Spontaneous growth of Single Crystalline Layers Induced by the Asymmetry of Organic Metallic Molecules

Jun Hong Park¹, Lalitasri Ravavar³, Iljo Kwak¹, Susan K. Fullerton-Shirey⁴, Pabitra Choudhury³, Andrew C. Kummel¹, ².*

¹Materials Science & Engineering Program and ²Departments of Chemistry & Biochemistry, University of California, San Diego.
³Department of Chemical Engineering, New Mexico Tech.
⁴Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA, 15213, USA.

Abstract: To avoid defects associated with grain boundaries that degrade organic device performance, the deposition of single crystalline organic active layers is required. Here, the spontaneous growth of large, single domains of the asymmetric, organic semiconducting molecule, titanyl phthalocyanine (TiOPc), is demonstrated on highly ordered pyrolytic graphic (HOPG). The first monolayer of TiOPc lies flat on HOPG with a face-up orientation with domains spanning from one step edge to another. A flat-lying, thin multilayer of TiOPc is obtained with negligible increase in roughness compared to the substrate, consistent with monolayer-by-monolayer growth. With increasing thickness of the TiOPc, the growth mode transitions from monolayer-by-monolayer to bilayer-by-bilayer with the repeated stacking of bilayers, each of which has face-to-face pair pairs. The asymmetric stacking provides the driving force to maintain nearly constant surface order during growth, allowing precise, subnanometer thickness control and single domain growth.
Introduction

Although inorganic Si and III-V materials have led the modern semiconductor industry for half a century, the integration of organic thin films have been expanded to microelectronics for displays, solar cells, and platforms for electronic skins\(^1\text{-}^8\). These organic thin film transistors (OTFT) and organic photovoltaic (OPV) provide low cost, mechanical flexibility, and direct bandgap modulation for electroluminescence. In flexible organic electronics, molecular orientation, degree of crystallinity and morphology govern carrier transport and injection between organic layers and electrodes\(^9\text{-}^{14}\); therefore, the development of single-crystalline organic channels on flexible electrodes is crucial. Taking advantage of its high strength and enhanced photovoltaic efficiency during deformation, graphene has recently been employed as a flexible electrode for OTFTs and OPV\(^{15}\text{-}^{17}\). Therefore, to fabricate flexible organic devices integrated onto graphene electrodes, it is essential to deposit organic layers on graphene as a single crystal. Single crystal growth is not only required to template the growth of large-domain organic heterostructures, but to also enable bandgap engineering of the contacts.

The growth of aromatic organic films relies on extended $\pi$-$\pi$ (van der Waals) interactions between organic molecules\(^{18}\text{-}^{20}\). During the deposition of organic layers, the growth of the films can involve directional molecular packing, resulting from the shape anisotropy of molecules. In many cases, the molecular-substrate interaction is stronger than molecular-molecular interaction; therefore, the molecules form a flat monolayer on substrates in the initial growth stage\(^{20}\text{-}^{22}\). However, upon additional organic molecular deposition, the molecular-substrate interaction can be overwhelmed by molecular-molecular interactions, resulting in a new molecule-substrate geometry such as “standing” molecular orientation\(^{20}\text{-}^{24}\). Moreover, because the multilayer growth of organic molecules mostly involves step flow, island, or layer-plus-island growth modes during the deposition\(^{19}\text{-}^{28}\), it is hard to simultaneously obtain precise thickness control, ultra-flat topology, and single domain growth. These orientation transitions and absence of layer-by-layer growth normally result in inhomogeneous crystallites that induce charge trapping at interfaces in OTFT or unintentional recombination of excitons at grain boundaries in OPV\(^{29,30}\).
In this report, the quasi-2D (two dimensional), epitaxial growth of titanyl phthalocyanine (TiOPc) multilayers deposited on a graphite surfaces is observed via scanning tunneling microscopy (STM). The TiOPc has been employed for organic photovoltaic cells, due to its broad photoelectrical activity from the visible to the near IR. As shown in this report, the multiple ring structure in TiOPc along with the molecular dipole and asymmetric shape induce classic layer-by-layer growth of thin multilayers with negligible increase in roughness and near single-crystal films on each graphite terrace. However, for thick multilayers, a transition is observed from monolayer-by-monolayer (ML by ML) growth to bilayer-by-bilayer (BL by BL) growth. This growth behavior has not been previously observed for any organic molecule. Therefore, noble growth behavior of TiOPc may open a pathway for high performance organic transistors and photovoltaic cells.

