

## SEMICONDUCTING ORGANIC MOLECULAR MATERIALS

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This feature article gives an overview of recent advances in development of high performance molecular organic semiconductors for field-effect transistors with emphasis on the structure of molecular materials and requirements for high-performance.

**Key words:** organic electronics, charge carrier mobility, processability, stability

## 1 INTRODUCTION

Organic  $\pi$ -conjugated molecules have attracted widespread interest for potential application as semiconductors since first report in 1986 [1]. These materials offer an attractive alternative because their fabrication processes are much less complex compared to conventional inorganic technology [2]. These molecules have ability to afford high operating speed, large device densities, low cost and large area flexible circuit [3], so they can be used as “universal” materials in light-emitting diodes (OLED), organic photovoltaics (OPVs) and field-effect transistors (OFET). This review is focused on organic semiconducting materials, in particular those with low molecular weight (“small”, *eg* nonpolymeric).

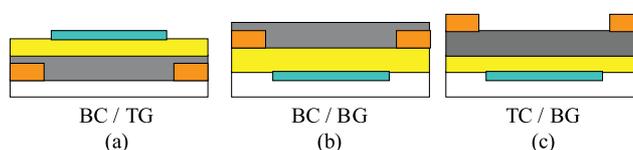
A significant improvement of charge mobility has been achieved from the initially reported  $\sim 10^{-5}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  for polythiophene in 1986 [1] to  $\sim 10^2\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  for present organic films [4], and  $\sim 15\text{--}40\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  for single crystals [5,6]. The high charge mobility of organic semiconductors compared to amorphous silicon indicate the great prospect of organic electronic devices for potential applications [7,8].

## 2 DEVICE STRUCTURES

The physical nature of the semiconductor as well as the employed gate dielectric may require or enable different device structures that can exhibit very different transistor behavior. The most commonly used structures (in relation of the surface) are the bottom contact/top gate (BC/TG Fig. 1a), bottom contact/bottom gate (BC/BG Fig. 1b) and top contact/bottom gate (TC/BG Fig. 1c) structures. Transistors with the same components, but different geometries can show very dissimilar behavior.

One of the major differences among these device geometries arises from the position of the injecting electrodes in relation to the gate. In the bottom contact/bottom gate

structure, charge is directly injected into the channel of accumulated charges at the semiconductor- dielectric interface.



**Fig. 1.** Common field-effect transistor configurations: (a) bottom contact/top gate (BC/TG); (b) bottom contact/bottom gate (BC/BG); (c) top contact/bottom gate (TC/BG)

In the other two structures, the source/drain electrodes and the channel are separated by the semiconducting layer. Thus, charges firstly have to travel through several tens of nanometers of undoped semiconductor before they reach the channel. However, in the staggered BC/TG and TC/BG configurations, charges are injected not only from the edge of the electrode, but also from those parts of the electrode that overlap with the gate electrode, contributing to the current depending on distance from the edge [9].

## 3 MATERIALS

Organic semiconductors can be divided according to charge carrier into p-type (positive charge or holes as the major carrier), n-type (negative charge or electron as the major carrier) or ambipolar (both electrons and holes are involved as charge carriers).

## 3.1 p-Type semiconductors

*Oligoacenes*

Fused-ring arene compounds, oligoacenes, and their derivatives are the key candidates for organic semiconductors. Special attention has been given to pentacene Fig. 2

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(1). Its efficient charge transport is mainly attributed to extended  $\pi$ -system with strong intermolecular overlaps as well as the proper energy level of the highest occupied orbital (HOMO : 5.1 eV) for efficient hole injection (*eg*, Au-5.1 eV) and transport. However, poor solubility in common organic solvents as well as its low stability in air significantly block its practical application. There is currently an interest in developing pentacene derivatives with improved solution-processability and ambient stability. Anthony and coworkers [10] synthesized a series of highly soluble and oxidatively stable functionalized pentacene compounds with ethyne group at the peri-position. It was found that the molecular packing motif strongly depended on the size and shape of substituent Fig. 2 (2a to 2e). The best results were reported for derivative Fig. 2 (2c) because of two dimensional brick wall arrangement of pentacene molecules with strong intermolecular interaction. Thin film of 2c exhibited a field-effect mobility of  $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $1.42 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for a single crystal nanowire.

