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Chapter

Crystal Polymorph Control for High-Performance Organic Field-Effect Transistors

Zhi-Ping Fan and Hao-Li Zhang

Abstract

Organic molecules are assembled together by weak non-covalent intermolecular interactions in solid state. Multiple crystalline packing states (crystal polymorphism) have commonly existed in the active layer for organic field-effect transistors (OFETs). Different polymorphs, even with the slightest changes in their molecular packing, can differ the charge transport mobility by orders of magnitude. Therefore, accessing new polymorphs can serve as a novel design strategy for attaining high device performance. Here, we review the state of the art in this emerging field of crystal polymorph control. We firstly introduce the role of polymorphism and the methods of polymorph control in organic semiconductors. Then we review the latest studies on the performance of polymorphs in OFET devices. Finally, we discuss the advantages and challenges for polymorphism as a platform for the study of the relationship between molecular packing and charge transport.

Keywords: organic field-effect transistors, organic semiconductors, polymorphism, structure-property relationship, carrier mobility

1. Introduction

An organic field-effect transistor (OFET) is a transistor using an organic semiconducting thin film as the active layer in its channel [1, 2]. Charge carriers are transported in the OFET active layer under the electric field. Through the design of new materials and the improvement of fabrication processes, many impressive developments in the field of OFETs have been achieved [3–6]. It has long been realized that the morphology of the active layer has a crucial impact on its charge transport properties. Tremendous efforts have been devoted to fabricate highly ordered crystalline films to achieve high device performance, including introduction of self-assembled monolayers [7–9], annealing [10, 11], off-center spin coating [4, 12, 13], and solution shearing [14, 15]. However, the lack of knowledge on the intrinsic properties of organic semiconductors remains the barrier for high-performance materials being efficiently developed.

Polymorphism of organic semiconductors has recently received much attention in the field of OFETs [16–18]. Different polymorphic crystals have the same molecular structure but a different molecular arrangement, which can be used as an ideal platform to correlate charge transport with respect to molecular arrangement. Through investigating OFETs with different polymorphs, the relationship between molecular packing and charge transport can be obtained. Recently, some ultra-high-mobility

OFETs have been obtained by controlling the polymorphic structures of organic semiconductors, revealing that the crystal polymorph control has become an efficient strategy for the manufacture of high-performance OFETs [4, 17].

1.1 What is polymorphism?

Polymorphism refers to the ability for the same compound to adopt multiple crystalline packing states. Organic molecules assemble into crystals by weak intermolecular interactions, typically via van der Waals and electrostatic interactions. Many thermodynamic and kinetics factors (such as temperature, solvent mixtures, speed of crystallization, seeding, and pH) can have significant impacts on crystal growth, leading to polymorphism prevalent among organic materials. For instance, a continuous investigation on polymorphism has indicated that approximately one-third of organic substances show polymorphism under normal pressure conditions [19, 20]. Different polymorphs often have distinct physical properties such as solubility, melting point, and electrical, optical, and mechanical properties [21]. The interest in polymorphism has increased significantly in recent years, particularly in the pharmaceutical and material science fields [17, 22].

1.2 The role of polymorphism in OFET

The charge transport property of organic semiconductors is sensitive to the molecular packing, where a slight change in molecular packing may result in huge difference in charge carrier mobility [23]. The side-chain engineering, which is efficient in tailoring the molecular packing, has been extensively applied to develop high-performance organic semiconductors [24–27]. However, the introduction of side chains alters the molecular structure, which makes the investigation on relationship between molecular packing and charge transport very complex.

Polymorphism offers an opportunity to tailor the molecular packing of a material, without affecting its chemical components. For example, rubrene can crystallize into three crystalline polymorphs, including an orthorhombic, a triclinic, and a monoclinic phase (**Figure 1a**) [28–30]. Taking advantage of polymorphism, it is possible to fabricate OFETs from the same organic semiconductor but with different polymorphs, hence, with different properties (**Figure 1b**). Importantly, by

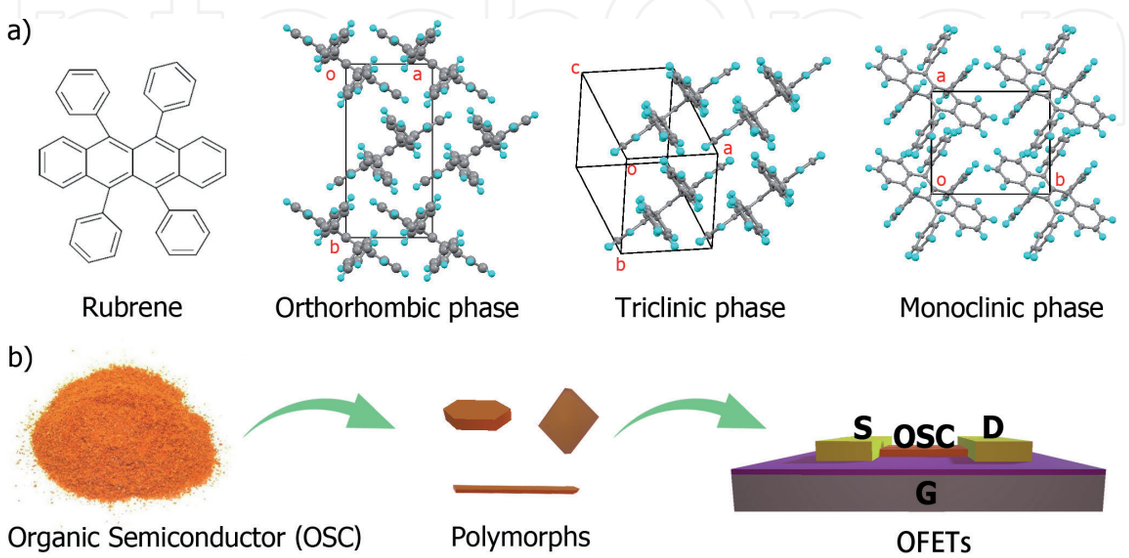


Figure 1.
(a) Molecular structure and the crystal phases of rubrene. (b) Schematic diagram for the fabrication of the OFETs from microcrystals of different polymorphs.

measuring charge transport performance in OFETs from different polymorphs, a direct relationship between molecular packing and charge transport can be established. Thus, many investigations on charge transport in different polymorphs have been performed in thin-film transistors, including some benchmark organic semiconductors like pentacene derivatives [15, 31, 32], rubrene [28–30], sexithiophene (6T) [33–36], and [1]benzothieno[3,2-b][1]benzothiophene (BTBT) derivatives [10, 37, 38]. However, the different factors affecting the device performance, including crystallinity, grain size, and grain boundaries, are difficult to be eliminated in thin-film transistors. Thus, tremendous efforts have been paid to manufacture OFETs from highly crystalline films even single crystals [39–44]. Especially, single-crystal OFETs from different polymorphs have attracted increasing attentions [45]. Compared to polycrystalline films, single crystals have the advantages of high molecular ordering and minimal grain boundaries, and its structure is much easier to determine.

