.66%.

2. 3. 2 OFET Device Fabrication

Single-crystal microribbons of BTBDT, TTBDT, and BFBDT were grown by means of the physical vapor transport technique with a horizontal-tube furnace. The source materials were evaporated at high temperature zone, and brought by carrier gas of pure Ar to the low temperature zone, forming microribbons.$^{13}$ For all OFET devices, heavily doped $n$-type Si wafers with a thermally grown 300-nm-thick SiO$_2$ layer were used as substrates. The SiO$_2$/Si substrates were pretreated with a piranha solution at 90 $^\circ$C for 0.5 h, and then copiously cleaned with sonication in deionized water, acetone, and isopropanol in this order. Then, about 30-nm-thick poly(methylmethacrylate) (PMMA) thin layer was dip-coated onto SiO$_2$/Si substrates as the dielectric to reduce charge trapping by the silanol groups on SiO$_2$. An individual single-crystal microribbon was picked up and placed onto the PMMA layer. The devices were completed by evaporating gold through a shadow mask to define the source and drain electrodes with a channel length of 30–50 $\mu$m on top of the single-crystal microribbon. The output and transfer characteristics of the OFETs were measured using an Agilent B1500A semiconductor parameter analyzer under ambient conditions at room temperature.

2. 4 Optical Properties

UV/vis absorption spectra of the three thienoacenes in solution and in deposited thin films are presented in Figure 2-2, and their optical data are listed in Table 2-1. It has been found that the optical properties of those thienoacenes in solid states are strongly affected by the difference of the heteroatomatic framework. The absorption spectra of BTBDT, TTBDT, and BFBDT in CH$_2$Cl$_2$ solution show the lowest energy absorption maximum ($\lambda_{\text{max}}$) in the range
of 385–390 nm (Figure 2-2a), reflecting that those compounds possess basically isoelectronic \(\pi\)-conjugation systems. However, obvious differences are observed between the absorption spectra in solutions and solid thin films. The absorption spectrum of \(\text{BTBDT}\) in the thin film (Figure 2-2(b)) exhibits an obvious red-shift (by approximately 30 nm) compared to that observed in the solution; while a blue-shifted absorption is observed in the thin film of \(\text{BFBDT}\). For \(\text{BTBDT}\) containing four sulfur atoms, greater intermolecular interactions enhanced by sulfur-induced orbital overlap would be expected, compared to furan-fused \(\text{BFBDT}\).

![Figure 2-2](image.png)

**Figure 2-2.** UV/vis absorption spectra of \(\text{TTBDT},\ \text{BTBDT},\ \text{and BFBDT}\) in (a) \(\text{CH}_2\text{Cl}_2\) solution and (b) thin films.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{abs}}^a) (nm)</th>
<th>(\lambda_{\text{em}}^b) (nm)</th>
<th>HOMO(^c) (eV)</th>
<th>LUMO(^d) (eV)</th>
<th>(E_g) (^d) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{BTBDT})</td>
<td>396,415</td>
<td>484</td>
<td>-5.36</td>
<td>-2.54</td>
<td>2.82</td>
</tr>
<tr>
<td>(\text{TTBDT})</td>
<td>396</td>
<td>519</td>
<td>-5.14</td>
<td>-2.38</td>
<td>2.76</td>
</tr>
<tr>
<td>(\text{BFBDT})</td>
<td>355,375,399</td>
<td>501</td>
<td>-5.43</td>
<td>-2.55</td>
<td>2.88</td>
</tr>
</tbody>
</table>

\(a)\) UV/vis absorption maxima in thin films. \(b)\) Emission maxima in thin films (see Supporting Information). \(c)\) Determined by photoelectron spectroscopy. \(d)\) LUMO = HOMO + \(E_g\), in which the optical energy gap, \(E_g\), was derived from the absorption onset of the thin film.
To further study the electronic properties of the thienoacenes, we have measured the ionization potentials of the thin films by photoelectron spectroscopy in air (Figure 2-3). The ionization potentials (or HOMO energy levels) of BTBDT and BFBDT are similar (ca. −5.4 eV), whereas that of TTBDT is found to be much smaller (−5.14 eV), which can be ascribed to the fusion of two electron-donating thiophene rings at the periphery in TTBDT. It is noted that replacing the outermost benzene rings with thiophene rings also raises the LUMO energy level (Table 2-1). All these new materials are expected to function as stable $p$-type semiconductors in air owing to their relatively low-lying HOMO energy levels compared to that of pentacene (−5.14 eV). Besides, the HOMO–LUMO energy gaps of the thienoacenes ($E_g = 2.76–2.88$ eV) are considerably larger than that of pentacene ($E_g = 1.77$ eV) because the replacement of benzene rings with thiophene (or furan) rings can increase the benzenoid character of the ladder $\pi$-conjugated architecture. These results indicate that in spite of their more elongated $\pi$-systems, the developed thienoacenes should possess better photooxidative stability compared to hydrocarbon oligoacenes under ambient conditions.