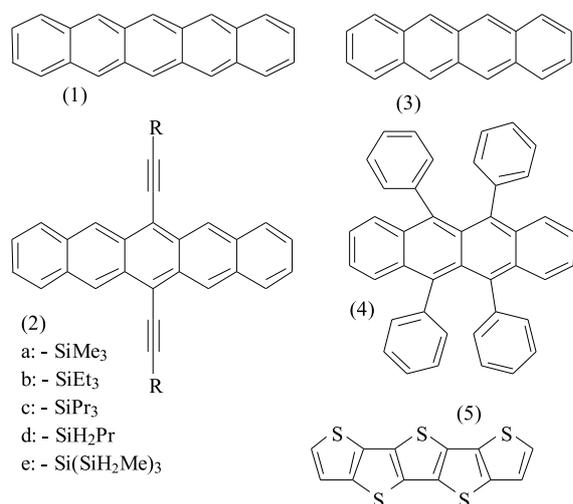


Fig. 2. (1) — pentacene, (2) — pentacene compounds, (3) — tetracene, (4) — rubene, (5) — pentathienoacene

Tetracene Fig. 2 (3) have attracted attention because of better solubility and air stability. Thin film of tetracene OFETs gave field effect mobility of  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [11]. Rubene, see Fig. 2 (4), similar to tetracene or pentacene, is present in a herringbone motif in solid state, but its phenyl substituents could lead to major steric interaction upon a large molecular long-axis displacement (around  $6.13 \text{ \AA}$ ) [12], so the mobility of rubene approached  $\sim 15\text{--}40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The molecule with similar shape to pentacene, having benzene rings replaced with thiophenes is called pentathienoacene, Fig. 2 (5). It was initially applied in OFETs by Xiao *et al* [13] in 2005. In comparison to pentacene, molecules of its thiophene analogue 5 interact together more tightly through additional intermolecular S-S contact in solid state, so that a slipped  $\pi$ -stacking model with a short distance of  $3.52 \text{ \AA}$  was demonstrated. Such planar and extended  $\pi$ -conjugation molecules gave a lower HOMO energy level of

-5.3 eV and a larger band gap of 3.29 eV. The best mobility achieved was  $0.045 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with pentathienoacene as the substrate at  $80^\circ \text{C}$ .

### Oligothiophenes

Another interesting class of p-type semiconductors are oligothiophenes. They represent a large group of organic materials because of unique properties of thiophene. A variety of their derivatives was prepared [14]. Well known defined are oligothiophenes, Fig. 3 (6) for  $n = 0, 1, 2, 3, 4, 5, 6$  [15]. The interest in this class of materials has increased since the first organic transistor, build with sexithienyl (Fig. 3 (6),  $n = 4$ ) as an active conducting material was reported [16]. By derivatization of the backbone, various materials can be prepared. For example Meng *et al* [17] prepared thiophene-antracene oligomers, Fig. 3 (7) which both exhibited a bandgap around 2.8 eV, larger than of pentacene (1.8 eV). Thin film of Fig. 3 (7b) exhibited a mobility of  $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which was about one order of magnitude higher than that of Fig. 3 (7a) due to the alkyl side chains improving molecular self-assembling in thin films. Ichikawa *et al*. [18] reported a thin film prepared from biphenyl derivative Fig. 3 (8) with mobility of  $0.66 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