There is no doubt that high-performance OFETs can be obtained by tailoring molecular packing motifs in the active layer. Among the investigations on polymorphism of organic semiconductors, several high-mobility OFETs have been manufactured by polymorph control, such as the TIPS-pentacene [46], C8-BTBT [4], C6-DBTDT [47], and TiOPC [48]. Tailoring polymorphs has become an emerging design strategy for high-performance organic electronics.

2. Methods of polymorph control in organic semiconductors

Though polymorphism is observed on many organic semiconductors, the fabrication of each polymorph with high purity is very difficult. For instance, even for the extensively studied organic semiconductors like pentacene and BTBT derivatives, only part of their polymorphs have been useful to establish the correlation between the material molecular packing and its charge transport properties [17]. The difficulties for the investigations on polymorphism include the fabrication of pure polymorphs and the determination of their crystal structures, where the polymorph control is fundamental. Some of the polymorph control methods most commonly applied to organic semiconductors are discussed below.

2.1 Solvent control

Solution process is important for the fabrication of organic semiconductor devices, which has the advantages of low-cost and large-area fabrication. In solution processes, solvent-induced polymorphism has been frequently observed in organic semiconductors such as DB-TTF [49], DT-TTF [50], TIPS-pentacene [51], and so on. Consequently, the solvent of choice for solution-processed organic semiconductors has become a commonly practiced method for high-throughput polymorph screening. For example, the triethylsilylethynyl anthradithiophene (TES-ADT) films can crystallize into two polymorphs from different solvents [52–54]. The polymorph selectivity for solution processes mostly relates to the polarity of solvents, while the concentration can also induce polymorphism [47, 55]. For instance, the C6-DBTDT molecules can crystallize into the α-phase and β-phase crystals from high concentration and dilute chlorobenzene solutions, respectively [47]. At the molecular level, the specific interactions between semiconductor and solvent molecules in the solution can induce the nuclei formation in a particular polymorph and therefore result in polymorph selectivity as a function of the solvent or the concentration [56].

2.2 Temperature control

The thermodynamic polymorphic selection is usually observed from deposition of organic semiconductors by physical vapor transport (PVT) processes [57]. In a study by Stevens et al., TMS-DBC crystals were synthesized in a crystallization tube by PVT method, where two polymorphs grew at different temperature regions [58]. The red low-temperature (LT) polymorph was obtained in regions with tube temperature about 25–65°C, while the yellow high-temperature (HT) polymorph grew in regions with temperature around 130–170°C. The two polymorphs were found extremely stable, which did not interconvert to the other crystal structure with subsequent solvent or thermal treatments. Temperature-induced polymorphism was also observed from TiOPC crystals fabricated by PVT technology [48]. Sheetlike α-phase TiOPC crystals were obtained on the substrate at the temperature zone of about 210°C, while ribbonlike β-phase crystals were grown at the temperature zone of about 180°C. For many polymorphic materials, most of the polymorphs are temperature sensitive, where thermal-induced phase transition is allowed. Consequently, temperature-induced polymorph selectivity is becoming an important strategy to access and study different polymorphs.

2.3 Crystallization through kinetics control

Crystallization through kinetics control is a powerful method for accessing metastable polymorphs, especially in thin-film geometry where kinetic trapping and thin-film confinement work in synergy. In a study by Wedl et al. [59], thin films of dihexylterthiophene (DH3T) were fabricated by spin coating, dip coating, drop casting, and physical vapor deposition, i.e., with very different crystallization speed. Three polymorphs of DH3T were discovered from the experiment, which was noted as the α-phase, β-phase, and the metastable thin-film phase. The crystallization speed was found to be a key parameter to control the respective polymorphs present in the films. The metastable thin-film phase was obtained from deposition techniques with fast crystallization speeds, such as physical vapor deposition, spin coating, drop casting with fast solvent evaporation, and dip coating with high withdrawal velocity. In contrast, a mixture of two stable polymorphs was observed in films fabricated by both drop casting and dip coating with slow evaporation of solvent. Crystallization kinetics control was also applied in a study by Giri et al. [14], wherein the solution shearing method with a function of shearing speed was utilized to fabricate thin films of TIPS-pentacene. Through fast solvent evaporation and quick crystallization, metastable states were kinetically trapped, which were relaxed to more stable states with toluene vapor annealing.

2.4 Templating via heterogeneous nucleation

Organic molecules are assembled by weak intermolecular interactions into their crystalline form, which can be affected by the molecule-surface interaction and the molecule-molecule interaction from additives. In other words, substrates and additives can act as templates to alter the crystal structure of organic semiconductors.

The substrate can promote heterogeneous nucleation of a particular polymorph due to specific interface interactions. On the substrate-thin-film interface, substrate-induced polymorphs (SIPs) are usually observed in the first few molecular layers, whose molecular packing are different from that in the bulk of the film. For example, two SIPs were firstly observed in thin films of pentacene, including a thin-film phase with d-spacing of 15.4 Å and a single-layer phase with d-spacing of 16.1 Å [32, 60, 61]. In contrast, the single-crystal phase of pentacene

exhibits the d-spacing of 14.1 Å [62–64]. SIPs were also observed in films of the 2,7-dioctyloxy-BTBT (C_8O-BTBT-OC_8) derivative [10]. The C_8O-BTBT-OC_8 molecules adopt a slipped π-π stacking in bulk crystal while exhibiting a herringbone packing motif in the thin-film phase. However, the SIP of C_8O-BTBT-OC_8 is a metastable form induced by the substrate, which is converted to the bulk form in 6 months or by chloroform vapor annealing. Although SIPs are commonly observed in thin films of organic semiconductors, studies on the formation of SIPs are limited [65].

Polymer additives have been demonstrated effective for polymorph control. In a study on polymorphism of TIPS-pentacene, conjugated polymer additives including poly(3-hexylthiophene) (P3HT) and region random TIPS-pentacene-bithiophene polymer (PnBT-RRa) were used to template the formation of a polymorph [66]. Two new polymorphs of TIPS-pentacene were obtained, including the phase II and phase III that were synthesized form TIPS-pentacene/PnBT-RRa blend and TIPS-pentacene/P3HT blend, respectively. Compared to the phase I obtained from pure TIPS-pentacene, the phase II exhibits very small changes in crystal structure, which is attributed to the structural similarity between TIPS-pentacene and PnBT-RRa as well as their strong intermolecular interactions. In contrast, the crystal structure of phase III exhibits a large difference compared to the phase I, due to the lack of structural similarity between TIPS-pentacene and P3HT. These results demonstrate the possibility of using polymer additives as templates for accessing various polymorph phases.

