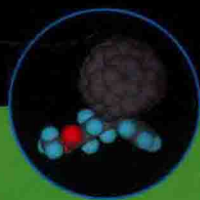


Self-Organized Organic Semiconductors

From Materials to Device Applications



Edited by **QUAN LI**

 **WILEY**

SELF-ORGANIZED ORGANIC SEMICONDUCTORS

From Materials to Device Applications

Edited by

Quan Li

Liquid Crystal Institute
Kent State University
Kent, Ohio



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SELF-ORGANIZED ORGANIC SEMICONDUCTORS

PREFACE

Organic semiconductors are attracting tremendous attention because of the promise of low cost and the possibility of roll-to-roll processing at ambient temperature and pressure. Among all organic semiconductors, self-organized organic semiconductors such as large π -conjugated liquid crystals and conjugated block copolymers undoubtedly represent a most exciting material today. The unique self-organized feature offers a brand new scientific frontier that holds immense opportunities as well as challenges in fundamental science that is opening the door for numerous applications such as organic photovoltaics, organic light-emitting diodes and organic field-effect transistors.

This book does not attempt to cover the whole field of self-organized organic semiconductors as this is extremely difficult to cover within a single book. Instead, the book focuses on the most fascinating topics in this field. Here self-organized organic semiconductors including crystal engineering organic semiconductors, conjugated block copolymers and cooligomers, charge transport and its modeling in liquid crystals, self-organized discotic liquid crystals, self-organized smectic liquid crystals, self-assembling of carbon nanotubes, and self-organized fullerene-based organic semiconductors are presented. The self-organized semiconducting materials, characterizations, and principles of devices are described. The applications of high-efficiency organic solar cells using self-organized materials and selective molecular assembly for bottom-up fabrication of organic thin-film transistors are also presented.

This book provides up-to-date and accessible coverage of self-organized semiconductors for graduate students and researchers in organic chemistry, polymer science, liquid crystals, materials science, material engineering, electrical engineering, chemical engineering, optics, optic-electronics, nanotechnology, and semiconductors. It can be used as a database and a reference by readers in both academia and industry. I sincerely hope that all those involved in research and education in this field will find the book to be useful.

Finally, I would like to express my gratitude to Jonathan Rose at John Wiley & Sons, Inc. for inviting us to bring this exciting field of research to a wider audience, and to all our distinguished contributors for their efforts. I am indebted to my wife Changshu and our two boys Daniel and Songqiao for their great support and encouragement.

Kent, Ohio
June 18, 2010

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CONTENTS

Preface	ix
Contributors	xi
1 Crystal Engineering Organic Semiconductors	1
<i>Joseph C. Sumrak, Anatoliy N. Sokolov, and Leonard R. MacGillivray</i>	
1.1 Introduction	1
1.2 Packing and Mobility of Organic Semiconductors	2
1.3 Overcoming the Packing Problem	4
1.4 A Modular Approach Toward Engineering π -Stacking	14
1.5 Conclusion	15
2 Conjugated Block Copolymers and Cooligomers	21
<i>Yongye Liang and Luping Yu</i>	
2.1 Introduction	21
2.2 Conjugated Copolymers/Cooligomers Containing Coil and Rod Blocks	22
2.3 Conjugated Copolymers/Cooligomers Containing All-Rod Blocks	31
2.4 Conclusion	35
3 Charge-Carrier Transport and Its Modeling in Liquid Crystals	39
<i>Jun-ichi Hanna and Akira Ohno</i>	
3.1 Introduction	39
3.2 General Features of Carrier Transport	42
3.3 Charge Transport Model for Liquid Crystals	53
3.4 Conclusion	74
4 Self-Organized Discotic Liquid Crystals as Novel Organic Semiconductors	83
<i>Manoj Mathews and Quan Li</i>	
4.1 Introduction	83
4.2 Semiconducting Properties of Discotic Liquid Crystals	85

