

# 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  $\pi$ -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  $\pi$ -conjugated surface. The extended packing of these molecules within single crystals or thin films establishes a degree of overlap

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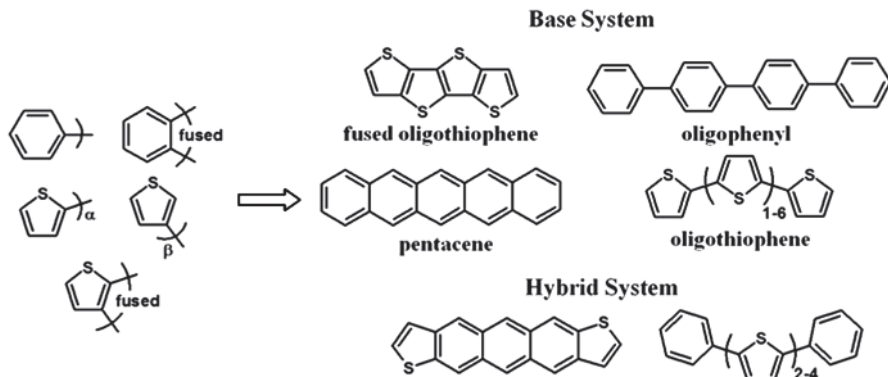
between neighboring  $\pi$ -faces, which is characterized as the transfer integral. The extent of the overlap plays a great role in the increase of the ease of charge transport within a solid, or charge-carrier mobility. Indeed, studies have shown that cofacial stacking can lead to higher mobilities owing to increased orbital-orbital overlap between neighboring molecules [6, 7]. However, the  $\pi$ -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  $\pi$ -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].

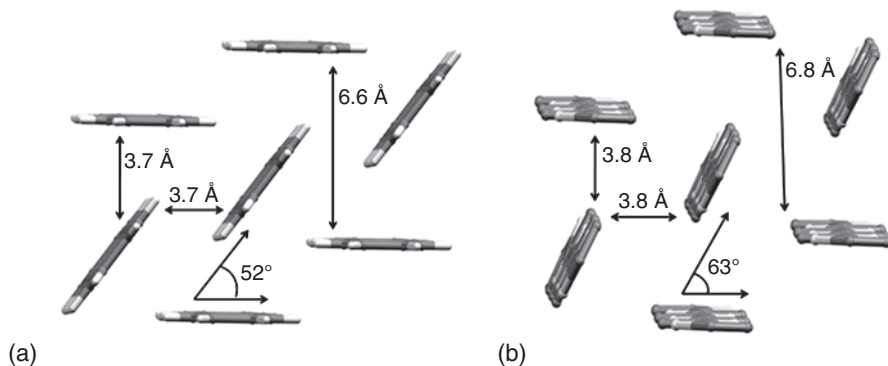
With these ideas in mind, this chapter discusses crystal engineering strategies in the context of semiconductor solids. It is first important to understand the nature of the structural problem that essentially plagues oligomer-based semiconductors (i.e., crystal packing). From there, strategies are described 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.,  $\alpha$ -linked,  $\beta$ -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... $\pi$  interactions, with an angle approximately  $52^\circ$  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 Å, with separations on the order of 6.6 Å 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 |