2.5 Postdeposition control

Postdeposition processing is a commonly used method to investigate phase transition, from which various polymorphs can be accessed. Solvent and thermal annealing is widely used for postdeposition treatments to increase crystallinity, to enlarge grain size, and in some cases to alter the molecular packing in films of organic semiconductors [67–69]. In a study by Hiszpanski et al. [70], three polymorphs of contorted hexabenzocoronene (c-HBC) have been obtained by the application of both thermal and solvent vapor annealing. The P21/c polymorph of c-HBC is obtained from the amorphous film by thermal annealing. In contrast, polymorph II is accessed from either the amorphous film or the P21/c polymorph by tetrahydrofuran vapor annealing. Subsequently, thermal annealing of polymorph II always yields polymorph II. From an investigation by Campione et al., α-tetrathiophene (α-4T)/LT single crystals were obtained by the floating-drop technique, and a crystal to crystal phase transition was observed at 191°C from α-4T/LT to α-4T/HT, obtaining large and thick α-4T/HT single crystals [71].

2.6 Other methods

In addition to the major methods summarized above, a variety of novel approaches have been developed to control polymorphs. A direct strategy to change the crystal phase is to apply pressure on crystals. For instance, pressure-induced phase transition was observed from rubrene and fullerene derivatives [72–76]. Ito et al. and Segara et al. reported mechanically induced phase transitions [77, 78]. The nucleation of a polymorph is often affected by many processing parameters. For example, Lee et al. successfully fabricated a metastable polymorph of quaterrylene diimide by flow-assisted crystallization [79]. He et al. synthesized a new polymorph of Cl2-NDI by vapor sublimation in air [18]. Even light can have effects on polymorph formation. As investigated by Pithan et al., two polymorphs of sexithiophene were obtained in dark and illumination environments [33].

3. Charge transport in OFETs with different polymorphs

Polymorphism is an important platform to study the charge transport mechanism in organic semiconductors because in polymorphs the crystal structure is the only variable, while the chemical structure remains identical [80]. By studying a polymorphic organic semiconductor, changes in charge transport can be directly associated with the differences in molecular packing. Many studies have attempted without success to reveal the relationship between charge transport and molecular packing, including experimental studies and quantum chemical calculations on different polymorphs.

3.1 Theoretical studies

Charge transport in inorganic semiconductors is well described by the band-like charge transport model. In contrast, to describe charge transport in organic semiconductors is much complex, where both electron–electron and electron–phonon interactions must be taken into account [81, 82]. A phonon is described as a particle-like quantized mode of vibrational energy, which arises from oscillating atoms within a crystal. In organic crystals, the molecule packing can be significantly disrupted by thermal functions due to the weak intermolecular interactions. Therefore, the charge transport behavior of organic semiconductors is temperature dependent [83]. It turns out that a charge-hopping model is commonly observed at near and above room temperatures [84], while a band-like transport model is typically observed in single crystals at lower temperatures [85].

The OFET devices mostly work at near and above room temperatures and follow a hopping transport mechanism. The hopping mobility can be deduced from the Marcus theory through Eq. (1) [17, 86]:

$$\mu_{\mathrm{hop}} = \frac{ea^2t^2}{k_B T\hbar}\left[\frac{\pi}{2E_{\mathrm{pol}}\,k_B T}\right]^{\frac{1}{2}} \exp\left(-\frac{E_{\mathrm{pol}}}{2K_{\mathrm{B}}T}\right) \tag{1}$$

where e is electron charge, a is the spacing between molecules, t is the charge transfer integral, k_B is the Boltzmann constant, T is temperature, $\hbar$ is Planck constant, and E_{pol} is the polaron binding energy. The polaron binding energy is related to the reorganization energy (λ_{reorg}) via $E_{\mathrm{pol}} = \lambda_{\mathrm{reorg}}/2$. The reorganization energy (λ_{reorg}) depicts both the intramolecular and intermolecular contributions to the change in the geometry of the molecules during charge transfer [87]. In organic crystals, two major parameters affect the charge carrier mobility, which are the transfer integral (t) and the reorganization energy (λ_{reorg}). The transfer integral and the reorganization energy can be quantitatively determined by quantum chemical calculations, and therefore, the hopping mobility can be estimated. In general, organic semiconductors with higher transfer integral and lower reorganization energy have higher charge carrier mobility.

Taking advantages of the quantum chemical calculations, the relationship between molecular packing and charge transport can be examined. For instance, Bredas et al. simulated the sexithiophene dimers to understand the effect of the molecular overlap on the transfer integral between adjacent molecules [88]. First, the HOMO and LUMO energy splittings were examined with a variation in the intermolecular distance between the conjugated planes. Next, by keeping the bottom molecule and the intermolecular distance between the sexithiophene (6T) dimers (4 Å) fixed, the effects of lateral molecular displacement along the conjugated plane on the energy splittings were examined by moving the top 6T molecule. The energy splitting is directly proportional to the charge transfer integral (t). The electronic splittings of HOMO and LUMO exhibit an exponential decay

as the intermolecular distance is increased. In contrast, the HOMO/LUMO energy splittings show large oscillations and tend to abate as the lateral displacement along the conjugated plane is increased. These results indicate that charge transport in organic semiconductors is sensitive to molecular packing. Consequently, altering the molecular packing, i.e., tuning the polymorph structure of organic semiconductors, provides an opportunity to improve the performance of OFETs.

3.2 Thin-film transistors with different polymorphs

Organic thin-film transistors are easy to fabricate in large area by solution processing and therefore have been widely used in various electronic devices like electronic paper [89] and medical sensors [90, 91]. However, the semiconductor processing method and conditions can greatly affect the molecular packing motif and consequently can dramatically affect the device performance (see Section 2). To date, the knowledge on how the charge transport in semiconductor films depends on molecular packing motif is still very limited. In this section, the relationship between molecular packing and charge transport will be discussed, giving some recent investigations as examples.

3.2.1 Pentacene

Pentacene is a benchmark organic semiconductor synthesized in 1912 [92], which exhibits excellent charge transport performance in thin-film transistor [93]. To date, there are five different polymorphs known for pentacene [9, 31, 32, 94]. As shown in **Figure 2**, the five polymorphs of pentacene are classified by their molecular layer thickness (d-spacing), where four thin-film forms exhibit d-spacing of 14.1, 14.4, 15.0, and 15.4 Å [31], and a monolayer form shows d-spacing of 16.1 Å [60]. However, among the five polymorphs, complete structural data have only been determined for the 14.1 and 14.4 Å polymorphs, where the 14.1 Å polymorph shares a similar packing as the single crystals. The single crystal of pentacene was reported with mobility around 5–40 $cm^2 V^{-1} s^{-1}$ [43, 95]. A recent study by Ji et al.

