Molecular orientation transformation in initial growth stage of disk-like phthalocyanine during organic vapor deposition process†

Tonghui Wang, Yongfu Zhu* and Qing Jiang*

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The device performance of organic field-effect transistors depends strongly on the morphology and molecular orientation of the first few molecular layers near gate dielectrics, which are in turn governed by the initial growth stage. In this work, we establish a unified thermodynamic model to characterize the initial growth stage of disk-like and rod-like organic molecules during an organic vapor deposition process. Under a high substrate temperature and low deposition rate, the initially grown parallel cluster can transfer to the normal one at a critical molecular number \( N_c \), which is determined by the competition between the surface energy of the molecule \( \gamma_f \) (surface energy of the molecular surface normal to the \( \pi-\pi \) interaction direction for a disk-like molecule or parallel to the molecular axis for a rod-like molecule) and that of the substrate \( \gamma_{sub} \). By thermodynamic analyses and molecular dynamics simulations, we further confirm this transformation from disk-like phthalocyanine. When \( N < N_c \), a parallel cluster is grown by self-assembly of individual lying down molecules driven by \( \gamma_f \). At \( N \geq N_c \), together with \( \gamma_f > (5/7)\gamma_{sub} \), the grown parallel cluster tilts down to form a normal one where \( N_c \approx \gamma_f/W\gamma_f \) (\( \gamma_f \) is the surface energy of the molecular surface parallel to the \( \pi-\pi \) interaction direction. \( W \) and \( H \) denote the molecular width and the intermolecular distance in the \( \pi-\pi \) interaction direction).

1. Introduction

Organic semiconductor films have attracted considerable attention due to their low-cost deposition, flexibility and large area processing in comparison with traditional inorganic counterparts. The promising application of organic thin films (OTFs) as active layers in devices such as organic field-effect transistors (OFETs), organic photovoltaic cells and organic light-emitting diodes has sparked a worldwide research activity in the controlled growth of OTFs. Device performance is mainly determined by the charge-carrier mobility (\( \mu \)), which can be described by the band theory for delocalized charges in structurally ordered materials, the tight-binding model for delocalized charges in weakly disordered systems and the hopping model for localized charges in strongly disordered materials. In these models, the electronic coupling is an important parameter, which is determined not only by the spatial overlap of orbitals, but also by the phase relationships between the orbitals of each molecule. To ensure high \( \mu \) values, strong intermolecular electronic coupling, which is associated with excellent overlap between the \( \pi \)-systems of neighbouring molecules, is essentially needed. Moreover, since the charge-carrier transport is effectively normal to the molecular axis and the light absorption/emission is polarized parallel to the molecular axis, organic molecules with normal orientation relative to the gate dielectric would be desired for OFETs, while the molecules oriented parallel to the contact could be ideal for electro-optical devices. For small organic molecules, organic vapor deposition (OVD) is an effective way to fabricate OTFs for use in OFETs. The typical deposition conditions are a background pressure of \( 10^{-4} \sim 10^{-8} \) Pa, a substrate temperature \( (T_{sub}) \) of \( 300 \sim 500 \) K and a deposition rate \( (\Phi) \) of \( 0.5 \sim 2.0 \) ML min\(^{-1}\). In general, organic molecules tend to stand upright on the substrate when they are deposited by the OVD method. Recently, the weak epitaxial growth method has been developed, where both the middle para-sexiphenyl layer and the following phthalocyanine layer are deposited by the OVD method. However, the causes and dynamics of the formation of normal orientation aren’t fully understood. As a result, the undesirable parallel orientation also appears in experiments.

It is well-known that the initial growth stage plays a decisive role in the subsequent growth and eventually determines the film qualities. Especially, since the charge-carrier transport in OFETs is confined in the first few molecular layers near gate dielectrics, investigations on the initial growth stage of OTFs during the OVD process become apparently urgent. Until now, many efforts have concentrated on the growth mechanism, morphology and growth dynamics of OTFs. However, the...
relevant studies on the initial growth stage have lagged far behind due to the limitations of spatial and temporal scales in direct experimental observation.

On the other hand, the inherent anisotropy of organic molecules, such as the typical disk-like and rod-like molecules, makes the initial growth stage of OTFs more complex than that of inorganic films. Using kinetic Monte Carlo simulations, Choudhary et al. investigated the sub-monolayer growth of rod-like pentacene by depositing a series of virtual molecules. Their simulations qualitatively show that the molecules flip up from a parallel orientation to an upright position once a critical nucleus is achieved and the conditions are favorable to forming an upright island. By the scaling and rate equation theory, Stadlober et al. found that the critical nucleus of rod-like pentacene consists of only three molecules when they are deposited on amorphous SiO₂ (α-SiO₂) and polymeric substrates at 298–343 K with Φ of 0.07–6.67 ML min⁻¹. The same critical nucleus size under different conditions means that OVD is actually under large supersaturation. Based on two fundamental orientations of the critical nuclei, Kubono et al. considered the initial growth stage of rod-like molecules via a complex kinetic model. The model shows that a higher degree of normal orientation at higher T_mel is induced by faster re-evaporation of the parallel clusters. However, it can’t elucidate the effect of Φ on the molecular orientation and the formation of complete normal orientation under negligible re-evaporation. In contrast to rod-like molecules, much less work, both theoretical and simulative, is carried out for disk-like molecules. All of these motivate us to study the initial growth stage of OTFs during the OVD process. Since molecular dynamics (MD) simulation has been successfully used to consider the self-assembly and ordering of organic molecules, an alternative way is thermodynamic modeling plus MD simulation, which can provide valuable insights for the initial growth process.