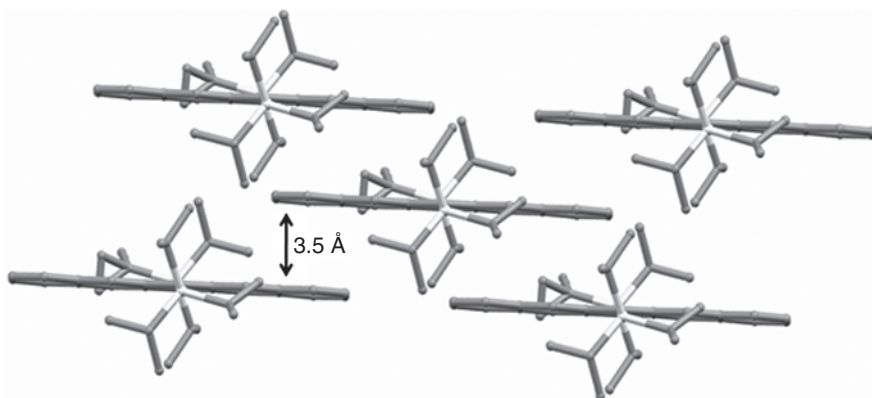
in the solid state (Fig. 1-2b). The angle between planar surfaces of oligothiophenes is typically  $63^\circ$ , which is slightly higher than the oligoacenes. The shortest distance between two thiophene rings is on the order of  $3.8 \text{ \AA}$ . A distance of approximately  $6.8 \text{ \AA}$  separates 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  $\pi$ - $\pi$  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  $\pi$ - $\pi$  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  $\pi$ -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  $\delta^+$  charges of H-atoms located on the edges of the rings and the  $\delta^-$  charges on the  $\pi$ -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 triisopropylsilylethynyl (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  $3.5\text{-\AA}$  separation between nearest-neighbor acenes (Fig. 1-3). Whereas such changes to packing led to a significant improvement in  $\pi$ -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

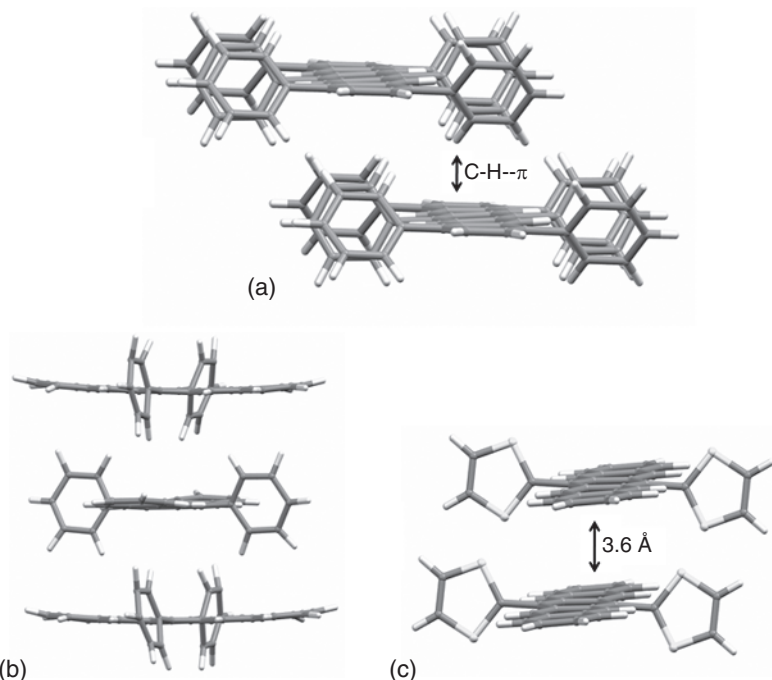


**Figure 1-3** Slip-stacked packing of triisopropylsilylethynyl (TIPS) functionalized pentacene.

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 $\cdots$  $\pi$  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  $\pi$ -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  $\pi$ -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 $\cdots$  $\pi$  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  $\pi$ - $\pi$  overlap (Fig. 1-4c). Each of these methods circumvented C–H $\cdots$  $\pi$  interactions to vary the packing