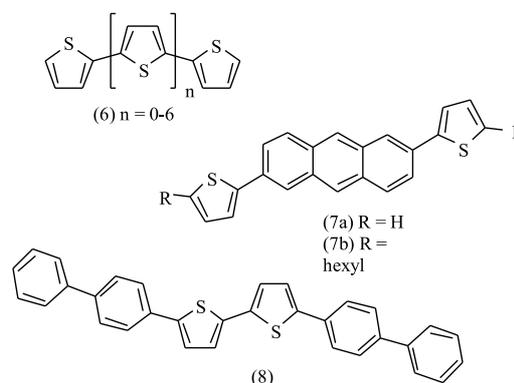


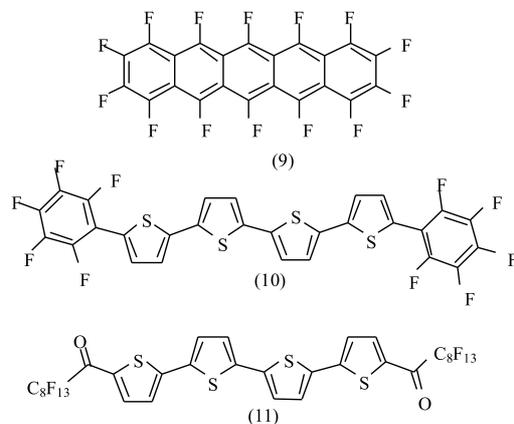
Fig. 3. (6) — oligothiophenes, (7) — thiophene-antracene oligomers, (8) — biphenyl-bithiophene compound

## 3.2 n-Type semiconductors

### Fluorine substituted p-type semiconductors

An effective approach for n-type organic semiconductors is to convert known p-type materials into n-type by modifying them with strongly electronegative fluorine atoms to lower the lowest unoccupied molecular orbital (LUMO) energy levels of materials for electron injection and transport. No matter the position or the type of electron-withdrawing substitution, perfluoroarene and perfluoroalkyl both greatly affect the crystal structure, orbital energies and charge transport.

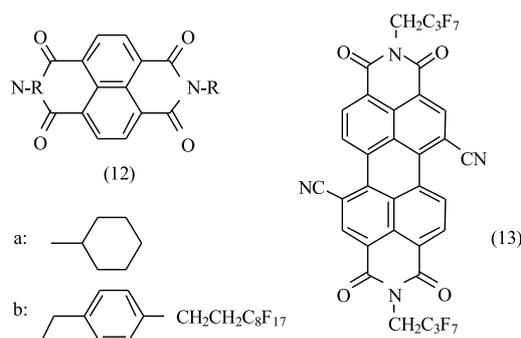
Representative examples are in Fig. 4 (9–11). The electron mobility for Fig. 4 (10) was up to  $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with on/of ratio of  $10^8$  [19]. Compound Fig. 4 (11) exhibited unprecedented solubility and stability [20], with high mobility both in solution cast (up to  $0.25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and vapor-deposition films (up to  $0.51 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ).



**Fig. 4.** (9) - perfluoropentacene, (10) - perfluorophenyl-quarternthiophene, (11) - perfluoracyl-quarternthiophene

#### Rylene diimides derivatives

Arene tetracarboxylic diimides represent another group of electron-deficient  $\pi$ -systems suitable for producing n-type semiconductors. They exhibit relatively high electron affinities, high electron mobilities, and excellent chemical, thermal and photochemical stabilities. The widely used rylene diimides include naphthalene diimides Fig. 5 (12, NDIs) and perylene diimides Fig. 5 (13, PDIs). Among NDIs, the highest mobility in inert atmosphere was found to be  $6.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for 12a [21], while the highest mobility under ambient condition was found to be  $0.57 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for 12b [22]. OFETs based on Fig. 5 (13) single crystals with poly(methyl methacrylate) (PMMA) as the gate dielectric exhibit electron mobilities of 6 and  $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in vacuum and in air, respectively, which are the highest reported for PDIs [23].