Results and discussion

A flat-lying TiOPc monolayer is deposited by molecular beam epitaxy (MBE) on highly ordered pyrolytic graphite (HOPG) with a high degree of 2D crystallinity, as shown in STM images of Fig. 1. Although all the STM measurements have been made on graphite, both graphite and graphene surface are inert, due to the sp² hybridization; therefore, they can be considered equivalent for this report. Figure 1(a) displays the molecular structure of TiOPc; the oxygen atom is located on the central Ti, consistent with a permanent dipole from the bonding of O to Ti. As shown in Fig 1(b), empty state STM images show a defect-free monolayer (ML) of TiOPc deposited on HOPG forming nearly single-crystalline domains on each HOPG step. The Fourier transform (FT) of the inset shows a four-fold symmetric crystal structure of a TiOPc ML.

A three-dimensional (3D), high-resolution STM image shows two different adsorption configurations in the ML with 1.6 ± 0.02 nm spacing, as shown in Fig 1(c). Most of TiOPc molecules possess a bright spot at the center of each TiOPc, assigned to the O atom, corresponding to the face up orientation of the molecule. However, a few TiOPc molecules show dark holes in their centers, which are
assigned to Ti atoms from inverted TiOPc, as shown in the white box. In empty-state images, the line trace of Fig 1(d) shows that the dark hole at the center of the TiOPc is about 0.08 nm lower than the bright protrusions of neighboring TiOPc molecules. Combining the STM images and line traces, the data is consistent with TiOPc molecules adsorbing on the substrate with face up (majority 98%) or down (minority 2%) orientation after annealing at 537 K as shown in Fig 1(e).

Scanning tunneling spectroscopy (STS) measurements in Fig. 1(f) show two different types of band structures depending on the position of the tip on one, face-up TiOPc molecule. The band structure obtained at the ring of TiOPc has large band edge states, while the band structure of the center of TiOPc has much smaller band edge states. As shown in Fig. 1(g), the STS range of -1.3 to – 0.7 V and 0.3 to 0.9 V from the center of TiOPc are expanded to show the onset bias at the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). To extract the position of onset bias from measured dI/dV/I/V, STS modeling was employed as shown by the dash lines; the detailed method is described in previous STM/STS studies. Note the standard error is obtained by the fitting process in STS. The given uncertainties provided by the present fitting employing least-squares fitting are statistical, are less than thermal broadening, and do not account for band edge states. The onset of the HOMO occurs at -0.91 ± 0.01 V, while the onset of the LUMO occurs at 0.64 ± 0.01 V. Therefore, although the Fermi level of center of TiOPc is still in the band gap, it is within ~0.27 V of the LUMO. It can be hypothesized that the Fermi level being closer to the LUMO can result from the localized dipole moments at center of the TiOPc molecules, which has been confirmed in previous experimental and DFT calculation data. It is noted that because of the existence of large band edge states in the ring of TiOPc, it is hard to define the exact position of the onset bias in STS of the TiOPc rings.