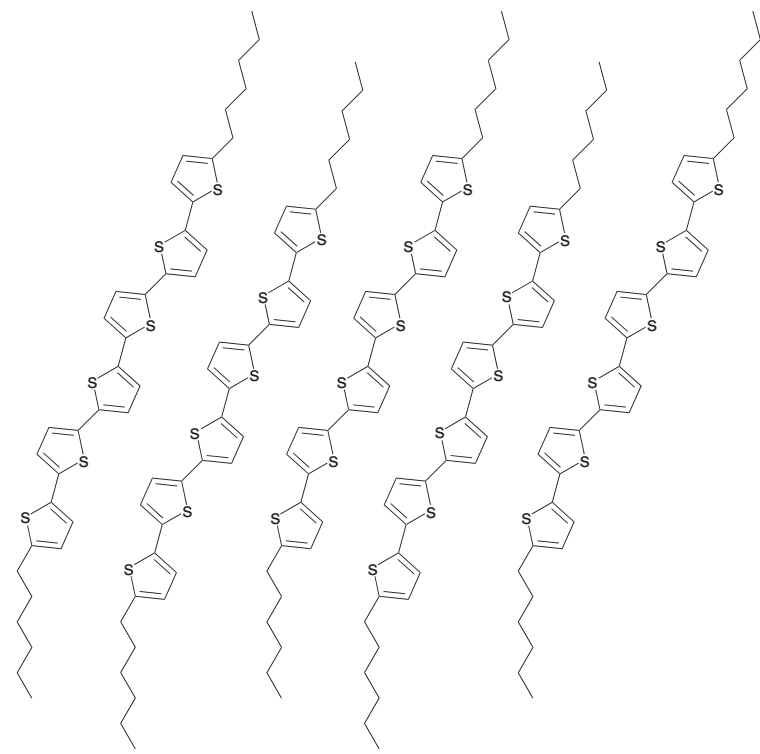


**Figure 1-4** X-ray structures of layered packings: a) hexylphenyl-, b) diphenyl-, c) dithienyl-pentacene.

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

### 1.3.2. Alkyl-Alkyl Interactions

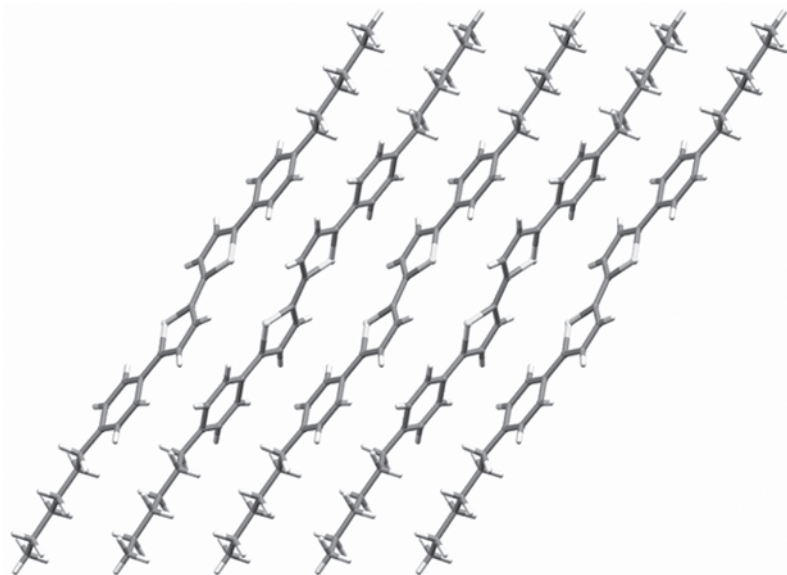
Alkyl chains are known to promote layered structures in the solid state through lipophilic interactions. Garnier et al. synthesized 2,5-dihexylsexithiophene (DH6T) to incorporate the self-assembly of alkyl chains into thin films of the semiconductor molecule [27]. Although X-ray diffraction (XRD) revealed 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  $\alpha$ -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  $\alpha$ ,  $\omega$ -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  $1.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ .  $\alpha,\omega$ -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  $\pi$ -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  $\pi$ - $\pi$  overlap. The growth modes of the branched substituents were also more 3-D, as opposed to the linear



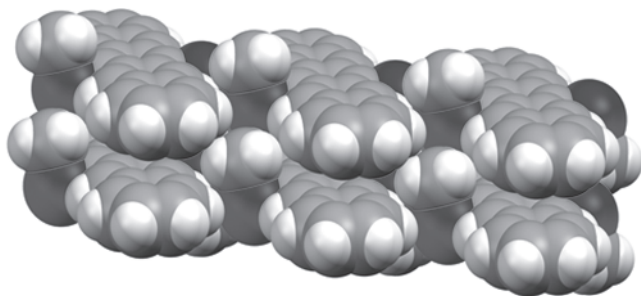
**Figure 1-6** Crystal structure of dHPTTP.

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  $\pi$ - $\pi$  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  $\pi$ - $\pi$  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  $\pi$ -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.