Among the explored organic materials, the family of planar phthalocyanines is recognized as one of the most promising candidates for fabricating OFETs due to their high mobility, long-term chemical and thermal stability and good processability at a relatively low cost. In addition, metal-phthalocyanine derivatives are one of the developed air-stable n-type organic semiconductors. These let phthalocyanine be an interesting model system for better understanding the initial growth stage of OTFs, especially for that of disk-like molecules.

In this contribution, we first build a unified thermodynamic model to characterize the initial growth stage of organic molecules in both disk-like and rod-like during the OVD process. Following this, a detailed thermodynamic analysis is carried out for a model system, namely, free-base phthalocyanine (H₂Pe) on the widely used α-SiO₂ substrate. Then, we identify the corresponding molecular process by MD simulations and determine the key parameters that control this process. Finally, the morphology and molecular orientation of OTFs in experiments are reasonably elucidated, while the basic requirements for getting normal orientation are given.

2. Thermodynamic model

In thermodynamics, the free energy required to form an N-molecule cluster, ΔG, can be given by:

\[ \Delta G = -N \Delta g + \sum S \gamma S, \]  

where the first term shows the energy gain induced by the difference of the chemical potential \( \Delta g \) between the vapor and bulk crystal phases and the second one denotes the energy loss due to the appearance of new surface \( S \) with surface energy \( \gamma \). The principle for the minimum of \( \Delta G \) can be reduced to the minimum of the total surface energies. In a highly supersaturated vapor phase, the molecules should aggregate into a cluster with minimal total surface energies too. For disk-like molecules, due to the large frontal surface and relatively strong π–π interaction between them, the molecules should firstly stack along the π–π interaction direction to expose the small lateral surface, as shown in Fig. 1. For rod-like molecules, a column-like cluster can be formed due to the cylindrical symmetry of the molecules and the preferential growth in the direction normal to the molecular axis (see the schematic diagram in ref. 22). The height of the column-like cluster corresponds to the molecular length \( L \). The free energy needed to form such clusters from disk-like and rod-like molecules, \( \Delta G_{\text{homo}} \), can be expressed as:

\[ \Delta G_{\text{homo}} = -N \Delta g + 2 \gamma l A_l + \sum N \gamma f A_l \]  

\[ \Delta G_{\text{homo}} = -N \Delta g + 2 \gamma_i L \sqrt{A_o \pi} \sqrt{N} + 2N \gamma_i A_o \]

In eqn (2a), \( \gamma_l \) and \( \gamma_i \) denote the surface energies of the frontal and the lateral surfaces of disk-like molecules, respectively. \( A_l \) and \( A_i \) are the surface areas per molecule of the frontal and the lateral surfaces, respectively. In eqn (2b), \( \gamma_l \) and \( \gamma_i \) denote the surface energies of the surfaces parallel and normal to the molecular axis of rod-like molecules, respectively. \( A_o \) is the cross-section area per molecule.

It is well-known that the thermodynamic amounts are size-dependent. However, since the intermolecular forces are the weak van der Waals forces in nature in the above case, the interactions among molecules can be neglected when the intermolecular distance is larger than 10 Å. Thus, the size-dependence on the thermodynamic amounts is negligible when \( N \geq 3 \), while the π–π interaction distance between two molecules is 3.30–3.70 Å.

When a foreign substrate appears, these clusters can keep all molecules parallel or normal to the substrate under the

![Fig. 1 Schematic diagrams of a single disk-like molecule and an initially grown cluster in a highly supersaturated vapor phase.](Image)
prerequisite that they can’t break down. For disk-like molecules, if the cluster keeps all molecules normal to the substrate, the contact between the substrate and the lateral surface with maximal $\gamma_{l}A_{l}$ value should be energetically more favorable. For rod-like molecules, if the cluster keeps all molecules parallel to the substrate, its shape changes from column to arch due to the substrate effect.44 Hereinafter, the clusters with all molecules parallel and normal to the substrate are referred to as parallel and normal clusters, respectively, which are denoted by subscripts $p$ and $n$. As a result, $\Delta G_{p}$ and $\Delta G_{n}$ for disk-like molecules can be expressed as:

$$\Delta G_{p} = \Delta G_{\text{homo}} + (\gamma_{l} - \gamma_{n} - \gamma_{l}A_{l}) (3a)$$

and for rod-like molecules as:

$$\Delta G_{p} = \Delta G_{\text{homo}} + (\gamma_{l} - \gamma_{n} - \gamma_{l}A_{l}) (3b)$$

Here, $\gamma_{l}$ and $\gamma_{n}$ are the interface energies between the substrate and the relevant surface. $\gamma_{\text{sub}}$ is the surface energy of the substrate. $\beta$ is the contact angle that satisfies Young’s equation of $\cos \beta = (\gamma_{\text{sub}} - \gamma_{\text{sub}})\gamma_{l}$. For disk-like molecules, $d\Delta G_{p}/dN - d\Delta G_{n}/dN = (\gamma_{l} - \gamma_{n} - \gamma_{l}A_{l})$ and for rod-like molecules, $d\Delta G_{p}/dN - d\Delta G_{n}/dN = (\gamma_{l} - \gamma_{n} - \gamma_{l}A_{l})$.