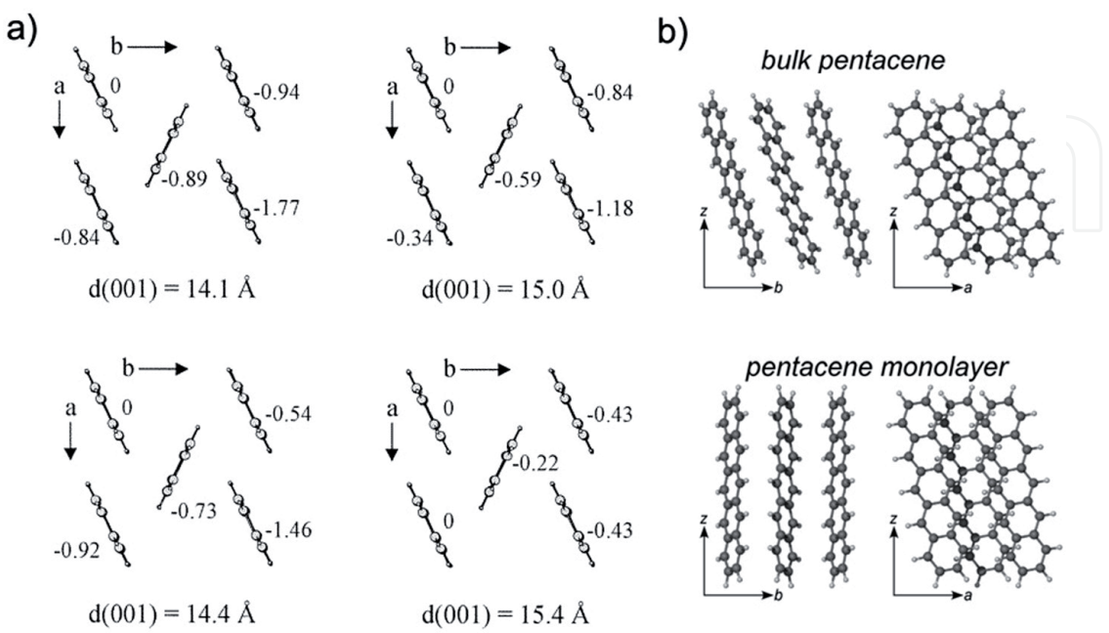


Figure 2.
(a) Schematic drawing of the crystal structures of the pentacene polymorphs [31]. Copyright 2003, American Chemical Society. (b) Normal views of the ab planes of the bulk and the monolayer structures of pentacene [60]. Copyright 2004, American Chemical Society.

reported that the polymorph with d-spacing of 16.2 Å has a mobility of up to 30.6 $cm^2 V^{-1} s^{-1}$ [93]. As for the other polymorphs, to stabilize and isolate a pure polymorph for transistor fabrication has been challenging. Thus, more investigation on the relationship between molecular packing and charge transport for pentacene remains a serious topic of research.

3.2.2 6,13-Bis(triisopropylsilylethynyl)-pentacene

In 2001, Anthony et al. introduced triisopropylsilylethynyl (TIPS) group to the pentacene core, obtaining a very soluble pentacene derivative, i.e. TIPS-pentacene [46]. Different from the herringbone-stacked pentacene molecules, the TIPS-pentacene molecules adopt a brick-wall stacking in solid state. Several recent investigations have revealed that TIPS-pentacene exhibits polymorphism. For instance, Diao et al. fabricated five different polymorphs of TIPS-pentacene by using the solution shearing technology [15]. The five polymorphs have been categorized into three families: I and Ib, II and IIb, and III. Within each family, there is only a slight change in one or two unit cell parameters between the polymorphs. Among different family (polymorphs I, II, and III), the main structural differences are changes in the π-π stacking distance and the extent of overlap between adjacent molecules (**Figure 3**). Form I has larger π-π stacking distance than that of forms II and III, where pair I in form III exhibits a record low-stacking distance of less than 3 Å. As a result, form I exhibits ambipolar charge transport property, with hole and electron mobility of 3.8 and 6.81 $cm^2 V^{-1} s^{-1}$, respectively. Form II shows the highest mobility up to 11 $cm^2 V^{-1} s^{-1}$. In sharp contrast, form III possesses the lowest mobility around 0.09 $cm^2 V^{-1} s^{-1}$. The quantum chemical calculations indicate a much smaller hole transfer integral for form III compared to form I and form II. Form II with moderate π-π stacking distance has the largest hole transfer integral

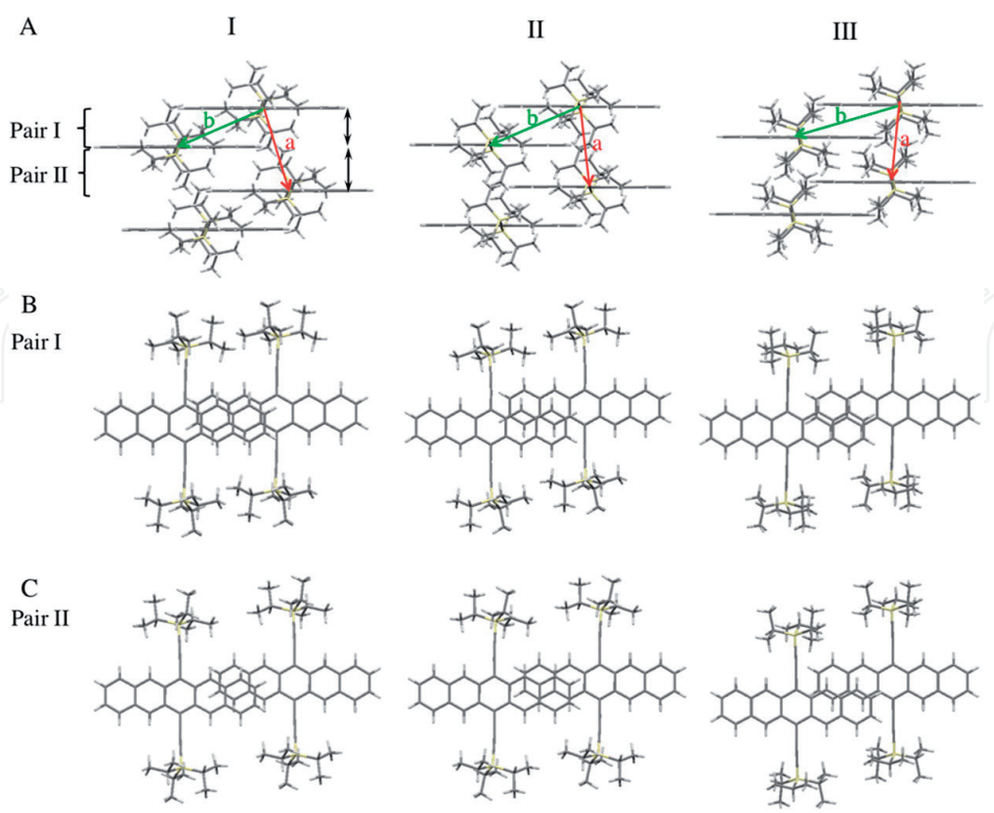


Figure 3.
Comparison of the three major polymorphs of TIPS-pentacene in their π-π stacking (A) and molecular offset along the conjugated backbone (B, C) as obtained from the crystallographic refinement calculations [15]. Copyright 2014, American Chemical Society.