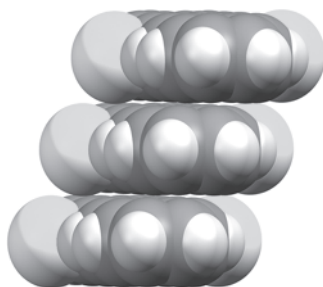


**Figure 1-7** Crystal structure of 6,13-bis(methylthio)pentacene.

Halogen-halogen interactions have been investigated by Bao and colleagues to increase  $\pi$ - $\pi$  stacking in crystals of 5-chlorotetracene (CT), 5,11-dichlorotetracene (DCT), and 5-bromotetracene (BT) [24]. CT and BT exhibited isostructural herringbone arrangements, while DCT adopted a face-to-face slipped  $\pi$ -stacking motif with an intermolecular distance of 3.48 Å (Fig. 1-8). Crystals grown by vapor growth methods for BT exhibited a mobility of  $0.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ . Crystals of DCT grown by the same method exhibited a mobility of  $1.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , which is the highest reported for tetracene. The increase in mobility in the case of DCT relative to tetracene was attributed to the enhanced  $\pi$ -orbital overlap in the mode of packing.

### 1.3.4. Quadrupole Interactions

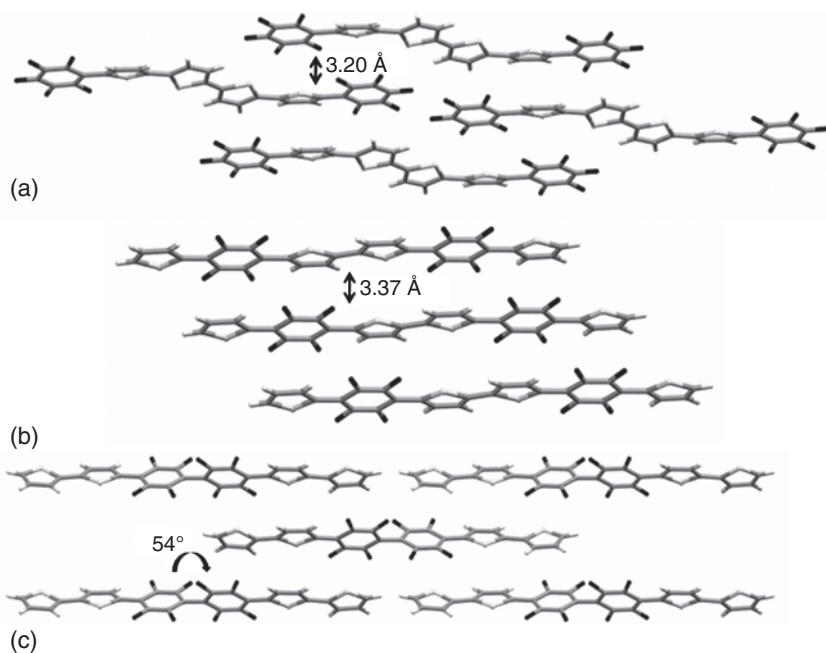
Molecular complexes between electron-rich and electron-poor aromatic rings have been known since 1960 [36]. Self-assembly via quadrupole interactions has been applied in supramolecular construction since the late 1990s [37, 38]. In 2003, Marks and colleagues reported organic semiconductors that incorporate quadrupole interactions. Two fluoroarene units were incorporated with four thiophene units to make three symmetrical molecules, specifically, 2,5'''-bis(2,3,4,5,6-pentafluorophenyl)-quaterthiophene, 5,5'-bis[2,3,5,6-tetrafluoro-4-