4.3	Discotic Liquid Crystals with High Charge-Carrier Mobility	91
4.4	Processing of Discotic Materials into Active Semiconducting Layers	103
4.5	Applications of Semiconducting Discotic Liquid Crystals	112
4.6	Conclusion	119
5	Self-Organized Semiconducting Smectic Liquid Crystals	131
	<i>Ji Ma and Quan Li</i>	
5.1	Introduction	131
5.2	Smectic Phases and Structures	132
5.3	Characterization Techniques	135
5.4	Charge-Carrier Transport in Smectic Liquid Crystals	140
5.5	Devices and Applications	150
5.6	Conclusion and Outlook	157
6	Self-Assembling of Carbon Nanotubes	165
	<i>Liming Dai</i>	
6.1	Introduction	165
6.2	Self-Assembling of CNTs by van der Waals Forces	166
6.3	Self-Assembling of CNTs by Specific Chemical Interactions	167
6.4	Self-Assembling of CNTs by Charge Transfer Interactions	176
6.5	Self-Assembling of CNTs by DNA Pairing	180
6.6	Self-Assembling of CNTs by Asymmetric Functionalization	183
6.7	Concluding Remarks	188
7	Self-Organized Fullerene-Based Organic Semiconductors	195
	<i>Li-Mei Jin and Quan Li</i>	
7.1	Introduction	195
7.2	Fullerene-Based Liquid Crystalline Donor-Acceptor Blends	196
7.3	Fullerene-Based Liquid Crystalline Covalently Linked Donor-Acceptor Dyads	199
7.4	Fullerene-Based Hydrogen-Bonded Donor-Acceptor Ensembles	205
7.5	Fullerene-Based Donor-Acceptor Blends Linked by Other Noncovalent Interactions	208
7.6	Fullerene-Based Self-Assembled Monolayers	212
7.7	Conclusion and Outlook	217
8	High-Efficiency Organic Solar Cells Using Self-Organized Materials	225
	<i>Paul A. Lane</i>	
8.1	Introduction	225

8.2	Small-Molecule Solar Cells	231
8.3	Polymer Solar Cells	244
8.4	Concluding Remarks	258
9	Selective Molecular Assembly for Bottom-Up Fabrication of Organic Thin-Film Transistors	267
	<i>Takeo Minari, Masataka Kano, and Kazuhito Tsukagoshi</i>	
9.1	Introduction	267
9.2	Fabrication of OFET Array by Surface-Selective Deposition	269
9.3	Improvement of Self-Organized OFET Performance with Aromatic Sam	271
9.4	Formation of Single-Crystal OFETs by Surface-Selective Deposition	274
9.5	Formation of OFET Array on Plastic Substrate	276
9.6	Evaluation of Variance in Characteristics of Self-Organized OFETs	278
9.7	Inverter Circuit Configured from Self-Organized OFETs	278
9.8	All-Solution-Processed Assembly of OFET Arrays	279
9.9	Conclusion	283
	Index	289

Crystal Engineering Organic Semiconductors

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1.1. INTRODUCTION

Organic semiconductors are of great interest owing to the promise of low-cost flexible electronics (e.g., RFID tags, displays, e-paper) [1–3]. A variety of conjugated organic polymers and oligomers have been synthesized and studied as semiconductors [4]. Research has demonstrated semiconductors based on oligoacenes or oligothiophenes to be some of the most promising candidates for organic electronics. Pentacene has been one of the most widely studied organic semiconductors and has set a benchmark with room temperature mobilities as high as $35 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for ultrapure single crystals [5]. Oligomers, compared to polymer counterparts, offer samples of high purity and well-defined structure. While both polymer- and oligomer-based materials have been extensively studied for electronics application, the materials show varying mechanisms for charge transport. In oligomers charge-hopping between overlapping wavefunctions of nearest neighboring π -faces dominates the transport mechanism, while intrachain transport is observed in polymeric materials. Thus, the packing of small molecules in the solid state plays a key role in the charge transport properties [6]. In this chapter, we discuss the influence of solid-state packing and the effects of recent attempts to establish control over the placement of molecules on the electronic properties of organic semiconductor solids.

A prerequisite for a molecule to function as an organic semiconductor is the presence of an extended π -conjugated surface. The extended packing of these molecules within single crystals or thin films establishes a degree of overlap

between neighboring π -faces, which is characterized as the transfer integral. The extent of the overlap plays a great role in the increase of the ease of charge transport within a solid, or charge-carrier mobility. Indeed, studies have shown that cofacial stacking can lead to higher mobilities owing to increased orbital-orbital overlap between neighboring molecules [6, 7]. However, the π -surfaces of most commonly used organic semiconductors (i.e., pentacene and oligothiophene) tend to crystallize in a herringbone, or edge-to-face, motif. Edge-to-face packing is nonideal to achieve maximum performance of an organic semiconductor owing to poor orbital overlap. Thus it is of great value to establish control of π -orbital overlap within semiconductor solids.