Hereinafter, the clusters with all molecules parallel to the substrate can remain up to $N > 34$ and that for rod-like molecules as:

$$\Delta G_{p} = \Delta G_{\text{homo}} + 2\gamma_{l}L\sqrt{A_{l}}(\sqrt{\beta - \sin \beta \cos \beta - \sqrt{\frac{\pi}{2}}} \sqrt{N}) (3c)$$

$$\Delta G_{n} = \Delta G_{\text{homo}} + (\gamma_{l} - \gamma_{n} - \gamma_{l}A_{l}) (3d)$$

where $\gamma_{l}$, $\gamma_{n}$, and $\gamma_{\text{sub}}$ are the interface energies of the substrate, the contacting free surface, and the substrate itself, respectively. $\gamma_{l}$ and $\gamma_{n}$ are the contact angles that satisfy Young’s equation of $\cos \beta = (\gamma_{\text{sub}} - \gamma_{\text{sub}})\gamma_{l}$. For disk-like molecules, $d\Delta G_{p}/dN - d\Delta G_{n}/dN = (\gamma_{l} - \gamma_{n} - \gamma_{l}A_{l})$ and for rod-like molecules, $d\Delta G_{p}/dN - d\Delta G_{n}/dN = (\gamma_{l} - \gamma_{n} - \gamma_{l}A_{l})$.

Accordingly, there must exist a critical size, $N_{c}$, where $\Delta G_{p}(N_{c}) > \Delta G_{n}(N_{c})$ and $\Delta G_{n}(N_{c} - 1) < \Delta G_{n}(N_{c} - 1)$ for both types of molecules. In other words, when $N > N_{c}$, the normal cluster becomes stable while the parallel one is metastable where a parallel–normal orientation transformation occurs. By making $\Delta G_{p} - \Delta G_{n} = 0$, $N_{c}$ can be determined as:

$$N_{c} = \frac{(\gamma_{l} - \gamma_{n})A_{l}}{(\gamma_{l} - \gamma_{n} - \gamma_{l}A_{l})}$$

and

$$N_{c} = \frac{(\gamma_{l} - \gamma_{n})A_{l}}{(\gamma_{l} - \gamma_{n} - \gamma_{l}A_{l})}$$

for disk-like and rod-like molecules, respectively. The prerequisite of the above transformation is that the parallel clusters don’t break down on the substrate till $N > N_{c}$ or the growth of the parallel clusters on the substrate can remain up to $N > N_{c}$. From eqns (3a) and (3c), one can get the free energy difference between two parallel $N$-2-molecule clusters (p2) and one parallel $N$-molecule cluster (p1) as:

$$\Delta G_{p2-p1} = 2\gamma_{l}A_{l} + (\gamma_{l} - \gamma_{n} - \gamma_{l}A_{l}) (4a)$$

for disk-like molecules and as:

$$\Delta G_{p2-p1} = (2\sqrt{2} - 2)\gamma_{l}L\sqrt{A_{l}}(\sqrt{\beta - \sin \beta \cos \beta} \sqrt{N}) (4b)$$

with $\cos \beta = (\gamma_{\text{sub}} - \gamma_{\text{sub}})\gamma_{l}$ for rod-like molecules.

As stated above, the required prerequisite for the transformation is satisfied by $\Delta G_{p2-p1} > 0$. Namely, $\gamma_{l} + \gamma_{n} - \gamma_{l}A_{l} > 0$ for disk-like molecules. For rod-like molecules, since $(2\sqrt{2} - 2)\gamma_{l}L\sqrt{A_{l}}(\sqrt{\beta - \sin \beta \cos \beta} \sqrt{N}) > 0$, $\cos \beta = (\gamma_{\text{sub}} - \gamma_{\text{sub}})\gamma_{l}$ must be smaller than one. Namely, $\gamma_{l} + \gamma_{n} - \gamma_{l}A_{l} > 0$, which is interestingly the same as that of disk-like molecules.

For an incoherent interface consisting of two different materials, the interface energy can be taken by the mean value of grain boundary energies of both materials approximately.46 Meanwhile, since the grain boundary energy is about 1/3 of the surface energy, $\gamma_{n} = (\gamma_{l} + \gamma_{n} + \gamma_{n})/2$. As a result, $\gamma_{l} > (5/3)\gamma_{n}$ is the prerequisite for both disk-like and rod-like molecules.

Although the model is developed based on the $\pi$-stacked structure for disk-like molecules, it can be applied to disk-like molecules in a herringbone structure. Taking $\pi$-H$_{2}$Pc’s herringbone structure as an example, the adjacent H$_{2}$Pc molecules are packed with two modes (i.e., face-to-face and face-to-edge) in 2-dimensional directions (see Fig. S1 in Supplementary Information).43 The former corresponds to the $\pi$-stack of H$_{2}$Pc molecules,43 while the latter is formed by the lateral interactions of the $\pi$-stacked H$_{2}$Pc clusters. Consequently, the formation of the herringbone structure for H$_{2}$Pc molecules is behind the orientation transformation of the $\pi$-stacked H$_{2}$Pc clusters, which will be discussed later. Thus, the model can be used to describe the orientation transformation of disk-like molecules in the herringbone structure too. Moreover, the model can also be employed to rod-like molecules in herringbone packing by taking $A_{o}$ as the cross-section area per molecule in the herringbone structure.