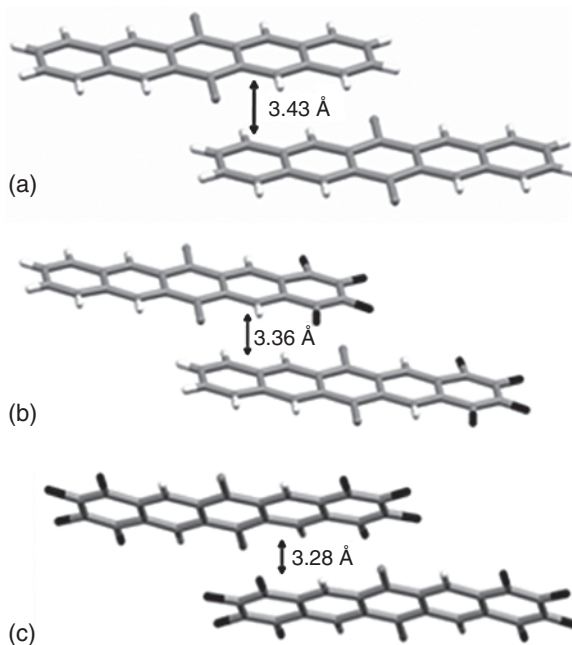
**Figure 1-8** Packing of DCT.

(2-thienyl)phenyl]-bithiophene, and 5,5''-(2,2',3,3',5,5',6,6'-octafluoro[1,1'-biphenyl]-4,4'-diyl)bisbithiophene [39]. All three molecules exhibited cofacial packing of the electron-rich thiophene units with the electron-deficient fluoroarene units. The compounds in which the fluoroarene units were spaced by a quaterthiophene or bithiophene space displayed cofacial  $\pi$ - $\pi$  stacking distances of 3.20 Å and 3.37 Å, respectively. The distances were remarkably short for thiophene-based oligomers (Fig. 1-9). The compound in which the fluoroarene units were adjacent to each other exhibited a torsion angle of approximately 54°, which disrupted the  $\pi$ -conjugation (Fig. 1-9c). Mobilities of 0.08, 0.01, and  $4 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  were reported for the fluoroarenes with the quaterthiophene spacer, bithiophene spacer, and no spacer, respectively, which generally compare to that of  $\alpha$ -6T ( $0.03 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) [39].

Anthony et al. have integrated quadrupole interactions into TIPS-based pentacenes to improve packing [40]. In particular, changing one or both of the end benzene rings in pentacene to TIPS-tetrafluoropentacene or TIPS-octafluoropentacene led to increased face-to-face  $\pi$ -interactions. Both compounds adopted similar 2-D  $\pi$ -stacked arrangements similar to TIPS pentacene. The compounds were stable in solution and the solid state when exposed to air and light. The intermolecular  $\pi$ -stacking distances decreased with an increase in the number of fluoro groups, with the average intermolecular distances being reduced from



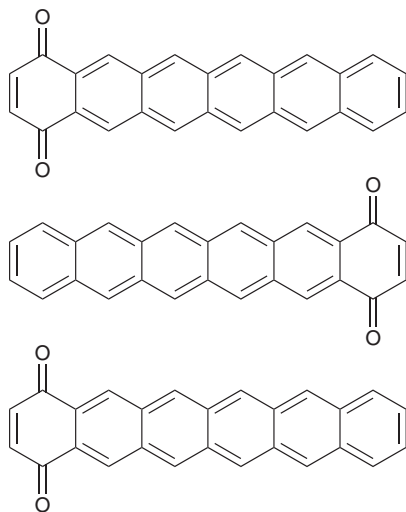
**Figure 1-9** Packing: a) 2,5''-bis(2,3,4,5,6-pentafluorophenyl)-quaterthiophene, b) 5,5'-bis[2,3,5,6-tetrafluoro-4-(2-thienyl)phenyl]-bithiophene, c) 5,5''-(2,2',3,3',5,5',6,6'-octafluoro[1,1'-biphenyl]-4,4'-diyl)bisbithiophene.



**Figure 1-10** Stacking of a) TIPS-pentacene, b) TIPS-tetrafluoropentacene, c) TIPS-octafluoropentacene (TIPS groups removed for clarity).

3.43 Å in the nonfluorinated compound to 3.36 Å in tetrafluoro and 3.28 Å in octafluoro compound (Fig. 1-10). However, in all cases the slip-stacked arrangement along the long axis of the pentacene molecules was prevalent. Nevertheless, the reduction in the intermolecular spacing was accompanied by an increase in mobility from 0.001 to 0.014 to 0.045  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  for TIPS-pentacene, TIPS-tetrafluoropentacene, and TIPS-octafluoropentacene when prepared under the same evaporation conditions, respectively. A similar introduction of perfluoroarene groups to improve stacking has been demonstrated by Swager et al. involving tetracene derivatives [41] and Watson et al. using polycyclic aromatics [42].