Crystal engineering is the use of intermolecular interactions to assemble molecules into a specific solid-state arrangement to achieve desired physical and chemical properties [8]. Examples of such intermolecular forces include lipophilic, dipolar, and quadrupole interactions, as well as hydrogen bonding. Control of dimensionality in the solid state with noncovalent bonds has been realized through the formation of zero-dimensional (0-D), 1-D, 2-D, and 3-D assemblies [8]. Recently, great interest has developed in the utilization of crystal engineering as a bottom-up approach to achieve increased overlap of molecular orbitals between neighboring semiconductor molecules. Improvement in the control of intermolecular interactions could also be used to stabilize the lattice of the transport media, resulting in increased maximum charge-carrier mobilities [9].

With these ideas in mind, this chapter discusses crystal engineering strategies in the context of semiconductor solids. It is first important to understand the nature of the structural problem that essentially plagues oligomer-based semiconductors (i.e., crystal packing). From there, strategies are described that utilize a range of interactions from steric crowding to circumvent edge-to-face packing to attractive forces (e.g., lipophilic) to enforce face-to-face geometries. We also describe a modular approach developed in our laboratory that achieves face-to-face stacking through hydrogen bonding in the form of molecular cocrystals. It should be noted that while the strategies described herein may be applicable for thin-film devices, the structure of a thin film will not necessarily correlate to that of a single crystal [10].

1.2. PACKING AND MOBILITY OF ORGANIC SEMICONDUCTORS

Organic semiconductors consist of one or more classes of molecular species that possess an aromatic structure (e.g., acenes, thiophenes) (Fig. 1-1). These materials typically begin to demonstrate field effect transistor (FET) mobilities upon reaching four units of conjugation. Molecules based on the aromatic moieties can be either covalently linked through single bonds (e.g., α -linked, β -linked thiophenes) or fused together (e.g., pentacene). Initial research on transport in organic semiconductor solids focused on the unsubstituted derivatives of the aromatic molecules. Indeed, knowledge of the packing and structure of unsubstituted organic semiconductors is generally required to draw comparisons to substituted products.

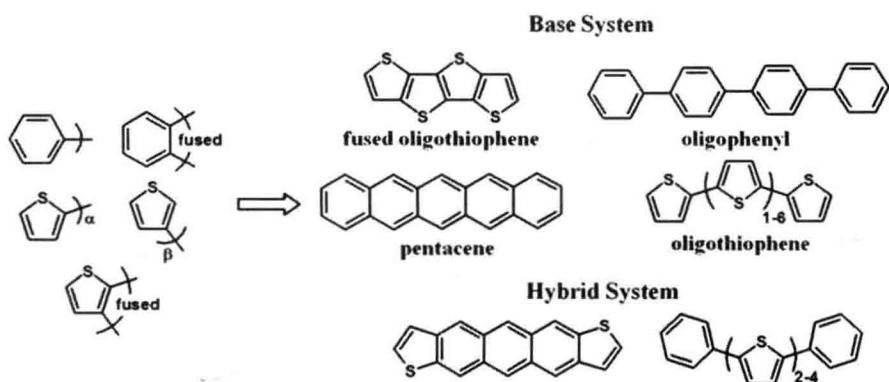


Figure 1-1 Base and hybrid organic semiconductors.

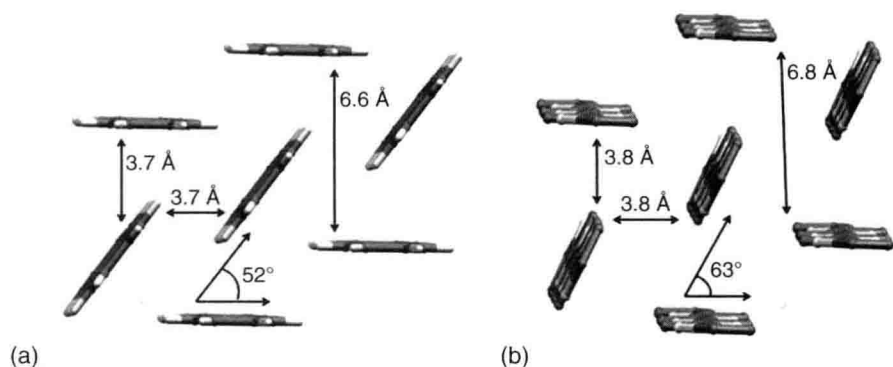


Figure 1-2 Crystal packing: a) pentacene and b) sexithiophene.