After the deposition of additional TiOPc molecules onto the ML, flat-lying bilayer growth and coherent island formation are observed resulting from “ML by ML” growth as shown in Fig. 2. In Figure 2(a), a 3D-rendered STM image shows partial bilayer (BL) growth on the TiOPc ML with a molecular ML by ML growth mode; after completion for the bottom face-up layer, each impinging molecule forms a new
single molecule second-layer island or attaches to an existing island, instead of diffusing to a step edge or starting third layer growth. The second layer growth maintains a square crystal structure, as shown in the FT image of the inset of Fig. 2(a). Because individual TiOPc molecules have a near square molecular shape, it is reasonable that they form square islands. Existence of single molecular islands on the first layer indicates the surface diffusion is limited and there is no step flow growth.

In the 3D rendered expanded STM image of Fig. 2(b), the orientation contrast between first and 2nd layer molecules is readily observed. To determine the adsorption configuration of molecules in the BL, two line traces are obtained from the first and second layer from Fig. 2(b), shown as red and purple arrows, respectively, in Fig. 2(c). The central atoms appear as bright spots in the first layer of TiOPc molecules, suggesting the face-up orientation of nearly all TiOPc molecules as indicated by the cross-sectional STM image and molecular structure superimposed on Fig. 2(c). Conversely, the central atoms appear as dark holes in the second layer molecules, consistent with the face-down orientation of TiOPc. This growth behavior does not appear in other planar molecules (such as CuPc) growth, as shown Fig. S1 - 3.

In order to elucidate the stacking configuration of the TiOPc bilayer, high resolution STM is performed, as shown Fig. 2(d). The second layer of adsorbed TiOPc molecules in Fig. 2(d) are observed nearly at the center of four TiOPc molecules in the first layer. It is noted that the isolated second layer molecules adsorbed on ML are shifted to the right side slightly in Fig. 2(d), consistent with the existence of strong dipole-dipole interaction between the top and the bottom molecules\textsuperscript{33}. However, this shifting of isolated TiOPc molecules on ML could be absent in fully filled second TiOPc layer because of close packing of TiOPc molecules. Based on the STM image and the line trace, the stacking of second layer molecules is shown in the schematic diagram of Fig. 2(e). It is noted that for simplification, the shifting of the isolated TiOPc molecule in second layer is not considered in the diagram. Assuming the central O of TiOPc is a vertex in first layer (which is an approximation), the square unit cell, indicated by the dashed, red box, is obtained by drawing lines along four neighboring TiOPc molecules. Based on this unit cell, the second layer TiOPc molecule is positioned near the center of square unit cell.
Growth behavior identical to the BLs can be observed in the thin (~2 – 3 nm), multilayer growth of TiOPc. Similar with the BL, Fig. 3(a) shows the topmost layer is grown with a ML-by-ML mode, forming a four-fold symmetric lattice structure as shown by the FT in the inset. In the molecularly resolved image of Fig. 3(b), the topmost molecules appear with dark holes at the centers consistent with face down orientation, while the underneath layer shows bright centers consistent with face up orientation, as shown by the superimposed molecular structure. It is proposed that most of the topmost TiOPc are in the face down orientation, indicating stable stacking as shown in a 3D STM image of Fig. 3(c). Therefore, the growth of face up oriented layers is not initiated until completion of the underneath layer with face down TiOPc molecules. The filling process in the face down oriented layer is shown by STM in Fig. S4. It is hypothesized that during the formation of face-up oriented layers on face-down oriented layers, the diffusion speed of TiOPc molecules in the face-up layer is very fast, as shown by the formation of large face-up domains in contrast the small face-down islands.

The permanent dipole and asymmetric shape of TiOPc lead not only to molecular layer-by-layer growth in the thin multilayer, but also termination by face-down molecular orientation in the BL and multilayers. In multilayer TiOPc, two distinct molecular orientations exists depending on the direction of the protruding central O-Ti group: “back-to-back (BTB) pair” and “face –to-face (FTF) pair” orientations, as shown in Fig. 3(d). In the BTB pair, the protruding O-Ti group faces outward, while the benzene rings of the two molecules face each other with strong π - π interaction. Conversely, the FTF pair involves TiOPc molecules with the protruding of O-Ti groups facing a benzene ring of another TiOPc, and benzene rings are faced outward. Therefore, the multilayers are grown by repeating BTB and FTF pairs, as shown in Fig. 3(e). Because the O-Ti group of TiOPc face towards each other in FTF pairs, this configuration can have favorable dipole-dipole interactions that minimize the net dipole.