Nuckolls et al. have used quinone moieties to achieve a quadrupole interaction that improved stacking. The syntheses, packings, and mobilities of three acene-quinone compounds, namely, 2,3-dimethyl-1,4-hexacene-quinone, 2,3-dimethyl-1,4-pentacene-quinone, and 5,6-hexacene-quinone were described. Single crystals of the pentacene-quinone revealed a head-to-tail arrangement with an intermolecular distance of 3.25 Å between  $\pi$ -surfaces and a mobility of  $2 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  was obtained for thin films based on pentacene-quinone. Single crystals for dimethyl hexacene-quinone were determined to be unsuitable for X-ray diffraction; however, a mobility of  $5.2 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  with an on/off ratio of greater than  $10^6$  was obtained for thin films. Experimental data suggested that dimethyl hexacene-quinone adopted the same head-to-tail arrangement as the pentacene-quinone (Fig. 1-11) [26]. Chang et al. have also recently

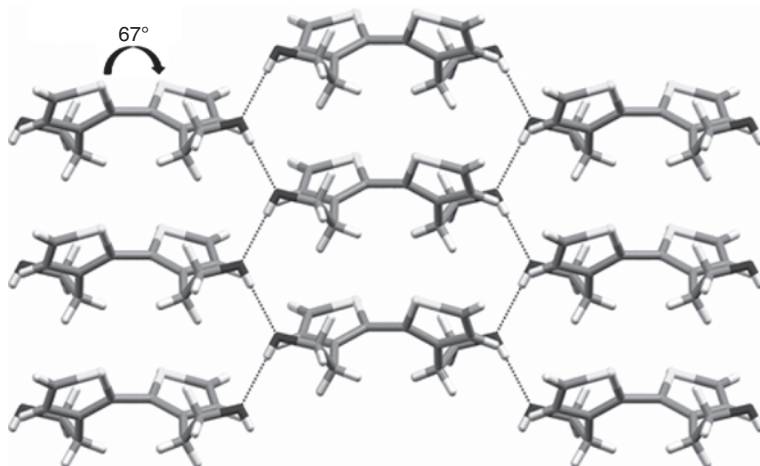


**Figure 1-11** Head-to-tail orientation of 5,6-hexacene-quinone.

described a donor-acceptor interaction integrated into a thiophene. In particular, the solid-state structure of 2,5-di(pyrimidin-5-yl)thieno[3,2-*b*]thiophene revealed  $\pi$ -stacking achieved via the stacked electron-rich S-atom of the thiophene and the electron-poor C-atoms of the pyrimidine [43]. The use of such quadrupolar interactions is promising to control  $\pi$ - $\pi$  arrangements; however, low mobilities may be attributed to the electronegative substituents (i.e., O-atom) along the aromatic core. The direct placement may cause a trapping effect, effectively lowering the observed performance.