![Figure 2-3. Photoelectron spectra of deposited thin films of TTBDT, BTBDT, and BFBDT.](image)

2.5 Organic Field-Effect Transistor Properties

Single-crystal microribbons of BTBDT, TTBDT, and BFBDT have been epitaxially grown by means of the physical vapor transport technique with a horizontal-tube furnace. The length of individual microribbons varies from several tens to several hundred micrometers and the width ranges from ca. 10 to 40 µm, with the thickness less than 100 nm. The resulting
microribbons have been placed onto a 30-nm-thick poly(methylmethacrylate) (PMMA)-coated SiO\textsubscript{2}/Si substrate, and successively contacted by evaporated gold source and drain electrodes with the channel lengths ($L$) of 30–50 µm, in this way establishing a bottom-gate, top-contact OFET configuration (Figure 2-4(a)). Under the polarizing optical microscope, the BTBDT microribbon displays homogeneous birefringence (Figure 2-4(b)), ensuring its crystalline nature and macroscopically uniform molecular orientation. The flat and sheet-like morphologies of the crystals are favorable for the formation of close contacts between the gate insulator and the crystal all over its surface. In the out-of-plane X-ray diffraction (XRD) pattern of BTBDT crystals, predominant peaks assignable to (00$l$) reflections are clearly observed (Figure 2-4(c)). The first-order diffraction peak with the $d$-spacing of 1.74 nm is coincident with the molecular length of BTBDT (1.72 nm), indicating that the molecules are arranged with their long axes perpendicular onto the substrate (layer-by-layer assembly) to form a lamellar structure.

We envision that the self-organization into such well-defined 1D microribbons driven by strong intermolecular interactions will facilitate efficient charge carrier transport along the crystal longitudinal direction in OFET applications.

\textbf{Figure 2-4.} (a) Schematic representation of OFET based on single-crystal microribbons. (b) Polarizing optical microscopic image of a typical device with a BTBDT microribbon. The arrows indicate the directions of polarizer and analyzer axes. (c) XRD pattern of BTBDT
microribbons on a substrate. The inset shows a magnified view.
Likewise, the out-of-plane XRD pattern for the TTBDT microribbons exhibits a set of (00l) reflections (see Supporting Information). It is reasonably anticipated that TTBDT adopts an edge-on molecular orientation similar to the case of BTBDT, and the interlayer distance ($d = 1.67$ nm) calculated from the XRD pattern is identical to its molecular length of TTBDT (1.68 nm). On the other hand, furan-fused BFBDT tends to show tilted molecular orientation with respect to the substrate normal in the microribbons, as confirmed by the XRD pattern, regardless of the similar molecular framework.

Figure 2-5. Output (left panels) and transfer characteristics (right panels) of OFETs based on BTBDT (a,b), TTBDT (c,d), and BFBDT (e,f) microribbons operated in ambient conditions. The insets show the optical microscopic images of representative devices (scale bar: 20 µm).
Table 2-2. OFET characteristics of thienoheptacenes\textsuperscript{a})

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{\text{max}}$\textsuperscript{b)} (cm$^2$/Vs)</th>
<th>$\mu_{\text{ave}}$\textsuperscript{c)} (cm$^2$/Vs)</th>
<th>$V_{\text{th}}$\textsuperscript{d)} (V)</th>
<th>$I_{\text{on}}/I_{\text{off}}$\textsuperscript{e)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTBDT</td>
<td>0.47</td>
<td>0.27 ± 0.12</td>
<td>−16</td>
<td>$10^6$</td>
</tr>
<tr>
<td>TTBDT</td>
<td>0.10</td>
<td>0.08 ± 0.02</td>
<td>−3</td>
<td>$10^5$</td>
</tr>
<tr>
<td>BFBDT</td>
<td>0.04</td>
<td>0.02 ± 0.01</td>
<td>−48</td>
<td>$10^4$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}) Measured in ambient conditions at room temperature. \textsuperscript{b}) The maximum hole mobility recorded. \textsuperscript{c}) The average value obtained for 8 individual devices. \textsuperscript{d}) Threshold voltage was determined by extrapolating the $|I_D|^{1/2}$ vs $V_G$ plot to $I_D = 0$ (cf. Figure 3). \textsuperscript{e}) On/off current ratio was determined from the $I_D$ at $V_G = 0$ V ($I_{\text{off}}$) and $V_G = −100$ V ($I_{\text{on}}$).

