



## Review

## Tailoring crystal polymorphs of organic semiconductors towards high-performance field-effect transistors

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## ABSTRACT

As a quite ubiquitous phenomenon, crystal polymorph is one of the key issues in the field of organic semiconductors. This review gives a brief summary to the advances on polymorph control of thin film and single crystal of representative organic semiconductors towards high-performance field-effect transistors. Particularly, the relationship between crystal polymorph and charge transport behaviour has been discussed to shed light on the rational preparation of outstanding organic semiconducting materials with desired crystal polymorph.

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## 1. Introduction

Polymorphism is the ability of a chemical substance to exist in more than one crystal structure. McCrone defined a polymorph as “the existence of a solid crystalline phase of a given compound resulting from the possibility of at least two different arrangements of the molecules of that compound in the solid state” [1], which is the most widely accepted, but the meaning is still developing [2–4]. Packing polymorphism exists as a result of difference in crystal packing whereas conformational polymorphism results from the existence of different conformers of the same molecule. The first example of polymorphism in organic materials was observed by Wöhler and Liebig when they examined the solution of benzamide in 1832 [5]. It is quite ubiquitous for organic molecules to crystallize in two or more polymorphs with various packing arrangements due to the weak non-directional Van der Waals forces. Crystal polymorphism has been found in typical organic semiconductors such as acenes [6–8], phthalocyanines [9], tetrathiafulvalenes [10,11] and oligothiophenes [12–14]. Generally, the polymorphic modifications exhibit different band

structures, electronic couplings and electron–phonon couplings, thus leading to a big discrepancy in charge transporting behaviours and other optoelectronic properties. On the other hand, although less considered than chemical impurity, polymorphism tend to give phase inhomogeneities, which is an intrinsic source of disorder to pose detrimental effects on charge carrier mobility [15,16]. Therefore, the tailoring of crystal polymorphs has become a crucial issue in the field of organic semiconductors towards high device performance as well as practical applications [17,18].

Like most chemical processes, crystallization in polymorphic systems is governed not only by thermodynamic factors but also by kinetic pathways [19]. The minimization of free energy will be offset by the kinetic tendency to crystallize as fast as possible to relieve the imposed supersaturation. The specific polymorph can be tailored by vapour deposition, solution and thermal techniques such as physical vapour transport, hot-wall deposition, organic molecular beam epitaxy, liquid–liquid interfacial precipitation, drop-casting, solution-sheared and thermal gradient methods, wherein the substrate nature plays a significant role in formation of defined crystal phase in some cases. In addition, the crystal polymorphs can be interconverted by subsequent treatment through tuning the physical parameters.

This review will summarize the studies on polymorph control of thin film and single crystal of representative organic semiconductors towards high-performance field-effect transistors. The relationship

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between crystal polymorph and charge transport behaviours will be discussed.

## 2. Crystal polymorphs and carrier mobility

### 2.1. Rubrene

As a tetraphenyl derivative of tetracene, rubrene is one of the superstars in organic semiconductors, which has been found to show three crystal polymorphs: orthorhombic, triclinic and monoclinic as shown in Fig. 1 [6]. Orthorhombic single crystals of rubrene, which are usually grown by the physical vapour deposition method (PVD) [20–23], have been reported to exhibit the record charge-carrier mobility of  $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [24]. Triclinic and monoclinic forms of rubrene with much lower mobilities have been facily prepared by reprecipitation method [6].

Close  $\pi$ -stacking arrangement of rubrene molecules in the orthorhombic polymorph lead to a high value of the transfer integral along the [0 1 0] direction, accounting for the outstanding carrier mobility [25,26]. Although  $\pi$ -stacking with a similar stacking distance is observed in the triclinic polymorph, the absence of a herringbone disposition of the molecules together with a small short-axis displacement is responsible for a poor mobility [27]. As for monoclinic polymorph, no  $\pi$ -stacking is present in the packing motif.

Very recently, Kim and coworkers reported epitaxial growth of highly ordered, orthorhombic rubrene films on hexagonal boron nitride (h-BN) layers as a van der Waals substrate and demonstrated high mobility up to  $11.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  comparable to those

of single-crystal counterparts (Fig. 2) [28]. The epitaxial approach to fabricate organic/inorganic van der Waals heterostructures can be further extended to numerous other organic and layered materials for various electronic applications.

### 2.2. Pentacene

Pentacene, a fused-ring polycyclic aromatic hydrocarbon, is another important organic semiconductor with several crystal polymorphs, particularly for thin films deposited by thermal evaporation [7,8,29–31]. Phase inhomogeneities almost invariably exist as a diffusion of one polymorph inside the other, irrespective of phase impurity amount, crystal shape, or grain size [32]. It has been demonstrated that pentacene thin film evolves from orthorhombic phase in the first several layers to the thin film phase and triclinic bulk phase with the increased film thickness [30,31].