Of the oligoacenes, tetracene and pentacene have been the main focuses of research. Pure tetracene and pentacene pack in a similar manner (Fig. 1-2a) [11]. Both molecules exhibit herringbone packing that is directed by C-H $\cdots\pi$ interactions, with an angle approximately 52° between the planar surfaces of nearest-neighbor molecules. The shortest carbon-carbon (C-C) distance between pentacene and tetracene molecules in the solid state is approximately 3.7 \AA , with separations on the order of 6.6 \AA being between columns. Reported mobilities for pentacene are as high as $35 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for extremely pure single crystals [5]. Without rigorous purification, mobilities of approximately $3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ have been reported [12]. The highest reported mobility for a single crystal of unsubstituted tetracene is $1.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [13].

Oligothiophenes are of great interest owing to ease of synthesis and modifications. Thus far, the solid-state packings for all unsubstituted oligothiophenes up to octithiophene have been determined via single-crystal X-ray diffraction [14–17]. As with the oligoacene counterparts, oligothiophenes exhibit herringbone packing

Table 1-1 Mobilities of [*n*]-Oligothiophenes.

Number of Thiophenes	4	5	6	7	8
Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	0.006	0.08	0.075	0.17	0.33

in the solid state (Fig. 1-2b). The angle between planar surfaces of oligothiophenes is typically 63° , which is slightly higher than the oligoacenes. The shortest distance between two thiophene rings is on the order of 3.8 \AA . A distance of approximately 6.8 \AA separates thiophenes in the column of the herringbone structure. As expected, an increase in the number of thiophene rings in an oligothiophene tends to lead to an increase in mobility (Table 1-1).

1.3. OVERCOMING THE PACKING PROBLEM

The solid-state structures of unsubstituted organic semiconductors are not ideally suited to achieve high mobilities. To improve mobilities, the structures must be designed to produce more efficient π - π overlap. To this end, attempts to control the arrangements of organic semiconductors have typically involved modifying the intermolecular forces that govern the solid-state packing. Changes to packing have been accomplished through the introduction, or modification, of substituents along the periphery of semiconductor molecules. Steric interactions using bulky groups, for example, have been used to destabilize edge-to-face $\text{C-H} \cdots \pi$ forces. The introduction of bulky groups to obtain reduced π - π separations may appear counterintuitive; however, the approach has been reliable. Electronic interactions can also be used to compete with $\text{C-H} \cdots \pi$ interactions. Quadrupole and dipolar interactions, as well as hydrogen bonds, have all been used to improve π -stacking.

1.3.1. Steric Interactions to Prevent $\text{C-H} \cdots \pi$ Interactions

One method to improve packing has been the use of bulky side groups to destabilize or eliminate close $\text{C-H} \cdots \pi$ contacts. $\text{C-H} \cdots \pi$ forces are based on electrostatic interactions between the δ^+ charges of H-atoms located on the edges of the rings and the δ^- charges on the π -face of the internal ring C-atoms. With the driving force for edge-to-face packing eliminated, there is an increased likelihood for face-to-face stacking. The approach has been developed by Anthony et al., where a pentacene functionalized with triisopropylsilyl ethynyl (TIPS) groups not only prevented herringbone packing but improved solubility and stability [18, 19]. With a reduction in $\text{C-H} \cdots \pi$ interactions achieved, the TIPS-functionalized pentacene packed in a brick motif based on cofacial columns with a 3.5-\AA separation between nearest-neighbor acenes (Fig. 1-3). Whereas such changes to packing led to a significant improvement in π -orbital overlap compared to unsubstituted pentacene, control of a slip-stack arrangement of the pentacenes on a long molecular axis remained difficult to achieve [20]. Mobilities as high as $1.8 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ were obtained for TIPS-functionalized pentacenes prepared via solution process