It has been found that the devices featuring single-crystal microribbons of BTBDT, TTBDT, and BFBDT are indeed well-operated as p-type transistors under ambient conditions. Representative output and transfer characteristics of the OFETs are highlighted in Figure 5, where the field-effect mobilities ($\mu$) could be evaluated from the transfer properties in the saturation regime ($V_D = −100$ V).\textsuperscript{10} Table 2-2 summarizes the OFET characteristics of the thienoacene microribbons. Among those devices, the BTBDT-based ones show the highest electrical performance presumably due to the formation of the layer-by-layer structure with more effective intermolecular interactions. The hole mobility of the BTBDT-based devices reaches the value as large as 0.47 cm$^2$/Vs (on average 0.27 cm$^2$/Vs from eight individual devices) with on/off current ratio ($I_{\text{on}}/I_{\text{off}}$) of $10^6$, and threshold voltage ($V_{\text{th}}$) of −16 V (Figure 5a,b). Previously, it has been reported that thinner crystals often lead to better OFET performances because the bulk resistance should reduce with decreasing active-layer thickness in the bottom-gate, top-contact OFETs.\textsuperscript{11} In the present study, however, all of microribbons formed by $\pi$-extended thienoacenes are thin enough (< 100 nm) to minimize the effects of the resistance, so that can fabricate high performance single-crystal transistors.

The OFETs employing the TTBDT microribbons likewise give relatively high hole mobility up to 0.10 cm$^2$/Vs (Figure 5c,d); whereas the mobility for the BFBDT-based devices (0.04 cm$^2$/Vs; Figure 5e,f) is one order of magnitude lower than that obtained with BTBDT. The lower mobility for BFBDT-based devices should be attributed to less effective intermolecular $\pi$-overlap in the crystal by replacing two outer thiophene rings with furan rings, which can be seen from the photophysical and XRD data. Note that the threshold
voltages ($V_{th}$) obviously decrease in the order of BFBDT > BTBDT > TTBDT. This propensity is in accordance with reduction of the energy difference between the HOMO level of the thienoacene semiconductors (see Table 2-1) and the work function of the gold electrodes (ca. −5.1 eV).  

### 2.6 Conclusions

We have designed and synthesized π-extended thienoacenes, BTBDT, TTBDT, and BFBDT, as a novel platform for $p$-type organic semiconductors. As revealed by their optical and electronic characterization, the thienoacenes still possess relatively large HOMO–LUMO energy gaps and higher stability, compared to conventional hydrocarbon oligoacenes such as pentacene, in spite of their elongated π-systems with seven fused rings. The OFETs employing BTBDT single-crystal microribbons exhibit excellent OFET performance even in air, with hole mobility as high as 0.47 cm$^2$/Vs and on/off ratio of approximately $10^6$. 
2.7 References


[10] Field-effect mobilities (µ) of the devices were calculated in the saturation regime using the equation: \( I_D = \frac{W}{2L} \mu C_i (V_G - V_{th})^2 \), where \( I_D \) is the source–drain current, \( W \) and \( L \) are channel width and length, respectively, \( C_i \) is the capacitance per unit area of the gate dielectric (10.9 nF/cm\(^2\)), \( V_G \) is the gate voltage, and \( V_{th} \) is the threshold voltage.


Chapter 3

High-Performance Field-Effect Transistors Based on Organic Single-Crystal Microribbons and Microsheets of Solution-Processed Dithieno[3,2-b:2',3'-d]thiophene Derivatives
3.1 Introduction

One-dimensional (1D) organic nano- or microstructures have been intensively developed in recent years because of their high crystallinity, good process ability, flexibility, and potential for large area fabrication. Relative to many other materials currently being studied, fused-ring thienoacenes have more rigid structures, better conjugation, and larger band gaps. Furthermore, the π-extended system in such molecules is expected to provide more efficient π-orbital overlap and lead to high charge carrier mobility. Particularly, in sulfur-rich annulated oligomers, the molecular packing is characterized by a combination of multiple S···S interactions and π-π interactions, which can increase the effective dimensionality of the electronic structure, leading to enhanced transport properties. Relevant examples are sulfur decorated oligoacenes, in which S···S interactions provide an alternative charge transport pathway other than π-π interactions. Unfortunately, there are only a few examples using fused thiophene systems for organic field-effect transistors because of the limited synthetic approaches and the poor solubility of these compounds.

Another effective approach is to obtain good ordering is to use the self-assembly of organic molecules induced by alkyl groups. Alkyl groups can act as the driving force for molecular ordering in the solid state owing to van der Waals intermolecular interactions between the groups that subsequently lead the semiconducting core to highly-ordered packing, thus enhancing carrier mobility. Furthermore, alkyl groups can improve the solubility of molecules in a variety of organic solvents.

In this chapter, we focus on developing fused thiophene systems that are highly soluble in organic solvents and can be synthesized with very simple methods based on a core of dithieno[3,2-b:2',3'-d]thiophene combined with alkyl side chains. By choosing this structure, 1D nano and microstructures can be formed because of the van der Waals interactions between the alkyl chains and S···S interactions between neighboring cores. Owing to the enhanced solubility and molecular interactions, one-dimensional (1D) single-crystalline microribbons of DTT-8 and microsheets of DTT-12 with structurally perfect single crystals are easily prepared by solution processing.
3.2 DTT-8 and DTT-12

Scheme 3-1 shows the synthetic routes for new semiconductors, 2,6-bis-(4-octyl-phenyl)dithieno[3,2-b;2',3'-d]thiophene (DTT-8, yield 89%) and 2,6-bis-(4-dodecyl-phenyl)dithieno[3,2-b;2',3'-d]thiophene (DTT-12, yield 86%), which were synthesized by palladium-catalyzed Suzuki coupling reactions. The molecules can be obtained in three steps with key intermediates of 2,6-dibromo-dithieno[3,2-b;2',3'-d]thiophene (4).