The model-predicted transformation mechanism is consistent with the Monte Carlo simulation result of rod-like pentacene.28 Furthermore, the transformation mechanism can explain the formation of complete normal orientation under negligible re-evaporation. When organic molecules are deposited under a high $T_{\text{sub}}$ or a low $\Phi$, they can adequately diffuse on the substrate, thus ensuring more parallel clusters being transferred. Especially for rod-like molecules, as $T_{\text{sub}}$ increases, $\beta$ becomes larger. Accordingly, $N_{c}$ decreases and the parallel-normal transformation becomes easier. These correspond to the experimental phenomena that a high $T_{\text{sub}}$ or a low $\Phi$ generally results in normal orientation.33,36,44

3. Simulation methods

All MD simulations were performed using the DISCOVER code under constant particle number, volume and temperature conditions (i.e., in $NVT$ ensemble).38 The COMPASS force field was adopted for all atom–atom interactions.39 $T_{\text{sub}}$ was chosen at 350 K, which was controlled by the Berendsen algorithm.40 The equations of motion were integrated by the Verlet leap-frog algorithm with a time step of 1 fs.41 The configurations were saved every 5 ps. The non-bonded van der Waals interactions were treated by truncating atom pairs with an interatomic distance greater than 10 Å, coupled with a long-range tail correction.42 The Ewald method was used for the long-range treatment of electrostatic interactions.42 For the sake of accuracy and computing time saving, only the energies of the equilibrium configurations were calculated by the Ewald method for both
van der Waals and electrostatic interactions. For simplicity, a completely hydrated \( \alpha \)-SiO\(_2\) substrate was used. From the heated bulk \( \alpha \)-SiO\(_2\), we obtained a periodic slab with an area of 82.94 \( \times \) 84.07 A\(^2\) and a thickness of about 12 A. Then, the slab was modified by deleting Si atoms at the surface and then saturated by H atoms according to the experimental results.\(^{44}\)

Finally, a vacuum of 40 A was added to avoid the interaction between repeated slabs in the direction normal to the surface. For this superlattice, the period lattice lengths in three dimensions are much larger than the width of a H\(_2\)Pc molecule. Thus, the amorphous slab in this superlattice can approximately render an amorphous surface, since the size of the superlattice is large enough to neglect the interactions from outside the superlattice.

In simulations, only the atoms in the bottom 6 A were constrained. Increasing the slab from 12 to 16 A did not change the interaction between the H\(_2\)Pc molecule and the substrate within an error of 3.98\%, which implies that both the slab and the constrained thickness are thick enough. For simulating the deposition under high \( T_{\text{sub}} \) and low \( \Phi \), we placed only several H\(_2\)Pc molecules on the substrate with enough equilibrium time. The time of each simulation was 6–30 ns and the data production time was 1 ns. For several vapor molecules in this periodic cell, \( P \) is about 1 atm at 350 K, treating the vapor as ideal gas. Then, \( \Delta g \) can be determined as \( \Delta g = 1.46 \text{ eV} \) H\(_2\)Pc\(^{-1}\).\(^{14,44}\)

In our simulations, the concentration corresponds to 0.022 N ML or 0.006 N ML when all H\(_2\)Pc molecules are initially placed parallel or normal to the substrate. Additional details about the procedures are placed in the Supplementary Information\(^{\dagger}\).

4. Results and discussion

4.1 Thermodynamic analyses

For H\(_2\)Pc in \( \alpha \)-phase that usually appears during the OVD process, H\(_2\)Pc(010) is the frontal surface while H\(_2\)Pc(100) and H\(_2\)Pc(001) are the lateral surfaces.\(^{33}\) Adding these data into eqn (2a), \( \Delta G_{\text{homo}} = -N\Delta g + 2\gamma_{(010)}A_{(010)} + 2N\gamma_{(100)}A_{(100)} + 2N\gamma_{(001)}A_{(001)} \), \( \gamma_{(100)} \), \( \gamma_{(010)} \) and \( \gamma_{(001)} \) at 350 K are 71.30, 81.93 and 67.64 mJ m\(^{-2}\), respectively (see Supplementary Information\(^{\dagger}\)).

Because the structure of a cluster should differ from the bulk, \( A_{(100)} \), \( A_{(010)} \) and \( A_{(001)} \) are directly taken from a H\(_2\)Pc molecule. Namely, \( A_{(100)} \approx A_{(001)} = 12.39 \times 3.40 \text{ A}^2 \) and \( A_{(010)} = 12.39 \times 12.39 \text{ A}^2 \). H\(_2\)Pc(100) is obviously the lateral surface with the maximal \( \gamma_{(100)} \) value. The contact of H\(_2\)Pc(100) with iner substrates has also been experimentally reported.\(^{4,33}\) Since \( \gamma_{\text{sub}} \) of the completely hydrated \( \alpha \)-SiO\(_2\) substrate is only slightly larger than \( \gamma \) of liquid water,\(^{45}\) the latter (62.67 mJ m\(^{-2}\) at 350 K)\(^{46}\) is used for \( \gamma_{\text{sub}} \). For H\(_2\)Pc molecules vapor-deposited on \( \alpha \)-SiO\(_2\) substrate at 350 K, since \( \gamma_{(100)} > (5/7)\gamma_{\text{sub}} \), the growth of a parallel cluster can remain. Hence, in light of eqns (3a) and (3b), there are:

\[
\Delta G_p = \Delta G_{\text{homo}} + (\gamma_{(010)} - \gamma_{\text{sub}} - \gamma_{(100)})A_{(100)} \tag{5a}
\]

\[
\Delta G_n = \Delta G_{\text{homo}} + (\gamma_{(001)} - \gamma_{\text{sub}} - \gamma_{(001)})A_{(001)}, \tag{5b}
\]

where \( \gamma_{(010)} \) and \( \gamma_{(001)} \) are 21.53 and 29.56 mJ m\(^{-2}\), respectively (see Supplementary Information\(^{\dagger}\)).