Density function theory (DFT) calculations elucidate the difference in binding strengths between the BTB and FTF pairs. The favorable alignment of the dipole moments in the FTF pair results in a stronger interaction (1.45 eV) compared to the BTB pair (1.20 eV); therefore, the intermolecular distance of the FTF
orientation is shorter than the BTB pair\textsuperscript{36}. It is noted that the binding energies of the FTF and BTB pairs are calculated in gas phase; both binding energies on the surface of graphite or graphene may differ slightly. In summary, during the deposition of TiOPc multilayers, once TiOPc molecules form the FTF orientation, the position of the TiOPc molecules are locked due to maximizing the dipoles attractive interactions and the $\pi-\pi$ interactions in the thin film while minimizing steric repulsion. The locking of the TiOPc molecules suppresses surface diffusion, resulting in ML-by-ML growth instead of step-flow growth.

Although, this layer-by-layer growth mode persists with increasing TiOPc multilayer thickness, the growth behavior transitions from ML growth to BL growth for thick films, as shown in Fig 4(a). When a TiOPc multilayer is deposited over 5 min at 373 K, only a large, topmost layer is observed as shown by the STM image in Fig. 4(a). In the top layer, although square shaped vacancies are observed, they can be fully filled by further deposition of TiOPc molecules. The height of this topmost layer is 0.70 $\pm$ 0.02 nm as shown in Fig. 4(b), consistent with BL growth. Although low tunneling conductivity in thick multilayers results in noisy STM images, a molecularly resolved STM image in Fig. 4(c) displays each TiOPc molecules possessing a dark hole at the center, which is assigned to the Ti atoms in face-down TiOPc. In Fig. 4(c), TiOPc molecules still form a square lattice structure as shown by the FT in the inset, similar to ML, BL and thin multilayers. Therefore, it can be concluded as the TiOPc film becomes thicker, the growth mode transitions to BL-by-BL growth, forming FTF pairs in thick multilayers. This growth mode transition from ML-by-ML to BL-by-BL can be suppressed by decreasing the deposition temperature, as shown in Fig. S6.

Based on the molecular observations from STM imaging, the BL growth behavior is described schematically in Fig 4(d). Initially, few TiOPc molecules arrive and form face up oriented clustered islands on the thick TiOPc layer, thereby forming BTB pairs with underneath face-down oriented TiOPc molecules. Afterwards, face-up oriented TiOPc molecules act as nucleation seeds. TiOPc molecules adsorb on face-up oriented molecules to create FTF pairs. By repeated creation of FTF pairs and formation of face-up oriented islands, uniformly thick layers are deposited by epitaxial BL growth. DFT calculation shows that the FTF bonding is stronger than BTB bonding, consistent with diffusion of TiOPc molecules to form FTF pairs.
Due to the unique BL-by-BL growth mode of TiOPc molecules, molecularly flat, thick TiOPc multilayers are observed on graphite surfaces, forming near single crystalline layers spontaneously on each HOPG step, as shown in the large area AFM image of Fig. S7. Conversely, the growth mode of other organic molecules, such as pentacene or PTCDA, transitions to multiple islands formation in thick film, resulting in the polycrystalline films\textsuperscript{19,25-28,40-42}.