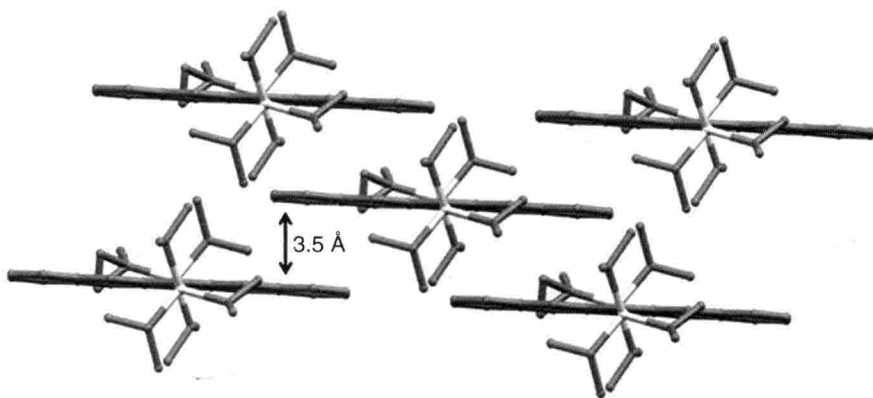


Figure 1-3 Slip-stacked packing of triisopropylsilyl ethynyl (TIPS) functionalized pentacene.

methods [21]. Anthony et al. have also successfully extended the method to hexacene and heptacene [22]. The method has been highly successful in both single crystals and thin-film devices, which demonstrates the robustness of steric interactions for potential applications in organic electronics.

Along with TIPS groups, phenyl groups have been used to reduce C–H \cdots π interactions. Ultrapure single crystals of 5,6,11,12-tetraphenyltetracene, or rubrene, have afforded a hole mobility of $20\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [23]. The mobility is significantly higher than that for single crystals of the parent tetracene [24]. The increase in mobility can be attributed to the increase in cofacial π -stacked interactions along the a -axis in single crystals of the molecule [25]. Mobilities of rubrene in thin films, however, have underperformed single crystals owing to difficulties in achieving crystalline films of the compound.

Nuckolls et al. have extended phenyl substitution to pentacene with a series of cruciform-based π -systems; specifically, with 6-phenyl-, 6,13-diphenyl-, 6,13-dithienyl-, 5,7,12,14-tetraphenyl-, 1,4,6,8,11,13-hexaphenyl-, and 1,2,3,4,6,8,9,10,11,13-decaphenylpentacene [26]. The phenyl substituents circumvented herringbone packing; however, the packing motifs varied depending upon number of phenyl substituents. A single phenyl substituent resulted in both edge-to-face and face-to-face packing in the solid. Hexaphenyl- and decaphenylpentacene packed in layered structures directed by edge-to-face C–H \cdots π interactions between the phenyl substituents with the pentacene backbones being separated by 5 Å. The resulting solids did not display measurable mobilities as thin films (Fig. 1-4a). The diphenyl-substituted pentacene packed cofacially; however, the long axis of nearest-neighbor acenes were oriented orthogonally and resulted in cagelike superstructures. The solid exhibited a mobility of $8 \times 10^{-5}\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (Fig. 1-4b). A mobility of $0.1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was obtained for the dithienyl derivative, which exhibited the greatest π - π overlap (Fig. 1-4c). Each of these methods circumvented C–H \cdots π interactions to vary the packing