Fig. 2a shows \( \Delta G_p \) and \( \Delta G_n \) functions in light of eqns (5a) and (5b) under the simulation conditions. As shown in Fig. 2a, both \( \Delta G_p \) and \( \Delta G_n \) monotonically decrease with \( d\Delta G_p/dN > d\Delta G_n/dN \). When \( N < 5 \), the parallel cluster is more stable than the normal one. When \( N \geq 5 \), \( \Delta G_p > \Delta G_n \). As a result, the parallel–normal transformation takes place. For H\(_2\)Pc molecules vapor-deposited on the \( \alpha \)-SiO\(_2\) substrate at 350 K under the typical \( \Phi \) of 0.5–2.0 ML min\(^{-1}\)\(^{14}\), \( \Delta g = 1.29–1.33 \text{ eV} \) H\(_2\)Pc\(^{-1}\) (see Supplementary Information\(^{\dagger}\)). Though the simulated \( \Delta g \) value is larger than the experimental one, their \( \Delta G_{\text{p(n)}} \) values have similarities (Fig. S2\(^{\dagger}\)).

To further understand the effects of the surface and interface energies on the relative stability between the parallel and the normal clusters, \( \Delta G_p - \Delta G_n \) can be divided into three parts, namely, \( \Delta G_p - \Delta G_n = \Delta G_{\text{surf}} + \Delta G_{\text{sub}} + \Delta G_i \). Here, \( \Delta G_{\text{surf}} = N(N_{(100)}A_{(100)} - \gamma_{(100)}A_{(100)}) \), \( \Delta G_{\text{sub}} = N(N_{(010)}A_{(010)} - \gamma_{(010)}A_{(010)}) \) and \( \Delta G_i = \gamma_{(010)}A_{(010)} - N\gamma_{(100)}A_{(100)} \) denote the parts contributed by the surface energy of the clusters, surface energy of the substrate and interface energy between the clusters and the substrate, respectively. Fig. 2b shows \( \Delta G_p - \Delta G_n, \Delta G_{\text{surf}}, \Delta G_{\text{sub}}, \Delta G_p - \Delta G_n \) and \( \Delta G_f \) functions. When \( N < 5 \), \( \Delta G_i = 0 \text{ eV} \), \( \Delta G_p - \Delta G_n \) is mainly determined by \( \Delta G_{\text{surf}} \) and \( \Delta G_{\text{sub}} \). In other words, when H\(_2\)Pc(010) contacts with the substrate, an interface is formed during the coalescence of H\(_2\)Pc(010) and the relevant substrate. This exothermic process stabilizes the parallel cluster. However, as \( N \) increases, more areas of H\(_2\)Pc(100) and H\(_2\)Pc(001) appear, which makes the parallel cluster metastable. When \( N \geq 5 \), \( \Delta G_i > \gamma_{(010)}A_{(010)}, \) which stabilizes the normal cluster. Thus, the parallel cluster should tilt down to expose H\(_2\)Pc(100).
Meanwhile, H$_2$Pc(100) contacts with the substrate. Although the interface energy becomes more important to stabilize the parallel cluster, its effect is weaker than the energetic increase due to the product of the surface energy and surface area. Near $N_c$, the change of $\Delta G_{\text{surf}}$ with $N$ is almost the same as $\Delta G_p - \Delta G_n$. Namely, $\Delta G_p - \Delta G_n \approx \Delta G_{\text{surf}} = N\gamma(100)A(100) - \gamma(010)A(010)$ around $N_c$. Let $\Delta G_p - \Delta G_n = 0$, $N_c$ can be further simplified as:

$$N_c = \frac{\gamma(010)A(010)}{\gamma(100)A(100)} = \frac{\gamma(010)}{\gamma(100)} \cdot \frac{W}{H}$$  \hspace{1cm} (6)

where $W$ and $H$ denote the width of the H$_2$Pc molecule and the distance between two H$_2$Pc molecules in the $\pi-\pi$ interaction direction, respectively. For disk-like molecules, since $H = 3.30$–3.70 Å, $N_c$ is mainly determined by other three amounts. Namely, larger $\gamma(010)$, $W$ and smaller $\gamma(100)$ result in a larger $N_c$ and vice versa.

In simulations, 2$\gamma_dA_f$ and $(\gamma_{id} - \gamma_{sub} - \gamma_d)A_f$ in eqn (4a) can be related to interactions by $E_{\pi-\pi} = 2\gamma_dA_f$ and $E_{\text{inf}}(N) = -(\gamma_{id} - \gamma_{sub} - \gamma_d)A_f$, where $E_{\pi-\pi}$ is the $\pi-\pi$ interaction between molecules and $E_{\text{inf}}(N)$ is the interaction between a parallel $N$-molecule cluster and substrate. Then, eqn (4a) can be rewritten as $\Delta G_{32-p1} = E_{\pi-\pi} - E_{\text{inf}}(N)$. Since $E_{\pi-\pi}$ and $E_{\text{inf}}(N)$ can be directly obtained and are the needed sum of thermodynamic amounts, we will use them to describe the simulation results. Furthermore, to describe the molecular process clearly, the adsorption energy of the $i$th H$_2$Pc molecule $E_{\text{ads}}(ith)$, the total energy release $E_{\text{total}}(N)$ and the average energy release per molecule $E_{\text{per}}(N)$ after equilibrium are calculated by: $E_{\text{ads}}(ith) = -(E_{\text{sub}} + N(T) - [E_{\text{sub}} + N(\gamma(T) + \gamma_d)])$, $E_{\text{total}}(N) = E_{\text{sub}} + (T) - E_{\text{sub}}(T) - N\gamma_d(T)$ and $E_{\text{per}}(N) = E_{\text{total}}(N)/N$, where the subscripts $\text{sub}$, $N$, $\gamma_{id}$, $\gamma_d$ and $\gamma_{\text{on}}$ denote the equilibrium system with $N$ H$_2$Pc molecules, the equilibrium system with $N + 1$ H$_2$Pc molecules, a H$_2$Pc molecule in vapor and the bare $a$-SiO$_2$ substrate, respectively.