**Fig. 5.** ((12) - naphthalene diimides, (13) - perylene diimide

#### Fullerene

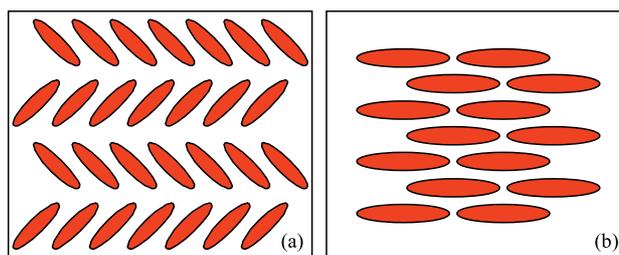
$\text{C}_{60}$  Fig. 6 (14) is an important n-type organic semiconductor. According to theoretical calculations  $\text{C}_{60}$  exhibit a relatively low lying LUMO energy level that is triply degenerated. Thus  $\text{C}_{60}$  behaves as an electron acceptor that is able to accept up to six electrons in solution. The performance of  $\text{C}_{60}$ -based OFETs has experienced tremendous advances with electron mobilities from 0.08 to  $\sim 6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [24]. Despite rapid performance degradation upon exposure to air, the application of  $\text{C}_{60}$ -based devices is challenging.



**Fig. 6.** (14) — fullerene

## 4 MATERIAL REQUIREMENT FOR HIGH PERFORMANCE

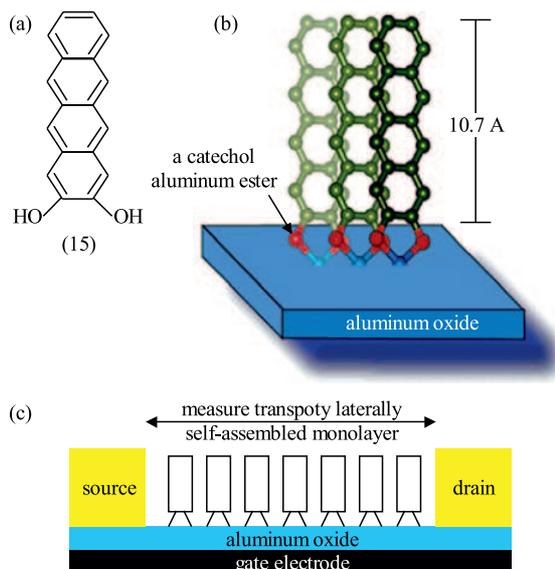
Efficient charge transport in molecular materials requires that the charges are able to move from molecule to molecule and are not trapped or scattered. Therefore, charge carrier mobilities are influenced by many factors including molecular packing, disorder, presence of impurities, temperature, electric field, charge-carrier density, size/molecular weight, and pressure. Some of these factors are discussed below.



**Fig. 7.** Molecular packing motifs existing in organic solid states: (a) common one dimensional herringbone  $\pi$ -stacking motive; (b) planar brickwork  $\pi$ -stacking motive providing two dimensional stacking

### 4.1 Molecular packing

The anisotropy of charge transport in single crystals point shows that the efficiency of transport is intimately related to the relative positions of the interacting molecules, and hence to crystal packing. In most instances, unsubstituted  $\pi$ -conjugated molecules crystallize into layered herringbone packing (Fig. 7a). Such packing gives rise to 2D transport within the stacked organic

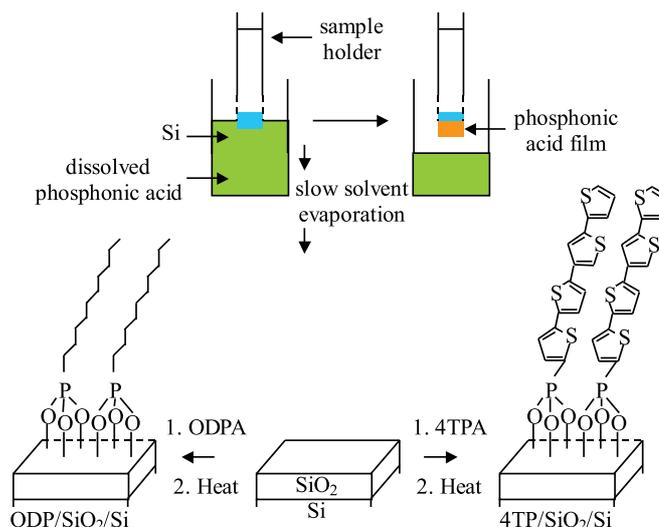


**Fig. 8.** (a) End functionalized tetracene 15. (b) Scheme of bonding and orientation of 15 on aluminium oxide (not intended to indicate in-plane ordering). (c) Scheme of self-assembled monolayer transistor (adapted from ref. [27])