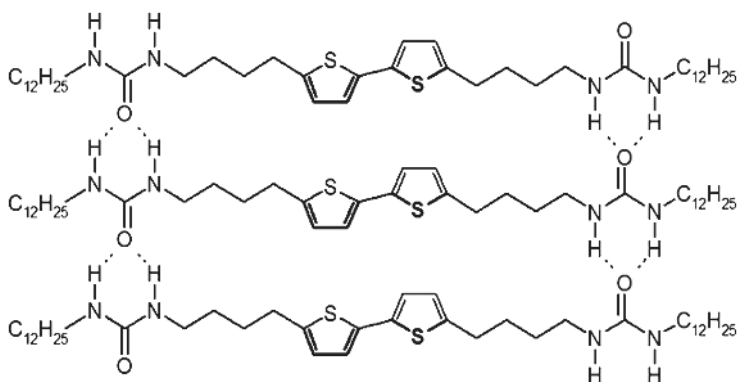
### 1.3.5. Hydrogen Bonding

The first study that incorporated hydrogen bonds as a means to affect the self-assembly of an organic semiconductor in the solid state was reported by Barbarella et al. in 1996. 2-Hydroxyethyl groups were added to the backbones of 2T, 4T, and 6T in the forms of 3,3'-bis(2-hydroxyethyl)-2,2'-bithiophene, 3,3',4'',3''''-tetrakis(2-hydroxyethyl)-2,2' : 5',2'' : 5''',2''''-quaterthiophene, and 3,3,4'',3''',4''''',3''''''-hexakis(2-hydroxyethyl)-2,2' : 5',2'' : 5''',2'''' : 5''''',2'''''' : 5''''''',2''''''''-sexithiophene. Although a crystal structure of the bithiophene revealed intermolecular O-H $\cdots$ O hydrogen bonds, a large twist angle of approximately 67° between thiophene units of the backbone effectively disrupted the conjugation of the molecule (Fig. 1-12) [44] and circumvented the formation of face-to-face stacking. The bithiophenes, however, packed into a columnar arrangement. Crystal structures were not obtained for the quaterthiophene or sexithiophene derivative. UV adsorption studies involving the longer derivatives suggested each to exhibit a largely twisted conformation, a nonideal conformation for achieving high mobility, in solution similar to the bithiophene derivative.



**Figure 1-12** X-ray structure of hydrogen-bonded network of 3,3'-bis(2-hydroxyethyl)-2,2'-bithiophene.

Feringa et al. have synthesized a series of bisurea compounds with a thiophene spacer in an attempt to form infinite 1-D  $\pi$ -stacked columns. Specifically, 2,5-di(4-(3-dodecyl-ureido)butyl)thiophene and 5,5'-di(4-(3-dodecylureido)butyl)-2,2'-bithiophene were described. Organogels formed upon cooling of each compound to room temperature in tetralin and 1,2-dichloroethane. Characterization of the gels by infrared spectroscopy, scanning electron microscopy, and powder X-ray diffraction revealed the formation of lamellar fibers formed through the hydrogen-bonded urea groups. It was suggested that the lamellar arrangement of the bithiophene derivative corresponds to cofacially stacked bithiophene moieties with an intermolecular distance on the order of 3.0 Å (Fig. 1-13). Conductive properties of the bisurea compounds

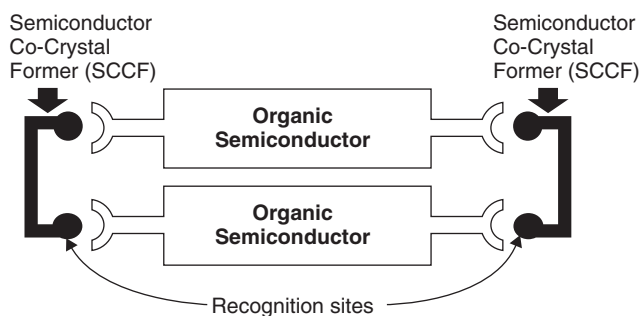


**Figure 1-13** Schematic representation of hydrogen-bonding of 5,5'-di(4-(3-dodecylureido)butyl)-2,2'-bithiophene.

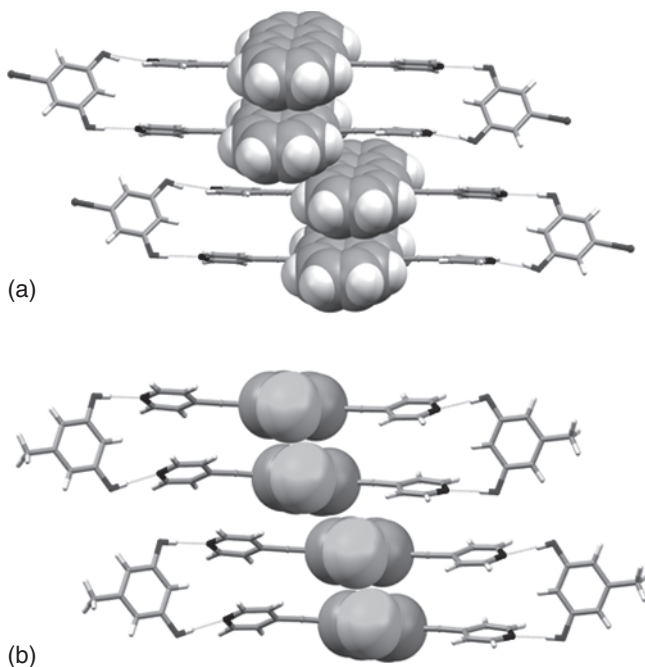
were studied via pulse-radiolysis time-resolved microwave conductivity. The bithiophene bisurea displayed a mobility of  $(5 \pm 0.2) \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , which is higher than unsubstituted quarterthiophene ( $1 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) when studied by the same technique [45]. The growth mechanisms of the fibers from solution and electronic properties were further probed by Rep et al. and DeSchryver et al., respectively [46, 47]. While the mobilities have not resulted in devices, the finding is an encouraging step toward the use of hydrogen bonds to direct molecular self-assembly where electronegative substituents do not appear to have an adverse effect on transport properties.