and therefore exhibits the highest mobility. This result shows that small π-π stacking distance does not always help to improve charge transport properties.

3.2.3 2,7-Dioctyl[1]benzothieno[3,2-b][1]benzothiophene

2,7-Dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT) is an extensive studied air-stable organic semiconductor, which often shows very high hole mobility in OFET devices [4, 96, 97]. In a recent study by Yuan et al., ultra-high mobility up to 43 $cm^2 V^{-1} s^{-1}$ was obtained from thin-film transistors based on a metastable polymorph of C8-BTBT film [4]. The metastable polymorph was fabricated by introducing polystyrene additive and using an off-center spin-coating method. After thermal annealing, the metastable polymorph was relaxed to the equilibrium polymorph, along with a sharp decrease of carrier mobility. However, the correlation between molecular packing and charge transport for the C8-BTBT films is difficult to establish. The authors stated that the beam damage during grazing incidence X-ray diffraction (GIXD) measurements made it impossible to obtain the precise crystal packing structure for the metastable polymorph. Moreover, the crystal alignment was also disrupted after thermal annealing, making it difficult to attribute the mobility drop entirely to crystal structure change.

3.2.4 5,11-Bis(triethylsilylethynyl)anthradithiophene

5,11-Bis(triethylsilylethynyl)anthradithiophene (TES-ADT) is a high-performance organic semiconductor with good solubility [53]. In a study by Yu and colleagues, four polymorphs of TES-ADT was obtained in thin films, including three thin-film forms (α, β, and γ polymorphs) and one amorphous form [98]. The α-phase film exhibited the highest hole mobility of 0.4 $cm^2 V^{-1} s^{-1}$, which was about two orders of magnitude higher than that of the β and γ polymorphs. However, in a study by Chen et al., the β-phase film fabricated from toluene by drop casting had a higher mobility (0.22 $cm^2 V^{-1} s^{-1}$) than that of α-phase film from tetrahydrofuran (0.06 $cm^2 V^{-1} s^{-1}$) [52]. The opposite results from these two investigations reveal that to directly correlate mobility to molecular packing from thin-film transistor with different polymorphs is challenging. It is known that many factors can affect the charge transport in thin-film transistors, including film morphology, degree of crystallinity, orientation, grain size, grain boundaries, and so on.

3.3 Single-crystal transistors with different polymorphs

Single-crystal transistors are preferred for fundamental studies on structure-charge transport relationships owning to their high molecular ordering and no grain boundaries. However, structure-property investigations have been successfully performed for only a small number of organic semiconductors by means of single-crystal transistors. Compared to thin-film transistors, the manufacture of single-crystal OFETs is more complicated, which generally requires the use of high-precision deposition or micromanipulation techniques. Moreover, the preparation of single crystals with different polymorphs is very difficult. In this section, some examples of single-crystal OFETs are introduced.

3.3.1 Rubrene

Rubrene is an excellent organic semiconductor with single-crystal mobility up to 20 $cm^2 V^{-1} s^{-1}$ [99]. Four polymorphs of rubrene, including a monoclinic, a triclinic, and two orthorhombic forms, have been known for a long time [30],

but the structure-charge transport relationship has only been discussed recently. In an investigation by Matsukawa et al., an orthorhombic single crystal exhibited high carrier mobility up to 1.6 $cm^2 V^{-1} s^{-1}$, while that of the triclinic form was only 0.1 $cm^2 V^{-1} s^{-1}$ [29, 100].

The two polymorphs share similar π-π stacking distances, while the density of the π-stacking column in the (001) plane of orthorhombic crystal structure (**Figure 4a**) is much higher than that of the (0−11) plane of the triclinic crystal structure (**Figure 4b**). In other words, the π-π overlap along the carrier conduction direction in orthorhombic crystal is significantly larger than that in the triclinic crystal. Consequently, the orthorhombic crystal exhibits higher carrier mobility than the triclinic crystal.

3.3.2 Tetrathiafulvalene

Two polymorphs of tetrathiafulvalene (TTF), including a monoclinic orange crystal and a triclinic yellow crystals, were found many years ago [101]. The single-crystal transistors of the two polymorphs were fabricated by Jiang and colleagues recently [102]. Based on single-crystal transistors, the charge transport performance associated with molecular packing was discussed. The monoclinic *α*-form yielded a higher mobility of approximately 1.2 $cm^2 V^{-1} s^{-1}$, while that of the triclinic *β*-form was around 0.23 $cm^2 V^{-1} s^{-1}$. Compared to the *β*-form, the *α*-form shows strong π-π stacking along the short b axis and short contacts between S atoms (**Figure 5**), which may be the main factor contributing to the higher mobility.

3.3.3 Dibenzotetrathiafulvalene

Brillante et al. investigated the polymorphism of dibenzotetrathiafulvalene (DB-TTF), and four polymorphs were found [49]. The pure *α*-phase crystals were obtained from chlorobenzene or dimethylformamide solution [103]. In contrast, the *β*-phase crystals were synthesized from hot saturated toluene solution and were usually accompanied with the α-phase crystals. Moreover, *γ*-phase thin films were fabricated by ultra-high vacuum (UHV) vapor deposition on SiO_x substrates at temperatures of 50–70°C and drop casting of colloidal composite solutions of polystyrene (PS) and DB-TTF. The fourth polymorph, the *δ*-phase, was obtained physically pure by crystallization from a mixture solution of isopropanol and nitromethane, as well as by vapor deposition under vacuum. However, among the four polymorphs, only the full-unit-cell parameters of the *α*- and *β*-phase crystals have been obtained (**Figure 6**).