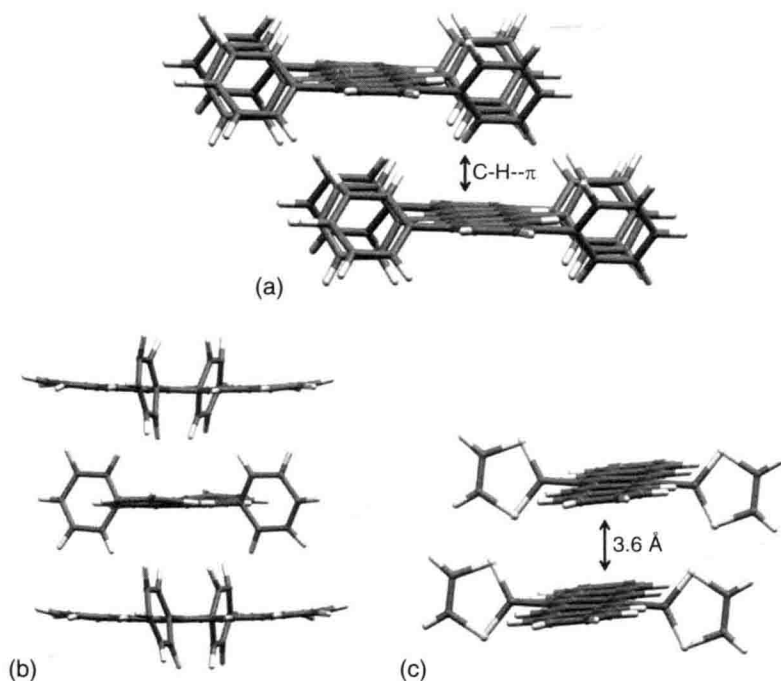


Figure 1-4 X-ray structures of layered packings: a) hexylphenyl-, b) diphenyl-, c) dithienyl-pentacene.

motifs. The lack of mobility in hexaphenyl- and decaphenyl-substituted pentacene demonstrated the importance of π - π overlap to improve mobility.

1.3.2. Alkyl-Alkyl Interactions

Alkyl chains are known to promote layered structures in the solid state through lipophilic interactions. Garnier et al. synthesized 2,5-dihexylsexithiophene (DH6T) to incorporate the self-assembly of alkyl chains into thin films of the semiconductor molecule [27]. Although X-ray diffraction (XRD) revealed the thin film to exhibit herringbone packing similar to unsubstituted sexithiophene (6T), mobility measurements showed a 40-fold increase compared to 6T when both were deposited at room temperature ($6T = 2 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, $\text{DH6T} = 8 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) [28]. The increase in thin-film mobility in α -alkyl-substituted oligothiophenes was attributed to an increase in long-range order owing to a change in the growth mechanism of the thin film from a 3-D island to a more 2-D layered structure (Fig. 1-5) [29]. Halik et al. compared diethyl, dihexyl, and didecyl α , ω -substituted sexithiophenes to study the impact of alkyl substituent length on mobility. Diethyl- and dihexyl-substituted sexithiophene were determined to exhibit superior thin-film mobilities compared to sexithiophene, with the respective mobilities being

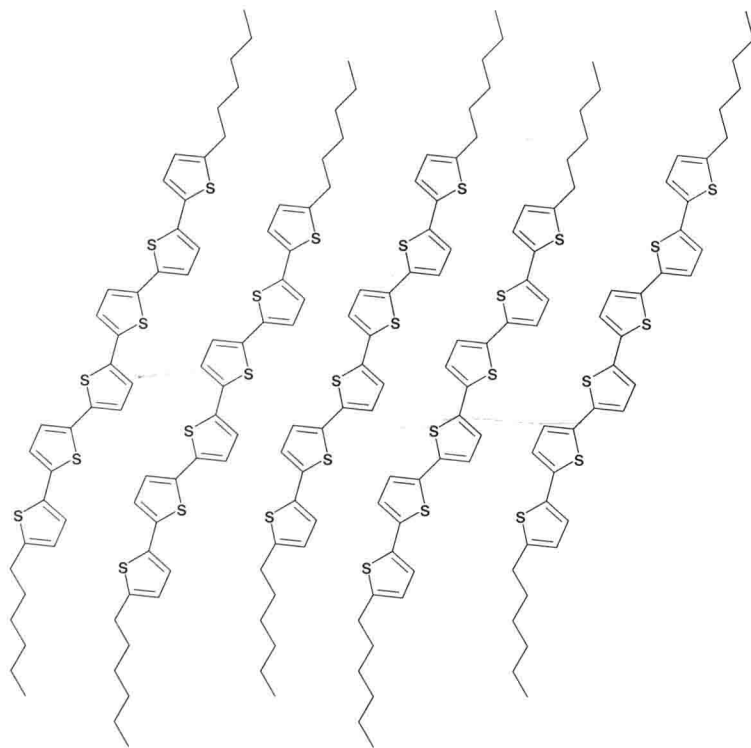


Figure 1-5 Schematic representation of DH6T thin film.