3.3 Experimental

3.3.1 Synthesis

The synthesis of DTT-8 and DTT-12 was completed according to the synthetic route in Scheme 3-1. Commercially available reagents and solvents were used without further purification unless otherwise noted. All of the reactions were performed under an N₂ atmosphere in dry solvents using standard Schlenk techniques. 2-(4-Octylphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2a) and 2-(4-dodecylphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2b) were prepared according to a method from literature, and were obtained as colorless oils in 92% and 65% yields, respectively. Dithieno[3,2-b;2',3'-d]thiophene (3) was purchased from Aldrich. The final products were purified by sublimation and characterized by MALDI-TOF mass spectra (MS), Elemental Analysis (EA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).
3. 3. 1. 1 Synthesis of 2,6-dibromodithieno[3,2-b:2',3'-d]thiophene (4)

N-bromosuccinimide (NBS, 4.57 g, 25.7 mmol) was added slowly to a stirred solution of 3 (2.47 g, 12.5 mmol) in dry DMF (50 mL) at 0 °C. The mixture was allowed to warm up to room temperature and stirred overnight. The reaction mixture was poured into water to form a precipitate. The precipitate was collected by filtration and washed with methanol. The product was recrystallized from CHCl₃/methanol and dried under vacuum to give 3 as an off-white solid (yield = 4.20 g, 95%). M.p. 171 °C. ¹H NMR (500 MHz, CDCl₃): 7.28 (s, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃): 139.11, 130.88, 123.23, 112.38. MS: m/z 353.64 [M]+. Anal. calcd (%) for C₈H₂Br₂S₃: C 27.13, H 0.57; found: C 27.38, H 0.61.

3. 3. 1. 2 Synthesis of 2,6-bis(4-octylphenyl)dithieno[3,2-b:2',3'-d]thiophene (DTT-8)
Pd(PPh₃)₄ (0.92 g, 0.8 mmol) and aqueous K₂CO₃ (2.0 M, 30 mL; Ar bubbled before use) were added to a mixture of 2a (5.57 g, 17.6 mmol) and 4 (2.83 g, 8.0 mmol) in dry THF (60 mL). The mixture was vigorously stirred for 24 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into water, and then extracted with CHCl₃. The combined organic layers were washed with water, and dried over anhydrous Na₂SO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: CHCl₃), recrystallized from CHCl₃/methanol, and dried under vacuum to afford DTT-8 as a yellow solid (yield = 4.08 g, 89%). This compound was further purified by repetitive temperature-gradient sublimation before use. Phase transition behavior: Cr 57 °C SmX 190 °C SmC 211 °C N 219 °C Iso (Abbreviations: Cr, crystalline phase; SmX, unidentified ordered smectic phase; SmC, smectic C phase; N, nematic phase; Iso, isotropic phase). ¹H NMR (500 MHz, CDCl₃): 7.55 (d, J = 7.8 Hz, 4H), 7.47 (s, 2H), 7.22 (d, J = 7.8 Hz, 4H), 2.63 (t, J = 7.7 Hz, 4H), 1.67-1.60 (m, 4H), 1.35-1.25 (m, 20H), 0.88 (t, J = 6.6 Hz, 6H). ¹³C{¹H} NMR (125 MHz, CDCl₃): 145.23, 142.99, 141.50, 132.01, 130.00, 129.11, 125.63, 116.02, 35.71, 31.90, 31.40, 29.49, 29.33, 29.27, 22.68, 14.10. MS: m/z 572.15 [M]+. Anal. calcd (%) for C₃₆H₄₄S₃: C 75.47, H 7.74; found: C 75.42, H 7.69.

3. 3. 1. 3 Synthesis of 2,6-bis(4-dodecylphenyl)dithieno[3,2-b:2',3'-d]thiophene (DTT-12)
This compound was prepared in a fashion similar to DTT-8, using 2b (1.82 g, 4.9 mmol), 3 (0.78 g, 2.2 mmol), and Pd(PPh₃)₄ (0.17 g, 0.15 mmol). The product was obtained as a yellow
solid (yield = 1.30 g, 86%). This compound was further purified by repetitive temperature-gradient sublimation before use. Phase transition behavior: Cr 83 °C SmX1 119 °C SmX2 167 °C N 194 °C Iso. 1H NMR (500 MHz, CDCl3): 7.55 (d, J = 8.2, 4H), 7.46 (s, 2H), 7.22 (d, J = 8.2 Hz, 4H), 2.63 (t, J = 7.8 Hz, 4H), 1.67-1.60 (m, 4H), 1.35-1.25 (m, 36H), 0.88 (t, J = 6.8 Hz, 6H). 13C{1H} NMR (125 MHz, CDCl3): 14 5.25, 143.00, 141.53, 132.03, 130.03, 129.11, 125.63, 116.02, 35.71, 31.94, 31.40, 29.68, 29.66, 29.61, 29.53, 29.37, 29.32, 22.70, 14.12. MS: m/z 684.34 [M]+. Anal. calcd (%) for C44H60S3: C 77.13, H 8.83; found: C 77.06, H 8.79.