In the *α*-phase crystal, the molecules adopt a face-to-face herringbone structure, possessing a good π-π overlap. Though the *β*-phase crystal also shows a herringbone

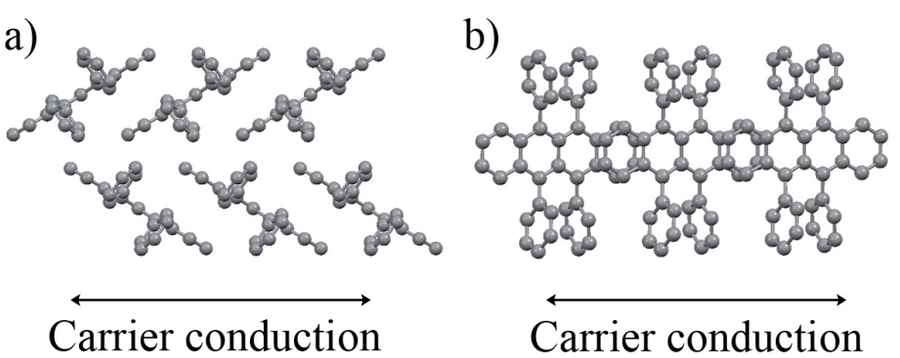


Figure 4.
Crystallographic structures of (a) the orthorhombic crystal (CCDC, 1025043) as viewed as the (001) plane and (b) the triclinic crystal (CCDC, 991020) as viewed as the (0−11) plane.

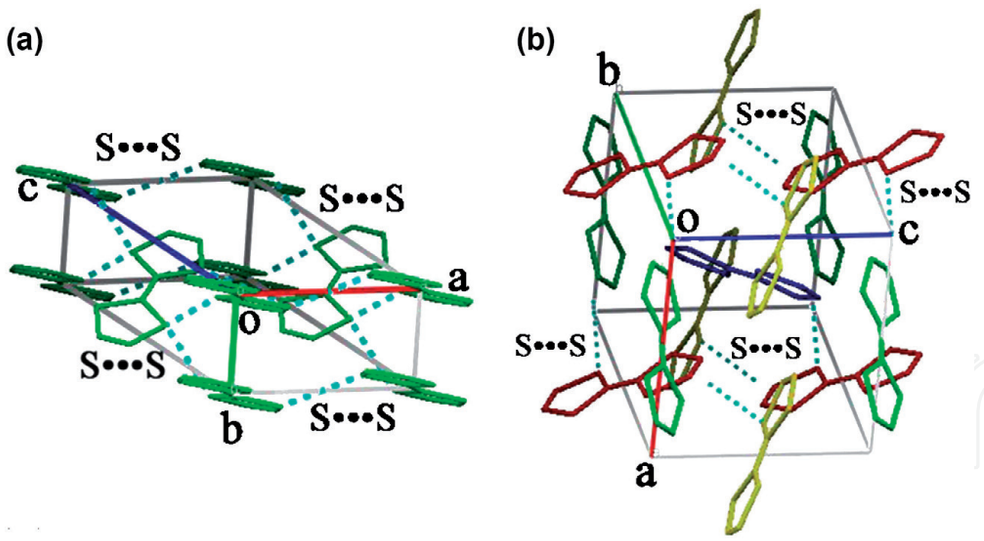


Figure 5.
Crystal packing of (a) α-TTF and (b) β-TTF with S···S interaction [102]. Copyright 2007, American Institute of Physics.

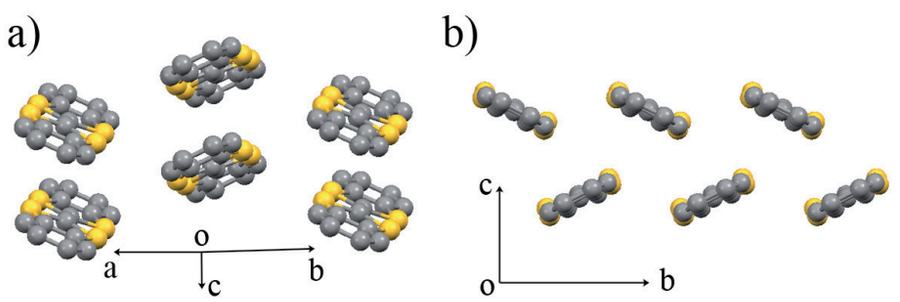


Figure 6.
The molecular packing of (a) the α-phase (CCDC, 1111519) and (b) the β-phase (CCDC, 696271) crystals of DB-TTF.

motif, the edge-to-face molecular packing neither results in π-π overlap between consecutive molecules in the stacks along b axis nor short contacts between adjacent columns. The solution-prepared single-crystal transistors based on α-phase crystal showed best hole mobility of up to 1.0 $cm^2\ V^{-1}\ s^{-1}$ [103].

3.3.4 Dithiophene-tetrathiafulvalene

Dithiophene-tetrathiafulvalene (DT-TTF) is a promising high-performance organic semiconductor, whose single-crystal OFETs were reported with high hole mobility up to 3.6 $cm^2\ V^{-1}\ s^{-1}$ [104]. Long plated crystals of DT-TTF can be easily prepared from a variety of solutions [104–106], which were named as the α-phase. In a study by Pfattner and colleagues, a new β-phase polymorph of DT-TTF was obtained as hexagonal-shaped platelet-like crystals [50]. The β-phase crystals were grown on some substrates from a solution of toluene or dichlorobenzene, mixed with crystals of the α-phase by ultrasonication of the solution before drop casting. The relative ratio of β-DT-TTF increased, whereas the α-phase was mostly obtained in the presence of small seed crystals. This indicates that the crystallization of α-phase probably starts in the solution, while the β-phase crystallizes directly on the substrate. The single-crystal OFETs of the two polymorphs were fabricated, and the device performances were measured, giving the hole mobilities of 1.18 and 0.16 $cm^2\ V^{-1}\ s^{-1}$ from the α-phase and β-phase crystals, respectively. Though the precise crystal structure of the β-phase crystal was not obtained, the analysis

of crystal structures for the two polymorphs revealed smaller distances between neighboring molecules in the α-phase crystal which may facilitate charge transport.

3.3.5 7,14-Bis((trimethylsilyl)ethynyl)-dibenzo[b,def]-chrysene

Stevens et al. found two polymorphs of 7,14-bis((trimethylsilyl)ethynyl)-dibenzo[b,def]-chrysene (TMS-DBC) using the physical vapor transport technology [58]. The first polymorph was obtained as red needles at low temperature, which was named as LT-phase (**Figure 7a**). The second polymorph was formed at high temperature as yellow plates and named HT-phase (**Figure 7b**). Further investigations found that the LT-phase can also be fabricated from solution and could not be converted into HT-phase by thermal annealing. Single-crystal OFETs of the two polymorphs were fabricated. The results revealed that the hole mobility of the HT-phase is up to 2.1 $cm^2 V^{-1} s^{-1}$, while that of the LT-phase is only 0.028 $cm^2 V^{-1} s^{-1}$.