### 4.2 MD simulations for a single H$_2$Pc molecule on a-SiO$_2$ substrate

MD simulations for a H$_2$Pc molecule with two ultimate initial configurations (i.e., lying down and standing upright), where each one lasts 6 ns, were performed to study the behavior of a single H$_2$Pc molecule on a-SiO$_2$ substrate at 350 K. Fig. 3 shows the projections of molecular centroid on a-SiO$_2$ substrate during simulations. As shown in Fig. 3a, H$_2$Pc molecule roughly undergoes a 2-dimensional random walk as in the case of tetraphiophene diffusing on an inert (010) surface of potassium hydrogen phthalate.\textsuperscript{23} This is because the confinement and diffusion barrier of a H$_2$Pc molecule on the isotropic a-SiO$_2$ substrate are small. The longest displacement in 6 ns is 51.12 Å, which is 4.13 times larger than $W$. As time increases, the diffusing distance becomes longer, which implies sufficient activity of the H$_2$Pc molecule on the a-SiO$_2$ substrate at 350 K.

For a H$_2$Pc molecule initially lying down on the substrate, the largest fluctuation normal to the substrate is 0.91 Å (Fig. 3b), which is much smaller than $W$. Thus, the H$_2$Pc molecule keeps lying down on the substrate. The distance between the molecular centroid and the substrate is $\delta(1) = 2.07 \pm 0.27$ Å, where the number in parentheses denotes the molecular number. For a H$_2$Pc molecule initially standing upright on the substrate (Fig. 3b), the initial $\delta(1)$ is 7.16 Å. It quickly decreases to 2.67 Å within the first 10 ps and then stays at 2.06 ± 0.32 Å. Furthermore, the H$_2$Pc molecule translates only 4.08 Å on the $XY$ plane within the first 10 ps. All of these imply that the life of the upright H$_2$Pc molecule is very short. The H$_2$Pc molecule prefers lying down on the substrate and it cannot stand up itself after lying down. This is consistent with the theoretical prediction of $\Delta G_d(1) < \Delta G_d(1)$. It has been experimentally reported that seixithiophene molecules exist among upright islands with a lying down configuration,\textsuperscript{17} which for a single molecule in OVD has also been found in another simulation work.\textsuperscript{23} After equilibrium, $E_{\text{total}}(1) = -0.98$ eV, $E_{\text{inf}}(1) = E_{\text{ads}}(1) = 0.98$ eV, which is at the same level of tetrathiophene on the (010) surface of potassium hydrogen phthalate,\textsuperscript{23} but much smaller than that of FePc on Ag (110) calculated by a DFT-D method.\textsuperscript{49}

### 4.3 MD simulations for more H$_2$Pc molecules on the a-SiO$_2$ substrate

Based on the simulation results of a single H$_2$Pc molecule, we consider the dynamic behaviors of more H$_2$Pc molecules on the a-SiO$_2$ substrate at 350 K. Initially, all H$_2$Pc molecules are placed parallel to the substrate. Fig. 4a presents the snapshots from a simulation of four H$_2$Pc molecules on the substrate. At 0.870 ns, two H$_2$Pc molecules meet each other and one H$_2$Pc molecule...
Fig. 4 Snapshots from simulations of four, five and six H$_2$Pc molecules deposited on the a-SiO$_2$ substrate at 350 K: (a) shows the configurations of four H$_2$Pc molecules at 0, 0.870, 0.880, 6.310, 6.315, 6.620, 6.655, 7.805, 23.240 and 24 ns; (b) shows the configurations of five H$_2$Pc molecules at 0, 0.955, 2.445, 2.715, 21.170, 21.180, 23.120 and 23.585 ns; (c) shows the configurations of six H$_2$Pc molecules at 0, 0.010, 0.395, 2.400, 3.360, 3.555, 3.830, 4.435 and 9.220 ns. XY, XZ and YZ denote projective planes. The yellow, red, white, gray and blue spheres denote Si, O, H, C and N atoms, respectively.
$E_{\text{ads}}(4\text{th})$ due to the tilting down of the five-H$_2$Pc cluster. To validate the above results, the deposition of six H$_2$Pc molecules is simulated with all of the H$_2$Pc molecules initially upright on the substrate (Fig. 4c). All of the H$_2$Pc molecules lie down quickly without clustering within the first 10 ps. At 9.220 ns, a six-H$_2$Pc cluster is formed. Differing from the five-H$_2$Pc cluster, all of the H$_2$Pc molecules in this six-H$_2$Pc cluster stand up. $E_{\text{total}}(6) = -7.53$ eV, $E_{\text{ads}}(6\text{th}) = 1.17$ eV, which is even 0.05 eV lower than $E_{\pi-\pi}$. This is because the standing up of H$_2$Pc molecules is an endothermic process. $d(6) = 6.33 \pm 0.49$ Å, which is 1.32 Å larger than $d(5)$. $\theta(6) = 76.13 \pm 4.31^\circ$. It has been reported that perylene molecules tilt about $73 \pm 5^\circ$ when they are deposited at 240 K with $\Phi$ of 0.4 ML min$^{-1}$. Note that the four-, five- and six-H$_2$Pc clusters are formed at 24, 21.180 and 9.220 ns, respectively. Since the direct impingement of the molecular vapor onto the surface of the clusters can be negligible, the molecular supply to the clusters is controlled by surface migration of the deposited molecules. As the molecular concentration increases, H$_2$Pc molecules meet each other more quickly with a shorter diffusion distance. Therefore, the faster clustering of the larger number of molecules meet each other more quickly with a shorter diffusion distance. Thus, $E_{\text{ads}}$ of the clusters can be negligible, the molecular supply to the clusters is controlled by surface migration of the deposited molecules.