3.3.2 OFET Device Fabrication

DTT-8 and DTT-12 were incorporated into OFETs with a bottom-gate and top-contact geometry. Single-crystal microribbons and microsheets of DTT-8 and DTT-12 were grown by drop casting. For all of the OFET devices, heavily doped n-type Si wafers with a thermally grown 300-nm-thick SiO2 layer were used as substrates. The SiO2/Si substrates were pretreated with a piranha solution at 90 °C for 0.5 h, and then cleaned by sonication in deionized water, acetone, and isopropanol in that order. Next, an approximately 30-nm-thick poly(methylmethacrylate) (PMMA) thin layer was dip-coated onto the SiO2/Si substrates as an additional dielectric to reduce charge trapping by the silanol groups on SiO2 in the final device.7 The hydrophilic PMMA also helps to make the drop-casting solution spread well on substrate and yield more high quality single crystals during casting. After dip coating, the substrates were annealed for 30 min in a glove box at 95 °C.

Single crystals were fabricated by drop-casting from a 0.4-1.0 mg/mL solution in 1,2-dichlorobenzene on to the PMMA-coated SiO2/Si substrates. The drop-cast solutions were then dried for 12h in a dry nitrogen-filled glove box at room temperature.

The devices were completed by evaporating gold through a shadow mask to define the source and drain electrodes (thickness of 50nm) with a channel length of 20–100 µm on top of the single-crystal microribbons and microsheets. The output and transfer characteristics of the OFETs were measured using an Agilent B1500A semiconductor parameter analyzer under ambient conditions at room temperature.
3.4 Optical Properties

The UV-vis absorption spectra (Figure 3-1(a)) of DTT-8 and DTT-12 in dichloromethane solution show absorption peaks at 373 nm and 374, respectively, and the peaks of drop-cast films are located at 362 nm and 364 nm for DTT-8 and DTT-12, respectively. The absorption spectra of both DTT-8 and DTT-12 in drop-cast films blue shift by about 10 nm compared to solution. These shifts are indicative of the formation of H-aggregates with close π-stacking in a face-to-face arrangement, which has previously been observed in crystalline dithieno[3,2-b:2',3'-d]thiophene derivatives.8 The band gap estimated from absorption edges of the drop-cast films is 2.91 eV for both compounds, which shows that these compounds are not easily oxidized and should have good stability in air.9 The HOMO energy levels of DTT-8 and DTT-12 calculated from the onset potentials of the photoelectron yield spectra measured by AC-3 (Figure 3-1(b)) are 5.08 and 5.12 eV, respectively. The LUMO levels of DTT-8 and DTT-12 were calculated roughly from the band gaps and HOMO levels as -2.17 eV and -2.21 eV, respectively. Moreover, the HOMO levels of these materials also match well with the workfunction of a gold electrode (-5.1 eV),10 which could enhance the hole injection between the electrode and semiconductor and improve the device performance.

Figure 3-1. Characterizations of DTT-8 and DTT-12: (a) UV-vis absorption spectra in CH₂Cl₂ solutions and drop-cast films. (b) Photoelectron spectroscopy.
Table 3-1. Optical properties of DTT-8 and DTT-12 in solution and drop-cast films

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{abs}} \text{a)} ) (nm)</th>
<th>( \lambda_{\text{abs}} \text{b)} ) (nm)</th>
<th>HOMO\text{c)} (eV)</th>
<th>LUMO\text{d)} (eV)</th>
<th>( E_g \text{d)} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTT-8</td>
<td>373</td>
<td>362</td>
<td>-5.08</td>
<td>-2.28</td>
<td>2.8</td>
</tr>
<tr>
<td>DTT-12</td>
<td>374</td>
<td>364</td>
<td>-5.12</td>
<td>-2.32</td>
<td>2.8</td>
</tr>
</tbody>
</table>

a) UV/vis absorption maxima in CH\(_2\)Cl\(_2\) solvent. b) UV/vis absorption maxima in drop-cast films. c) Determined by photoelectron spectroscopy (AC-3). d) LUMO = HOMO + \( E_g \), in which the optical energy gap, \( E_g \), was derived from the absorption onset of the drop-cast film.

3. 5 Single-Crystal Structure and Molecular Packing

Single crystals of DTT-8 and DTT-12 were easily grown from 1,2-dichlorobenzene and methanol for X-ray crystallography studies. The DTT-8 crystals belong to the orthorhombic crystal system, with 6 molecules in the unit cell and parameters of \( a = 70.25(3) \) \( \text{Å} \), \( b = 7.333(3) \) \( \text{Å} \), and \( c = 5.822(2) \) \( \text{Å} \). As shown in Figure 3-2(a), the DTT-8 molecules adopt a lamella-like structure in the \( a-c \) plane, which is similar to the packing of C\(_n\)-BTBT molecules in crystals.\text{11} In addition, a 2D network of intermolecular interaction exists through the short S···C contact distance (3.32 \( \text{Å} \)) between the edge-to-face molecules and the short S···S contact distance (3.34 \( \text{Å} \)) between the edge-to-edge molecules, which are both shorter than the sum of the corresponding van der Waals radii of S···C (3.56 \( \text{Å} \)) and S···S (3.68 \( \text{Å} \)) (Figure 3-2(b)).