#### 1.4. A MODULAR APPROACH TOWARD ENGINEERING $\pi$ -STACKING

The approaches discussed above achieve face-to-face  $\pi$ -stacking by introducing or modifying a substituent on the backbone of a semiconductor molecule. The methods share a common theme of utilizing interactions provided by covalently attached substituents to direct molecular packing. Recently, we have described how face-to-face stacking of semiconductor molecules can be achieved in two-component solids, or cocrystals. The method involves cocrystallizing a semiconductor molecule with a second molecule, termed the semiconductor cocrystal former (SCCF), which is designed to enforce, via intermolecular bonds, the stacking of the semiconductor in a face-to-face arrangement [48]. The key to the cocrystal approach is that the SCCF effectively decouples the organization of the semiconductor within the crystal from the effects of long-range crystal packing. More specifically, the bifunctional SCCF utilizes hydrogen bonds to enforce stacking of acenes and thiophenes functionalized with appropriate molecular recognition sites (Fig. 1-14). Using a series of 1,3-dihydroxybenzenes, or resorcinols, as SCCFs, the approach has been used to successfully enforce  $\pi$ - $\pi$  stacking between an anthracene and a thiophene within cocrystals of 2(5-iodoresorcinol)-2(9,10-bis(4-pyridylethynyl)anthracene) and 2(5-methylresorcinol)-2(2,5-bis(4-pyridylethynyl)thiophene), respectively. The acene and thiophene were forced into face-to-face stacks with separation



**Figure 1-14** Scheme of cocrystallization of organic semiconductor and SCCF.



**Figure 1-15** X-ray structures: a) 2(5-iodoresorcinol)·2(9,10-bis(4-pyridylethynyl)anthracene), b) 2(5-methylresorcinol)·2(2,5-bis(4-pyridylethynyl)thiophene). (A full color version of this figure appears in the color plate section.)

distances of 3.44 Å and 3.56 Å, respectively (Fig. 1-15). The hydrogen-bonded assemblies were shown to self-assemble into face-to-face arrangements, which enabled the formation of extended  $\pi$ -stacked structures. We are working to expand the components of the modular approach to semiconductors of increasing complexity and determine the mobilities of the resulting solids.

## 1.5. CONCLUSION

In this chapter, we have shown that crystal engineering can be used to improve the  $\pi$ -overlap of organic semiconductor molecules in the solid state. This goal is accomplished by several approaches, from disrupting C–H $\cdots\pi$  interactions that dictate edge-to-face arrangements, to enhancing intermolecular forces that overcome edge-to-face interactions, supporting face-to-face stacking. Face-to-face stacking typically results in higher mobilities in solids. Steric interactions have been shown to disfavor herringbone stacking, while attractive forces based on lipophilic, dipolar, quadrupolar, and hydrogen bonding interactions have overcome effects of long-range packing, resulting in face-to-face stacking arrangements. Whereas virtually all approaches have relied on covalent modification of a semiconductor substituent, a new approach describes a method that employs

a second component, in the form of a cocrystal, to direct face-to-face stacking. The approaches to date have been highly encouraging, and we anticipate that crystal engineering will continue to provide steps that lead to rational design of semiconductor solids with increasing mobilities and novel applications.

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