The crystal polymorph growth of pentacene thin film was found to be dependent on the substrate [33,34]. Hwang *et al.* presented a pentacene thin film field-effect transistor using silk fibroin as the gate dielectric with a very high mobility value of  $23.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in the saturation regime and a low operating voltage of  $-3 \text{ V}$  mainly because that a great reduction of amorphous pentacene occurred when pentacene was deposited onto silk fibroin [35]. For a typical fabrication process of pentacene film transistor, the thin film grown on a dielectric layer by vapour deposition usually contains amorphous and crystalline phases [36]. In contrast, silk fibroin served as a better substrate than  $\text{SiO}_2$  for the growth of the pentacene orthorhombic phase and thin film phase, respectively, at the beginning of pentacene deposition and in the subsequent

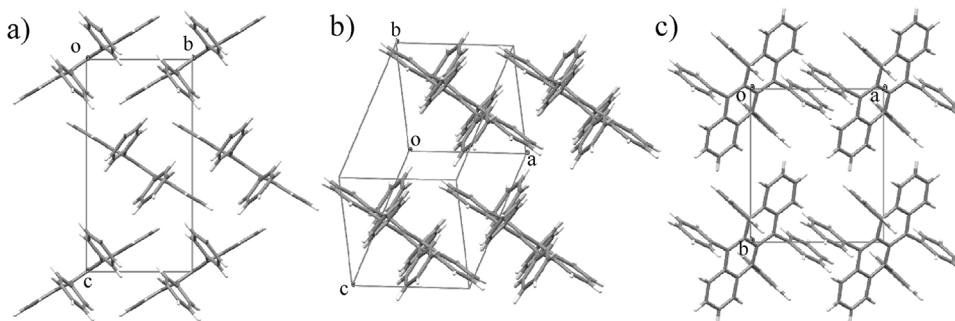


Fig. 1. Crystal structure of the orthorhombic (a), triclinic (b) and monoclinic (c) phases of rubrene.

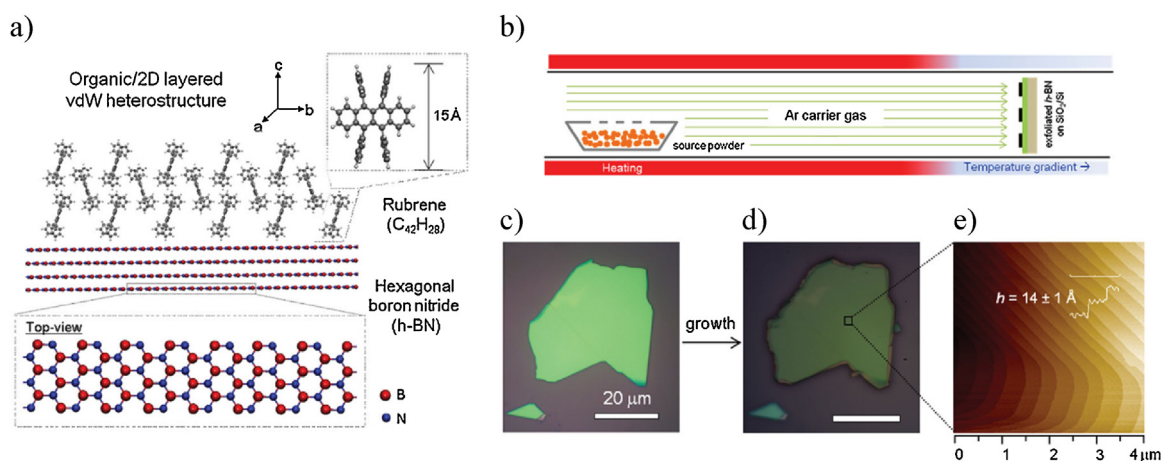


Fig. 2. Growth of organic/2D layered van der Waals heterostructures. Schematic illustration of: (a) the organic/2D layered van der Waals heterostructure composed of rubrene and h-BN and (b) the vapour-phase transport method for the growth. Optical images of: (c) the h-BN crystal exfoliated on a  $\text{SiO}_2/\text{Si}$  substrate and (d) the rubrene film grown on h-BN. (e) AFM image of the film surface and the height profile along the line. It shows a highly uniform terrace structure with the step height of  $14 \pm 1 \text{ \AA}$ . Reprinted with permission from Ref. [28], Copyright 2014, Wiley-VCH.

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