layers [25] while transport between layers is less efficient. Therefore, the overlap degree of neighboring molecular orbitals significantly determines the mobility of charges. Molecular packing with strong intermolecular overlaps is favorable for efficient charge carrier transport and high field-effect mobility. To enhance the stacking in crystal structure, several methods are evolved [26]. Recently, extensive work has been carried out on improving the stacking by introducing polarity, increasing the C/H ratio or adding heteroatoms to generate hydrogen bonds, halogen-halogen interaction, *etc* to enhance the intermolecular overlaps (such as observed in planar brickbone motive, Fig. 7b), and thus improving the charge transport properties.

Tulevski *et al* [27] reported attaching organic semiconductor molecules on gate oxide. They prepared tetracene derivative, Fig. 8a (15), that forms dense, upright monolayer on the surface of aluminium oxide (Fig. 8). These monolayers spontaneously self-organize into the active layer in nanoscale field-effect transistor device. With this method devices with highly organized monolayer that have source-drain distance less than 100 nm can be prepared.

Another approach is to anchor the semiconductor molecules on silicon surface through phosphonate bond to create a self-assembled layer. This method was demonstrated for octadecylphosphonate and  $\alpha$ -quarterthiophene-2-ylphosphonate [28]. Growing an organophosphonate film on SiO<sub>2</sub>/Si by self-assembly is straightforward process: the substrate is held vertically in solution of corresponding organo-phosphonic acid below its critical micelle concentration (CMC) [29], and the solvent is allowed to evaporate slowly. As the meniscus slowly traverses the substrate is transferred to the surface in inverse analogy



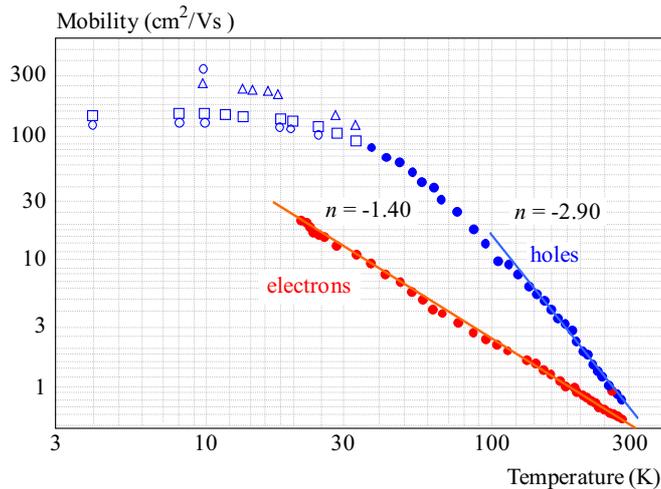
**Fig. 9.** The “tethering by aggregation and grow” setup and chemical reactions (adapted from ref. [31])

to Langmuir-Blodgett method (Fig. 9), but without application of pressure [30].

Another approach to improve the charge injection is to interpose an appropriately oriented dipole layer between contact and semiconductor. Marmont *et al.* [31] reported a preparation of OFET consisting of pentacene and gold as a drain/source contacts. The contacts were modified with self assembled monolayers (SAMs) made of alkane or fluorinated alkane thiols. They observed decrease/increase of the mobility depending on the SAM (Tab. 1). The molecules of pentacene are preferentially oriented perpendicular to the electrode. Work function of gold is reduced with an alkane chain, while it is increased in the case of fluorinated molecule, in good agreement with the direction of the respective molecules.