As shown in **Figure 7**, the LT-phase adopts one-dimensional (1D) slipped stacking, while the HT-phase exhibits two-dimensional (2D) brick-wall stacking. Quantum chemical calculations revealed that the LT-phase possesses 1D charge transport channel along the π-stacking direction with a transfer integral of -86.8×10^{-3} eV (**Figure 7b**). In contrast, the HT-phase possesses exhibits 2D charge transfer channels with transfer integrals of -77.3×10^{-3} and -41×10^{-3} eV along the t1 and t2 directions, respectively (**Figure 7e**). Though the HT-phase exhibits slightly smaller transfer integral (absolute value) than that of the LT-phase, its 2D charge transport channels benefit charge transfer, which allows charge carriers to take alternative pathways around defects or trap states. As a result, the HT-phase facilitates higher mobility than the LT-phase.

3.3.6 N,N′-bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide

Würthner et al. manufactured single-crystal transistors based on α-phase crystals of N,N′-bis-(heptafluorobutyl)-2,6-dichloro-1,4,5,8-naphthalene tetracarboxylic diimide (Cl2-NDI), which showed electron mobility up to 8.6 $cm^2 V^{-1} s^{-1}$,

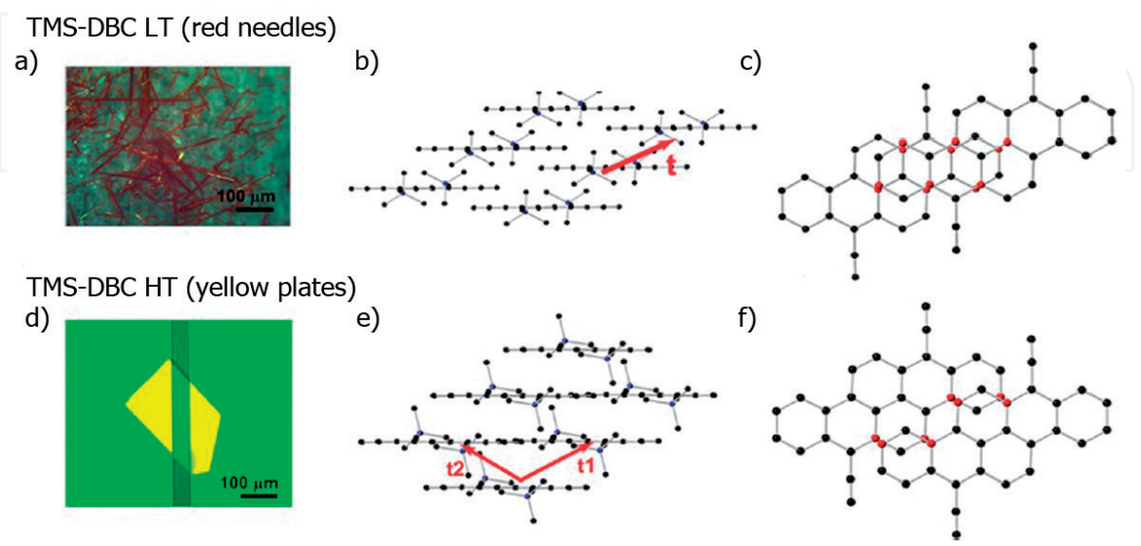


Figure 7.
(a) and (d) Crystal color, size, and shape of the LT red and HT yellow polymorphs of TMS-DBC. (b) and (c) Side and top views of the crystal packing in the red LT polymorph. (e) and (f) Side and top views of the crystal packing in the yellow HT polymorph. The directions corresponding to the largest calculated electronic couplings are indicated with arrows [58]. Copyright 2015, American Chemical Society.

achieving the best performance for air-stable n-type OFETs reported till now [107]. The α-phase polymorph of Cl2-NDI was grown on n-octadecyl triethoxysilane-modified substrates resulting in ribbon-shaped crystals by drop casting via $CHCl_3$ solution. In a study by He et al., the ribbon-shaped β-phase crystals were grown on various substrates like Si/SiO2 by sublimation in air ambient pressure [108]. The single-crystal transistors of β-phase crystals exhibited a maximum electron mobility of 3.5 $cm^2\ V^{-1}\ s^{-1}$.

In the α-phase crystal, Cl2-NDI molecules adopt a herringbone packing motif, where nearly half of each molecular skeleton overlaps with the adjacent molecule at a close π-stack distance of 3.27 Å. In contrast, molecules in the β-phase crystal exhibit a two-dimensional brick-wall packing arrangement with a π-stack distance of 3.29 and 3.32 Å. The selected area electron diffraction (SAED) studies revealed that single-crystal transistors for both the α-phase and β-phase crystals were measured along the π-π stacking direction. Compared to the α-phase crystal, the β-phase crystal possesses a weaker electronic coupling along the π-π stacking direction and a longer percolation pathway for electrons to cross the unit cell, which explains lower carrier mobility.

3.3.7 Dihexyl-dibenzo[d, d']thieno[3, 2-b; 4,5-b']dithiophene

In an investigation by He et al., dihexyl-dibenzo[d, d']thieno[3, 2-b; 4,5-b'] dithiophene (C6-DBTDT) was synthesized efficiently [47]; two polymorphs of C6-DBTDT were obtained by drop casting of solutions with different concentration in chlorobenzene or toluene. The platelet-like α-phase single crystals were prepared through drop casting from a high concentration chlorobenzene solution (5.0 mg/mL). In contrast, the micro-ribbonlike β-phase single crystals were formed from a relatively diluted chlorobenzene solution (0.3 mg/mL). Single-crystal transistors were fabricated, where the α-phase and β-phase crystals exhibited hole mobilities of 8.5 and 18.9 $cm^2\ V^{-1}\ s^{-1}$, respectively.

It is generally believed that only the HOMO level contributes to hole charge carrier transport from one molecule to another adjacent molecule. The electronic couplings of adjacent molecules in the α-phase and β-phase crystals were calculated by the quantum chemical calculations. The results indicated that the electronic couplings of HOMO between adjacent molecules in α-phase crystal are larger than that in β-phase crystal. On the other hand, the electronic couplings of HOMO demonstrate that the α-phase crystals may facilitate charge transport, which is in opposition to the experimental results. The authors noted that the electronic couplings of (HOMO-1)s for β-phase could be much larger than that of α-phase, which is near to the HOMO level. It was thought that (HOMO-1) level plays an important role in the charge transporting behavior.