The single crystals of DTT-12 also form an orthorhombic crystal system and exhibit a lamella-like structure in the \( a-c \) plane (Figure 3-2(c)). The unit cell of DTT-12 has dimensions of \( a = 88.90(8) \) \( \text{Å} \), \( b = 7.391(7) \) \( \text{Å} \), and \( c = 5.846(5) \) \( \text{Å} \). Again, intermolecular interactions exists through a short S···C contact distance (3.34 \( \text{Å} \)) between the edge-to-face molecules and a short S···S contact distance (3.36 \( \text{Å} \)) between the edge-to-edge molecules (Figure 3-2(d)). Furthermore, mobility has the potential to be high in these molecules with strong intermolecular interactions because interaction in closely packed molecules can lead to greater overlap of \( \pi \)-orbitals and consequently promote charge transport.\text{12}
Figure 3-2. Single crystal structure of DTT-8 and DTT-12: (a, c) lamella structure in the a-c plane. (b, d)) highly ordered S···S interactions within the c axis.

3.6 Organic Field-Effect Transistor Properties

After the drop-casting, either microribbons or microsheets were formed (Figure 3-3(a, c)) depending on the length of the alkyl-chains. The single-crystal microribbons had lengths of 200-500 μm, widths of 4-50 μm, and thicknesses <300 μm, while the microsheets had lengths, widths, and thicknesses of 90-200 μm, 40-100 μm, and <100 μm, respectively. Typical single
crystals scanned by an atomic force microscope (AFM) exhibit a highly uniform width and smooth surface (Figure 3-3(b,d)). The surface quality is expected to strongly influence carrier transport properties in OFETs because the field-induced carriers are mostly confined to the vicinity of the interface between the semiconductor and the gate dielectric. The high quality, smooth surface of these crystals may help to achieve high mobility in completed devices.

Figure 3-3. Growth method of self-assembled single crystals by drop-casting. Microribbons of DTT-8: (a) after drop-casting and drying for 12h (scale bar: 100 μm). (b) AFM image of single crystals (scale bar: 5 μm). Microsheets of DTT-12: (c) after drop-casting and drying for 12h (scale bar: 100 μm) (d) AFM image of single crystals (scale bar: 5 μm).

From the drop-cast crystals, OFETs with channel lengths ($L$) ranging from 20 to 100 μm and channel widths ($W$) from 4-100 μm were fabricated. The electrical characteristics of the OFETs measured at room temperature in ambient atmosphere are shown in Figure 3-4. The field-effect mobility was calculated in the saturation regime according to Equation 2 (see Chapter 1), and the extracted OFET parameters are summarized in Table 3-2. The highest mobility measured in the DTT-8 microribbons was 10.2 cm²/Vs with an on/off ratio of $10^7$. 

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and threshold voltage of -22V, while the DTT-12 microsheets achieved a mobility of 1.8 cm²/Vs with an on/off ratio of 10⁵ and a threshold voltage of -26V. The trend of higher mobility for DTT-8 compared to DTT-12 holds over several devices as the average mobilities of 8 devices were 5.3 and 0.9 cm²/Vs for the microribbons and microsheets, respectively (characteristics and parameters summarized in Figure 3-5 and Table 3-3).

![Figure 3-4. Illustrations of OFET based on single-crystal (a) microribbons of DTT-8 and (d) microsheets of DTT-12. FET characteristics of microribbons and microsheets: (b, c) output characteristics and (e, f) transfer characteristics.](image)

**Table 3-2.** OFET characteristics of DTT-8 and DTT-12

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \mu_{\text{max}} ) b) (cm²/Vs)</th>
<th>( \mu_{\text{ave}} ) c) (cm²/Vs)</th>
<th>( V_{\text{th}} ) d) (V)</th>
<th>ON/OFF ratio e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTT-8</td>
<td>10.2</td>
<td>5.3</td>
<td>-22</td>
<td>( 10^7 )</td>
</tr>
<tr>
<td>DTT-12</td>
<td>1.8</td>
<td>0.9</td>
<td>-26</td>
<td>( 10^5 )</td>
</tr>
</tbody>
</table>

a) Measured in ambient conditions at room temperature. b) The maximum hole mobility recorded. c) The average value obtained for 8 individual devices. d) Threshold voltage determined by extrapolating the \( |I_G|^{1/2} \) vs \( V_G \) plot to \( I_D = 0 \). e) On/off current ratio determined from the \( I_D \) at \( V_G = 0 \) (\( I_{\text{on}} \)) and \( V_G = -80 \) V (\( I_{\text{off}} \)).
Until now, the shortest intermolecular S···S contact distant that had been reported in a high hole mobility material was approximately 3.45 Å.\textsuperscript{14} The analyses in this study suggest that the new materials reported here obtained even shorter intermolecular S···S contact distant of 3.34 Å. This short length is thought to be one of the key reasons that such high mobilities could be achieved. However, the considerable difference in mobility between DTT-8 and DTT-12 despite having similar S···S contact distant indicates that other factors are also at work.