## 4.2 Tuning energy gap and energy alignment

The electronic structure of molecules not only plays an important role for charge injection and transport in organic semiconductors, but is crucial for its environmental stability too. Hence, it is important to design molecules with consideration of molecular energy gaps and levels. For p-type materials, the HOMO levels are typically 4.9–5.5 eV, while for n-type materials the LUMO levels are normally 34 eV. A simple example to tune the energy gap and levels of organic semiconductors is to use star organic semiconductors as the parent cores to rationally modify or structurally reorganize them. For example, judicious choice of appropriate conjugation units (such as acenes or oligothiophene cores) and incorporation of some weakly electron-donating groups (such as double/triple carbon bond or chalcogen atoms) and side chains in the molecule serve to lower the HOMO energy



**Fig. 10.** Log-log plot of electron and hole mobilities in ultrapure naphthalene as a function of temperature. The applied electric field is approximately parallel to crystallographic direction (adapted from ref [40])

**Table 1.** Saturation mobility of bare and SAM-modified pentacene-transistor (DT-decanethiol; PFDT-1,1,2,2-H-perfluorodecanethiol; PFHT-1,1,2,2-H-perfluorohexane-thiol)

SAM	None	DT	PFDT	PFHT
Mobility ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ )	0.040	0.016	0.065	0.105

level, as well as strengthen molecular interactions, resulting in many extraordinarily high performance and air stable p-type organic semi-conductors [17, 32–35]. Introducing strong electron-withdrawing groups to stabilize the organic anions against oxygen and water is another effective approach for highly stable n-type semiconductors [23, 36, 37].

### 4.3 Purity

Impurities in organic semiconductors introduced through the complex synthesis process or defects in the molecular structure itself can severely result in poor field-effect performance by forming a large amount of charge trapping sites in the active layer or acting as dopants for semiconducting materials. Currently, two approaches have been widely used to obtain highly pure materials, (i) simplifying synthetic routes, optimizing synthetic sequences, or beginning with purified starting materials [38], (ii) purifying products many times, such as by gradient sublimation, *etc.* [39]. These methods work effectively for small molecules.

### 4.4 Temperature

Temperature dependence is markedly different in single crystals and in disordered materials. In single crystal, the hole and electron mobility generally decrease with temperature according to a power law evolution:  $m \div T^{-n}$  [40]. This is illustrated in Fig. 10 for the case of electron and hole transport along a crystal axis direction of naphthalene. Similar evolution is observed along specific

direction for a large number of single crystals; the main difference lies in the value of  $n$ , which typically varies between 0.5 and 3.

In highly disordered systems, transport generally proceeds via hopping and is thermally activated. Higher temperatures improve transport by providing the requirement to overcome the barriers created by energy disorder.

### 4.5 Other factors

Many studies have also addressed the influence of film morphology on charge transport and OFET performances. In thin films, grain boundaries are the key to carrier transport. As intermolecular charge hopping across the grain boundaries, or through disorder domains, is not as efficient as that within ordered domains. Increasing grain sizes with good film continuity is a promising approach to improve charge transport and mobility. Interface quality and compatibility greatly influence the grain size and boundaries. Hence, numerous methods, including optimizing interface quality [7, 41] film treatments (such as thermal or solvent annealing) [42, 43] and other strategies [44, 45] have been studied recently to control the morphology of organic thin films. For example, it is effective to tune the surface energy by self-assembled monolayers (SAMs) prior to the deposition of organic semiconductors to improve the interface compatibility. Generally, a high surface energy leads to larger grain sizes and therefore results in high device performance with significantly increased mobility and reduced subthreshold slopes.

## 5 CONCLUSIONS

$\pi$ -Conjugated molecular organic materials with semiconductor properties, overviewed in this paper, represent promising functional materials for high performance field-effect transistors. They exhibit high charge carrier mobility and on/off ratio. In the same time, they are easily tun-

able by structural modifications and offer advantageous processability. However, stability issues should be considered.

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