1.1 and $1.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. α,ω -Didecylsexithiophene, however, showed little improvement versus sexithiophene, with mobilities of 0.1 and $0.07 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively, suggesting an optimum alkyl substitution length [30].

More recent studies on alkyl-substituted organic semiconductors have involved a hybrid phenyl-thiophene system. Marks et al. demonstrated entirely solution-processed devices composed of 5,5'-bis(4-*n*-hexylphenyl)-2,2'-bithiophene (dHPTTP) that exhibited higher than expected mobilities ($0.07 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) for a system with a relatively small conjugated π -system [31]. Single-crystal studies on dHPTTP revealed the molecule to exhibit herringbone packing similar to most oligothiophenes (Fig. 1-6). The improvement in mobility was attributed to a decrease in traps in the thin film owing to alkyl-alkyl interactions similar to DH6T [32]. In related work, Bao et al. have synthesized a series of alkyl- and alkoxy-substituted bisphenylbithiophenes (PTTP) and bisphenylterthiophenes (PTTTP) to study side chain effects on mobility. It was discovered that branching in the side chain leads to a decrease in mobility. The decrease was attributed to increased steric interactions to an extent that prevented close packing and efficient π - π overlap. The growth modes of the branched substituents were also more 3-D, as opposed to the linear

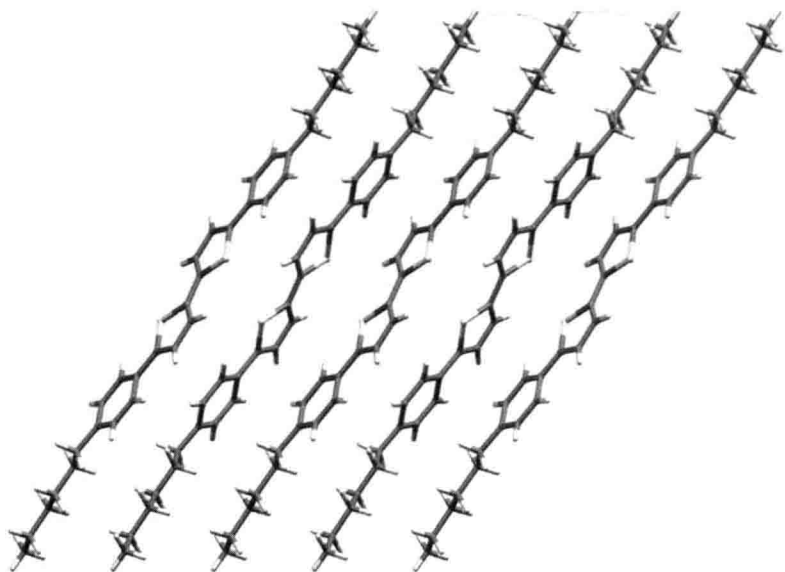


Figure 1-6 Crystal structure of dHPTTP.

chains, further contributing in the lowering of mobilities and making it difficult to decouple steric from growth mode effects. When the semiconductor core was changed from PTPP to PTTTP, the mobility peaked at a shorter side chain length, suggesting an optimal molecular dimension for charge transport [33]. The changes in alkyl lengths played an important role in altering the molecular packing, and thus can be considered a tool to gauge finer effects of packing on charge transport.

1.3.3. Dipolar Interactions

The introduction of dipolar interactions within an organic semiconductor molecule provides a means to enforce face-to-face π - π stacking arrangements. The arrangements are based on the stacked molecules adopting either an antiparallel or a parallel geometry. In this context, Kobayashi et al. have introduced chalcogens (O, S, Te) at the 9,10-position of anthracene and alkylthio groups at the 6,13-position of pentacene to induce π - π stacking through chalcogen-chalcogen interactions [34]. 9,10-Dimethoxyanthracene was determined to pack into a herringbone motif with a lack of heteroatom interactions. However, 9,10-bis(methylthio)-anthracene crystallized into 2-D sheets, directed by $S \cdots S$ interactions. Anthracene rings of adjacent stacked sheets formed 1-D π -stacked columns where the $S \cdots S$ interactions were preserved. The same packing motif was observed in the case of 6,13-bis(methylthio)pentacene (Fig. 1-7) [35]. 9,10-bis(methyltelluro)anthracene also formed sheets through $Te \cdots Te$ interactions [34]. Mobility measurements were not reported for the compounds.