Although, the structures of the microribbons and microsheets ascertained by the single crystal X-ray analysis were almost similar, the approximately six-fold increase in mobility for microribbons compared to microsheets might be explained by differences in crystal growth on the SiO\textsubscript{2} substrates. One possibility is that the c-axis epitaxial growth rate of DTT-8 single crystal was faster than that of DTT-12. Though not expected to be large since intermolecular spacing in the primary direction of current flow, the c-axis, is almost unchanged, the extent of the effects of the longer alkyl chain length and a dimension are also not clear. More studies will be needed to further understand the exact reasons for the difference in carrier mobility between DTT-8 and DTT-12.

Figure 3-5. FET characteristics for 8 individual devices: (a) output characteristics of DTT-8 microribbons and (b) output characteristics of DTT-12 microsheets.
Table 3-3. Key OFET parameters of DTT-8 and DTT-12 for 8 individual devices a)

<table>
<thead>
<tr>
<th>Compound</th>
<th>channel widths (µm)</th>
<th>channel lengths (µm)</th>
<th>µ (cm²/Vs)</th>
<th>Vᵇ</th>
<th>I on/I off</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTT-8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>17.7</td>
<td>38.6</td>
<td>10.2</td>
<td>-22</td>
<td>10⁷</td>
</tr>
<tr>
<td>2</td>
<td>19.7</td>
<td>43.0</td>
<td>3.8</td>
<td>-25</td>
<td>10⁷</td>
</tr>
<tr>
<td>3</td>
<td>9.4</td>
<td>42.3</td>
<td>7.0</td>
<td>-25</td>
<td>10⁷</td>
</tr>
<tr>
<td>4</td>
<td>21.2</td>
<td>51.3</td>
<td>3.5</td>
<td>-24</td>
<td>10⁷</td>
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<tr>
<td>5</td>
<td>21.1</td>
<td>50.2</td>
<td>4.0</td>
<td>-29</td>
<td>10⁶</td>
</tr>
<tr>
<td>6</td>
<td>16.2</td>
<td>39.5</td>
<td>3.4</td>
<td>-29</td>
<td>10⁵</td>
</tr>
<tr>
<td>7</td>
<td>19.8</td>
<td>42.1</td>
<td>3.9</td>
<td>-34</td>
<td>10⁶</td>
</tr>
<tr>
<td>8</td>
<td>3.8</td>
<td>68.1</td>
<td>6.5</td>
<td>-48</td>
<td>10⁷</td>
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<tr>
<td>DTT-12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>54.3</td>
<td>54.7</td>
<td>1.81</td>
<td>-26</td>
<td>10⁵</td>
</tr>
<tr>
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<td>69.2</td>
<td>21.6</td>
<td>1.01</td>
<td>-43</td>
<td>10⁵</td>
</tr>
<tr>
<td>3</td>
<td>118.0</td>
<td>49.9</td>
<td>0.57</td>
<td>-35</td>
<td>10⁷</td>
</tr>
<tr>
<td>4</td>
<td>104.6</td>
<td>53.4</td>
<td>0.65</td>
<td>-36</td>
<td>10⁶</td>
</tr>
<tr>
<td>5</td>
<td>60.1</td>
<td>41.2</td>
<td>0.60</td>
<td>-31</td>
<td>10⁶</td>
</tr>
<tr>
<td>6</td>
<td>65.0</td>
<td>90.7</td>
<td>1.00</td>
<td>-30</td>
<td>10⁵</td>
</tr>
<tr>
<td>7</td>
<td>41.1</td>
<td>72.0</td>
<td>0.75</td>
<td>-16</td>
<td>10⁵</td>
</tr>
<tr>
<td>8</td>
<td>52.2</td>
<td>42.1</td>
<td>0.65</td>
<td>-25</td>
<td>10⁴</td>
</tr>
</tbody>
</table>

a) Measured in ambient conditions at room temperature. b) Threshold voltage determined by extrapolating the |I_D|½ vs V_G plot to I_D = 0. c) On/off current ratio determined from the I_D at V_G = 0 V (I_off) and V_G = −80 V (I_on).