In order to elucidate the mechanism for the growth mode transition from ML to BL growth, the binding energies of adsorbed TiOPc molecules are calculated by density of function theory (DFT), as shown in Fig. 5. Calculated binding energies between the N\textsubscript{th} TiOPc molecule and the N-1\textsubscript{th} molecules on graphene are shown in Fig. 5(a), including the BTB and FTF pairs of TiOPc in the gas phase. In Fig. 5(b), a face-up oriented first layer TiOPc molecule has the highest binding energy (2.34 eV) with the graphene substrate. Afterwards, the binding energy of face-down oriented second layer adsorbed TiOPc with first layer face-up oriented TiOPc (FTF pair) decreases to 1.61 eV. As BTB pairs are formed by the adsorption of the face-up oriented third layer molecule to a face-down oriented second layer molecule, the binding energy decreases to 1.49 eV. However, the binding energy of FTF pair formed between a face-down oriented forth layer TiOPc and face-up oriented third layer TiOPc increases to 1.65 eV. The increase of binding energy in FTF pair results from favorable orientation of opposing intrinsic dipole moments and minimization of steric hindrance while maximizing $\pi - \pi$ interaction\textsuperscript{32}. Therefore, the growth mode transition from ML growth to BL growth is consistent with the strong influence of the pre-existing TiOPc layer on the stacking of TiOPc molecules\textsuperscript{43}. As the molecular-substrate interaction becomes weak during the growth of thick layers, the molecular-molecular interaction dominants growth behavior, rather than molecular-substrate, resulting in the intermolecular distance decreases, as shown in Fig. S8. In the thin multilayers, although the BTB pair has lower binding energy than the FTF pair, formation of the FTF pairs is not initiated until full filling of the BTB pair layer, due to the substrate effect, as shown in supplementary materials. However, because the substrate effect on the topmost layer is weak or eliminated by screening of pre-deposited layers in the thick
multilayer, the binding energy difference between FTF and BTB pairs dominate the growth behavior during the molecular packing for thick layer growth.

Conclusion

Unique molecular layer-by-layer growth of TiOPc is observed on the graphite surface, resulting from asymmetric molecular shape and intrinsic dipole moments$^{32-34,36}$. The deposition of TiOPc molecules onto the TiOPc monolayer results in flat-lying BLs and thin multilayers involving dispersed, single molecular islands or coherent cluster formation, consistent with ML-by-ML growth. Conversely, in thick multilayers, substrate effects are screened; therefore, the greater interaction energy for FTF vs BTB TiOPc pairs results in a growth-mode transition to BL-by-BL. As a results of the ML by ML and BL by BL growth modes, the deposited TiOPc films (10 nm) on the graphite surfaces are nearly single crystalline and molecularly flat, as shown in STM and AFM images. This unique growth mode results in the deposition of near single crystalline films on graphite surfaces without complicated seeding techniques. The results presented here demonstrate the impact of asymmetric charge density of organic molecules on the growth behavior of films. Therefore, this growth behavior of polar phthalocyanine opens the development of platform layers for organic transistors, OLEDs, and photovoltaic cells, and it can be applied to other 2D materials$^{17,44}$.