A normal seven-H$_2$Pc cluster can also be formed, as shown in Fig. S5f, which implies that the in-plane growth of the normal cluster starts. $d(7) = 6.43 \pm 0.45$ Å and $\theta(7) = 80.47 \pm 3.96^\circ$. The latter is only 4.34° larger than $\theta(6)$. $E_{\text{total}}(7) = -9.00$ eV, which is 1.47 eV smaller than $E_{\text{total}}(6)$. Thus, $E_{\text{ads}}(7\text{th}) = 1.47$ eV, being 0.25 eV larger than $E_{\pi-\pi}$ due to the lateral interaction between the H$_2$Pc molecule and the substrate. The simulation for the deposition of ten H$_2$Pc molecules shows a similar case of seven H$_2$Pc molecules. In these normal clusters, the average distance between H$_2$Pc molecules is about 3.39 Å, which is nearly the same as the interplanar stacking distance of the face-to-face mode (3.40 Å) in $\alpha$-H$_2$Pc’s herringbone structure. This suggests that the face-to-face mode is firstly formed. It has been reported that $\alpha$-H$_2$Pc’s herringbone structure is more stable (by ~6%) than the planar layered structure in edge-to-edge mode on amorphous substrates. Thus, when the formed normal clusters laterally interact with each other, H$_2$Pc molecules in these clusters should displace, which makes the $\pi$-stacks point in different angles with respect to the normal of molecular plane. Finally, H$_2$Pc molecules aren’t exactly situated on the top of each other and the herringbone structure is formed. This is consistent with the existence of $\alpha$-H$_2$Pc’s herringbone structure on inert substrates.

For comparison purposes, the deposition of H$_2$Pc molecules on Cu(100) at 300 K is simulated. Unlike the case of H$_2$Pc molecules on $\alpha$-SiO$_2$ substrate, a monolayer with all of the H$_2$Pc molecules parallel to Cu(100) forms without clustering, which is in agreement with the experimental results. $E_{\text{int}}(1) = 4.36$ eV, which is at the same level of FePc molecule on Ag(110), but much larger than $E_{\pi-\pi}$. Thus, H$_2$Pc molecules tend to combine with Cu(100) but not themselves. Although a normal six-H$_2$Pc cluster is directly placed on Cu(100), it quickly decomposes within 0.04 ns (Fig. S6f).

4.4 Mechanism of orientation transformation

For describing the transformation mechanism clearly, $E_{\text{per}}$, $d$ and $\theta$ versus $N$ are plotted in Fig. 5. Moreover, $d$ of a parallel six-H$_2$Pc cluster versus $\theta$ is shown in the insert of Fig. 5b. Note that the data of the eight- and nine-H$_2$Pc clusters are simulated by placing them directly on the substrate. As shown in Fig. 5a, the model-predicted $E_{\text{per}}$ are larger than the simulated $E_{\text{per}}$. This is because our simulations overestimate the molecule–molecule and substrate–molecule interaction energies. Except $E_{\text{per}}(5)$, the tendencies of $E_{\text{per}}$ for both model and simulation are similar, which implies the almost identical overestimates for the both interaction energies. The exception of $E_{\text{per}}(5)$ is induced by the fact that the assumed five-H$_2$Pc cluster in the model differs from the real one in the simulation. The stronger $\pi-\pi$ interaction accounts for the sharp drop from $E_{\text{per}}(1)$ to $E_{\text{per}}(2)$ in Fig. 5a. Due to the slight effect of the substrate on H$_2$Pc molecules at the third and fourth layers, $E_{\text{per}}$ becomes smooth from $E_{\text{per}}(3)$ to $E_{\text{per}}(4)$. When $N < 5, \theta = 0^\circ$ and $d$ is nearly a linear function of $N$, as shown in Fig. 5b and 5c. Namely, the layered parallel clusters are formed. $E_{\text{int}}(1), E_{\text{int}}(2), E_{\text{int}}(3)$ and $E_{\text{int}}(4)$ are all lower than $E_{\text{int}}(5)$. The insert in (b) denotes $d$ of a parallel six-H$_2$Pc versus $\theta$. 

![Fig. 5](image-url) (a) The average energy release per H$_2$Pc molecule $E_{\text{per}}$, (b) distance $d$ between the centroid of the clusters and the substrate, (c) average angle $\theta$ between H$_2$Pc molecules in the clusters and the substrate after equilibrium versus $N$. The model-predicted $E_{\text{per}}$ are also shown in (a). The insert in (b) denotes $d$ of a parallel six-H$_2$Pc versus $\theta$. 