3. 6 Conclusions

New organic semiconducting molecules based on dithieno[3,2-b;2’,3’-d]thiophene that could easily be fabricated into high-quality, single-crystal microribbons and microsheets by solution drop-casting were designed and synthesized using a relatively simple synthetic method. The molecules pack in a highly-ordered fashion to form a lamella-like array in the a-c plane in which the side-by-side intermolecular S⋯S interaction lengths are 3.34 Å and 3.36 Å in DTT-8 microribbons and DTT-12 microsheets, respectively, which are some of the shortest reported to date. This highly-ordered packing is driven by the intermolecular S⋯S...
interactions between alkyl chains which can facilitate the self-assembly. Single-crystal OFETs based on individual microribbons and microsheets were fabricated and found to exhibit excellent electric performance showing the highest mobility of 10.2 cm²/Vs in OFETs using single crystal microribbons, which is about 6 times higher than mobility in the microsheets.
Chapter 3. Sulfur-Containing Thienoacenes

Reference


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Chapter 4

Summary
In this research, two strategies were employed for the design and synthesis of new high-performance p-type organic semiconductors for organic field-effect transistors. One strategy focused on the application of π-extended heteroacenes, while the other explored sulfur-containing thienoacene-based materials. The molecular and film properties of the synthesized molecules were characterized, and performance of the compounds in OFETs was measured.

The first strategy (Chapter 2) dealt with new π-extended heteroacenes that include thiophene and/or furane rings and exhibit highly symmetric structures. We successfully synthesized the seven-ring fused π-extended heteroacenes bisthieno[2,3-d;2',3'-d']benzo[1,2-b;4,5-b']dithiophene (BTBDT), bisthieno[2',3':4,5]thieno[2,3-d;2',3'-d']benzo[1,2-b;4,5-b']dithiophene (TTBDT), and bisthieno[2,3-d;2',3'-d']benzo[1,2-b;4,5-b']dithiophene (BFBDT) as a novel series of p-type organic semiconductors. The thienoacenes have a large HOMO-LUMO energy gap and high stability inspite of their elongated π-systems due to their benzenoid character. OFETs employing single-crystal microribbons of the compounds exhibited good performance even in air, with hole mobilities as high as 0.5 cm²/Vs.

The second part (Chapter 3) dealt with OFETs using fused thiophene rings with favorable properties owing to S···S and S···π intermolecular interactions, which enhance intermolecular interactions, which promote compressed highly-ordered packing. DTT-8 and DTT-12 were synthesized using a dithieno[3,2-b;2',3'-d]thiophene core unit with side alkyl chains.

Single-crystal microribbons and microsheets of the compounds could be readily fabricated by drop-casting method. Single-crystal microribbons of DTT-8 and microsheets of DTT-12 were found to have very close intermolecular S···S contacts (3.34 Å and 3.36 Å) and S···π contacts (3.32 Å and 3.34 Å), respectively. The highest mobilities of DTT-8 and DTT-12 reached values of 10.2 and 1.8 cm²/Vs with on/off current ratios ($I_{on}/I_{off}$) of $10^7$ and $10^5$, respectively.

Chapter 2 showed that seven-ring-fused heteroacenes having hetero atoms (C, S, or O) are a viable system for obtaining better intermolecular π···π interaction, stability, and high mobility. The molecules using a dithieno[3,2-b:2',3'-d]thiophene core with side alkyl chains in Chapter
3 demonstrated that the better S···S intermolecular interactions offered by this core-chain combination are another viable route for better stability, and high mobility. The origin of the difference in mobility between **DTT-8** and **DTT-12** is still not completely understood, so further studies will be needed to better relate the effect of the length of the side alkyl chains on the crystal shape and device properties. Following the paths demonstrated in this research, S···S intermolecular interactions, side alkyl chain, and π-extended heteroacenes are expected to play a large role in the continued development of high performance materials for OFETs.
Appendix
Figure A1. $^1$H and $^{13}$C$^{1}$H NMR spectra of compound 2.
Figure A2. $^1$H and $^{13}$C{$_t^1$H} NMR spectra of compound 3.
Figure A3. $^1$H and $^{13}$C$^{1}$H NMR spectra of compound 4.
Figure A4. MALDI-TOF mass spectra of thienoacenes. Insets show the theoretical isotope patterns of the compounds.
Figure A5. Photoluminescence spectra of thienoacenes in (a) CH$_2$Cl$_2$ solution and (b) thin films.

Figure A6. XRD patterns of (a) TTBDT and (b) BFBDT microribbons.

The insets show postulated structural models.
Figure A7. $^1$H and $^{13}$C{$^1$H} NMR spectra of compound DTT-8.
Figure A8. $^1$H and $^{13}$C{$^1$H} NMR spectra of compound DTT-12.
Figure A9. DSC thermograms of (a) DTT-8 and (b) DTT-12 liquid crystals at a rate of 5 °C/min. The insets show the optical microscopic images (scale bar: 200 µm). (Abbreviations: Cr, crystalline phase; SmX, unidentified ordered smectic phase; SmC, smectic C phase; N, nematic phase; Iso, isotropic phase).
List of Publications

Original papers

[1] Organic Single-Crystal Transistors Based on π-Extended Heteroheptacene Microribbons

Y. S. Yang, T. Yasuda, H. Kakizoe, H. Mieno, H. Kino, Y. Tateyama, C. Adachi, 2013. (To be submitted)

Joint papers


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