Experimental detail

Highly Oriented Pyrolytic Graphite (HOPG) samples were cleaved freshly in air by mechanical exfoliation, then transferred into the UHV chamber immediately. After transferring the HOPG into the UHV chamber, samples were annealed at 750 K to remove tape residue and air induced adsorbates. The TiOPc powder (Sigma Aldrich) was purified by multiple sublimations with a differentially pumped effusion cell (Eberl MBE- Komponenten) in the UHV chamber. Each TiOPc monolayer was prepared by depositing thick-overlayers on clean HOPG or graphene at 473 K surface temperature by organic molecular beam epitaxy.
Subsequently, the multilayer was heated to 523K for 6 min, and a flat-lying TiOPc monolayer was formed. Formation of monolayer was confirmed by STM imaging. Afterwards, the TiOPc multilayer was deposited with 1 nm/min deposition rate onto the TiOPc monolayer at 373 K, which acts as seeding layer. STM and STS were performed at 100K with Omicron VT STM with etched tungsten tips.
Figure 1. Empty State STM Images and STS of Monolayer TiOPc on HOPG. STM images recorded with $V_s = +2.0 \text{ V}$, $I_t = 20 \text{ pA}$ at 100 K. (a) Molecular structure of TiOPc. (b) 1 ML TiOPc deposited by MBE on HOPG at 373 K. (c) 3D rendered submolecular-resolution STM image of ML TiOPc. Both face up (majority-tall) and down (minority-short) oriented molecules are shown. (d) Line trace of both face up and down oriented molecules. The corresponding STM images are superimposed. (e) Schematic diagram of TiOPc ML on graphene based on the STM image (f) $dI/dV/I/V$ data from TiOPc ML on HOPG. Two different types of STS are observed, depending on the STS location in the molecule. The locations of the STS measurements are marked as X in the superimposed STM image and TiOPc molecule. The position of $E_F$ is shown with an orange arrow. (g) Expanded STS from -1.3 to -0.7 V and 0.3 to 0.9 V where the onsets of differential current occurs; spectra taken at the center of the TiOPc.
Figure 2. Empty State STM Images of TiOPc Bilayer on HOPG. All STM images recorded at 100 K. (a) 3D rendered STM image of a partial TiOPc bilayer (Vs = +2.0 V, It = 20 pA). Examples of single layer TiOPc are in white boxes. The inset shows a Fourier transform (FT) of the full bilayer. (b) 3D rendered high resolution STM image of a partial TiOPc bilayer (Vs = +2.0 V, It = 40 pA). (c) Line trace analysis from Fig. 2(b). Line 1 corresponds to the first and second layers, while line 2 corresponds to the second layer. (d) High resolution STM image of single TiOPc molecules adsorbed on the TiOPc monolayer. (e) Stacking configuration with face up and down molecules.
Figure 3. Empty State STM Images of a Thin TiOPc Multilayer (about 3 nm thickness) and Schematic Stacking Model. (a) STM image of the initial TiOPc multilayer (Vs = +2.0 V, It = 20 pA); the corresponding thickness is estimated as ~3 nm. Inset shows the Fourier transform (FT) of an STM image. (b) Molecularly resolved STM image shows face up (layer 3 only) and down oriented TiOPc molecules (layer 4) from a region marked by a white rectangle in Fig 3(a) (Vs = +2.0 V, It = 40 pA). The molecular structure is superimposed. (c) 3D rendered STM image (Vs = +2.0 V, It = 60 pA). (d) Concave and convex pairs in the TiOPc layer. (e) Schematic of TiOPc multilayer grown via two dimensional molecular layer by layer growth.
Figure 4. Empty State STM Images of a Thick TiOPc Multilayer on HOPG. STM images recorded at 100K (Vs = +2.0 V, It = 20 pA). (a) STM image of a thick TiOPc multilayer deposited for 5 min on a TiOPc ML at 373 K (about 5 nm thickness). (b) 3D rendered STM image showing topmost layer and corresponding line trace. (c) High resolution STM image of the topmost layer. Yellow arrows indicate central dark hole of TiOPc. Inset shows the FT of the topmost layer of TiOPc thick multilayer. (d) Schematic model of thick TiOPc multilayer with bilayer growth mode.
Figure 5. Calculated binding energy of Nth adsorbed TiOPc molecules by Density Functional Theory. (a) Binding configurations of TiOPc molecules in ML, BL and multilayer, included gas phase adsorption. (b) Binding energy between Nth adsorbed TiOPc molecule and N-1th adsorbed TiOPc molecule. For gas phase adsorption, two values are provided.
Author Contributions

J.H.P and A. C. K conceived and designed this experiment. J.H. P performed the growth of TiOPc and STM experiments. J.H.P, S.F,S and A.C.K analyzed the STM/STS data. L.R and P.C performed DFT calculations and A.C.K. reviewed the calculations. I.K performed AFM. ALL data were discussed by J.H.P, S.F.S and A.C.K. J.H.P wrote most of manuscript.

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Reference