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The nucleation and growth are along the substrate plane in Frank–van der Merwe mode (layer-by-layer). This model prediction that high energy deposits are due to the standing up of all H$_2$Pc molecules. After this, the $E_{\text{per}}$ increases to $E_{\text{per}}(10)$ is only 0.03 eV (2.14%) lower than $E_{\text{per}}(9)$, which suggests that $E_{\text{per}}$ nearly saturates as $N = 10$. All of these imply that the orientation of H$_2$Pc molecules transforms at $N = 5$, which is indeed our model result. Since the simulations correspond to the deposition under relatively high $T_{\text{sub}}$ and low $\Phi$, the stable parallel cluster should exist when $N < N_c$. However, when $N \geq N_c$, the parallel cluster becomes metastable and transfers to the stable normal one. This transformation can be divided into two steps. Take the transformation of a metastable parallel six- H$_2$Pc cluster for example. As shown in Fig. 5b and the insert of Fig. 5b, the metastable parallel cluster firstly tilts down with decreasing $d$ and increasing $\theta$. At a critical point of $d = 5.21$ A and $\theta = 38.25^\circ$, H$_2$Pc(100) completely contacts with the substrate. After this, the interface between H$_2$Pc(010) and the substrate opens with increased $d$ and $\theta$. Namely, all H$_2$Pc molecules in the critical state stand up and a stable normal six- H$_2$Pc cluster is finally formed.

With these results in mind, the morphology and molecular orientation of OTFs in experiments can be reasonably interpreted. Meanwhile, the basic requirements for getting normal orientation can be considered. When organic molecules are deposited on metals,$^47,51,52$ metal halides$^45$ and semiconductor single-crystal substrates,$^53$ $E_{\text{int}}(1)$ is much larger than $E_{\text{per,\pi}}$. Thus, the molecules should combine with the substrate but not themselves. The nucleation and growth are along the substrate plane in Frank–van der Merwe mode (layer-by-layer).$^54$ Finally, ultrathin organic films can be grown with molecules lying down on the substrate.$^47,51–53$ However, if $E_{\text{int}}(1) < E_{\text{per,\pi}} < E_{\text{int}}(N_c)$, such as diindenoperylene on $a$-SiO$_2$ substrate,$^54$ F$_{16}$CuPc on pentacene thin film$^55$ and tetraphiopene on the (010) surface of potassium hydrogen phthalate,$^23$ the out-of-plane growth of a parallel cluster will stop without orientation transformation. The growth will follow the Wolmer–Weber mode (island).$^52$ Finally, the parallel and normal islands can coexist on the substrate,$^{21,24,55}$ which is unfavorable for OTFs quality. Only when $E_{\text{per,\pi}} > E_{\text{int}}(N_c)$ can the growth of a parallel cluster remain. Tilt $N \geq N_c$, a normal cluster is more stable than the parallel one where the parallel–normal transformation occurs. The following growth of the first few layers is in Frank–van der Merwe mode and is controlled by diffusion-limited aggregation mechanism.$^{15,17,19}$ Finally, the complete normal orientation can be formed, which is just the needed molecular orientation for use in OFETs.$^{10,11}$ However, if the deposition is under low $T_{\text{sub}}$ or high $\Phi$, the molecules cannot adequately diffuse on the substrate and the parallel orientation may remain.$^{56}$ By increasing $T_{\text{sub}}$ or decreasing $\Phi$, the metastable parallel clusters can be effectively transferred to the stable normal clusters. These correspond to general phenomena that high $T_{\text{sub}}$ or low $\Phi$ results in normal orientation while low $T_{\text{sub}}$ or high $\Phi$ gives rise to parallel orientation or an amorphous structure.$^{4,16,14}$

Besides controlling the morphology and molecular orientation of OFTs, one can increase the overlap of the intermolecular orbitals through molecular design. All phthalocyanines have widely delocalized $\pi$-orbitals sticking out of the molecular plane. Especially for metal–phthalocyanines, the $d$-orbitals of the central metal ions can significantly influence their electronic structures,$^{56}$ stacking and intermolecular electronic coupling. When they are deposited on $a$-SiO$_2$ substrate by the OVD method, $\mu$(CuPc) > $\mu$(SnPc) > $\mu$(ZnPc) > $\mu$(H$_2$Pc) > $\mu$(FePc) > $\mu$(PtPc) > $\mu$(NiPc),$^4$ and $\mu$(SnCl$_2$Pc) > $\mu$(F$_{16}$CuPc) > $\mu$(F$_{16}$FePc) > $\mu$(F$_{16}$ZnPc) > $\mu$(F$_{16}$CoPc) > $\mu$(Cl$_{16}$FePc),$^{28,57}$ Moreover, aromatic rings can be added to enhance the spatial overlap of the intermolecular orbitals. It has been reported that $\mu$ values of oligophenyl-based OFETs increase with the lengths of oligophenyls due to the increasing intermolecular overlap.$^{58}$ However, in any case, one must ensure $\gamma_s > (5/7)\gamma_{\text{sub}}$. Since $\gamma_s$ values are generally at the order of 100 mJ m$^{-2}$,$^{59}$ the size of $\gamma_{\text{sub}}$ should not exceed 140 mJ m$^{-2}$.

Conclusions

In summary, a unified thermodynamic model has been built to characterize the initial growth stage of disk-like and rod-like organic molecules during the OVD process. The model shows that a parallel–normal orientation transformation can take place at a critical molecular number, $N_c$, which is further confirmed by MD simulations for disk-like phthalocyanine. When $N < N_c$, a parallel cluster is grown by self-assembly of individual lying down molecules driven by larger $\gamma_f$. At $N = N_c$, the initially grown parallel cluster becomes metastable and transfers to the normal one through $\gamma$-controlled molecular orientation transformation while $N_c \approx \gamma_f W \gamma_f H$. The prerequisite for the emergence of the transformation is $\gamma_s > (5/7)\gamma_{\text{sub}}$. After $N > N_c$, the in-plane growth of the normal cluster starts.

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Notes and references

38 Materials Studio and Discover are products of Accelrys Inc. (see www.accelrys.com).