3.3.8 2,8-Bis(butyl(methyl)amino)-indeno[1,2-b]fluorene-6,12-dione (BMA-IFD)

In a recent investigation by Fan et al., a new molecule, indeno[1,2-b]fluorene-6,12-dione derivative, i.e., BMA-IFD, was designed and synthesized [55]. Two polymorphs of BMA-IFD were easily obtained by crystallization from solution. The ribbon-shaped α-phase crystal (**Figure 8a**) was obtained from chloroform (1 mg/ml), while the flake-shaped β-phase crystal (**Figure 8b**) was obtained from xylene solution (0.2 mg/ml). Single-crystal OFETs were fabricated and measured. The results showed that the β-phase polymorph exhibits hole mobility up to 1.26 $cm^2\ V^{-1}\ s^{-1}$, much higher than that of the α-phase crystals (0.21 $cm^2\ V^{-1}\ s^{-1}$).

The α-phase and the β-phase crystals, whose structures were experimentally determined, were investigated by quantum chemical calculations to associate the

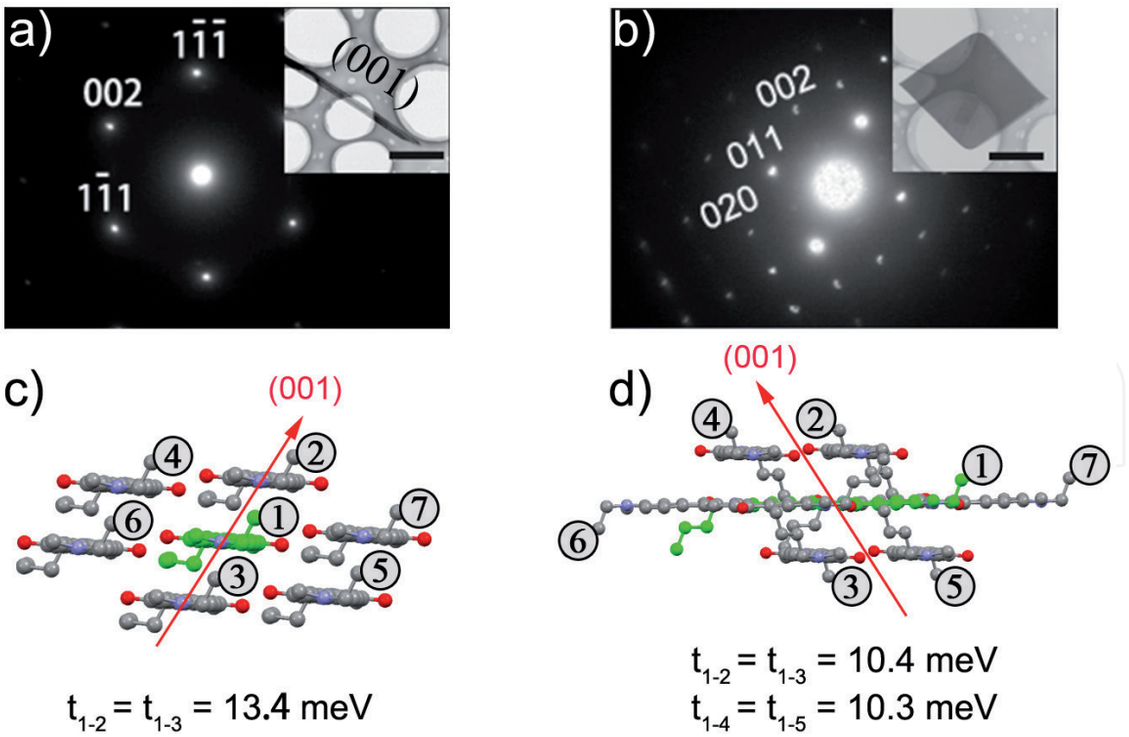


Figure 8.
SAED and TEM images of (a) the α-phase and (b) the β-phase crystals (the scale bar is 5 μm). The transfer integrals of (c) the α-phase and (d) the β-phase crystals along the (001) directions. The molecules in panels e and f are colored differently only for clarity purposes [55]. Copyright 2018, American Chemical Society.

charge transport properties with the molecular packing structures. The results show that a one-dimensional (1D) electron coupling between adjacent molecules is observed in the α-phase crystal (**Figure 8c**). In comparison, a two-dimensional (2D) electron coupling between adjacent molecules is found in the *β*-phase crystal (**Figure 8d**). Though the values of transfer integrals are close for the two polymorphs, the β-phase polymorph possesses a 2D charge transport network and therefore exhibits higher carrier mobility.

3.3.9 Titanyl phthalocyanine

Titanyl phthalocyanine (TiOPC) is a well-known organic semiconductor and photoconductor; however, it exhibits poor solubility in common solvents. In a recent study by Zhang et al., TiOPC crystals were synthesized by physical vapor transport (PVT) technique through a two-zone horizontal tube furnace [6]. Some sheet crystals were obtained at the temperature zone of about 210°C, while some ribbon crystals were grown at the temperature zone of about 180°C. The sheet and ribbon crystals belong to the *α*-phase and *β*-phase polymorphs, respectively. The measurements on single-crystal OFETs of the two polymorphs demonstrated that the *α*-phase crystals exhibit excellent charge transport property with mobility up to 26.8 $cm^2\ V^{-1}\ s^{-1}$, while that of *β*-phase crystals are only 0.1 $cm^2\ V^{-1}\ s^{-1}$.

The crystal structures of the two polymorphs were determined, where the *α*-phase and *β*-phase crystals exhibit a 2D lamellar brick stone motif and an unusual 3D framework, respectively. The main difference in electronic coupling of the two polymorphs was a strong interlayer electronic couplings perpendicular to the current direction in the *β*-phase crystal. The strong interlayer electronic couplings may result in destructive interference effects that remarkably diminish the charge carrier mobility.

4. Conclusion and outlook

Herein, the polymorphism in organic semiconductors is introduced, including the common strategies for polymorph control and investigations on OFETs from different polymorphs. Polymorphism is proved to be an excellent platform to directly correlate the molecular packing with charge transport for organic semiconductors; such investigations are very limited so far. A main challenge is to precisely tailor thermodynamic and kinetic factors of crystal nucleation and growth for large-area thin films or high-quality single crystals. Among the investigations on polymorphism, several polymorphs with outstanding charge transport performance have been obtained, demonstrating that altering the crystal polymorph structure of organic semiconductors is an efficient strategy to access high-performance OFETs. However, the majority of the high-mobility polymorphs are metastable. Consequently, getting insight into the relationship between molecular structure and crystal polymorph remains an important issue, which is essential for the rational design of molecular structures to further develop the desired crystal polymorphs with outstanding electrical characteristics.

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Conflict of interest

The authors declare no conflict of interest.

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