Hierarchical self-assembled structure and frictional response of phthalocyanine molecules

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Abstract: Solid evidence is needed to demonstrate the effect of molecular orientation and structure on the frictional property of boundary lubricants. In this work, the frictional properties of phthalocyanine self-assembled monolayers (SAMs) with face-on (aromatic cores parallel to the substrate) and edge-on (aromatic cores stand on the substrate) orientations have been compared and the in situ structural variation of edge-on SAMs under frictional shear has been revealed by atomic force microscope (AFM). Face-on oriented SAMs show lower adhesion, lower friction, and stronger wear resistance, compared with edge-on oriented SAMs. Hierarchical structures of edge-on oriented SAMs have been revealed by frictional topography, which are consisted of nanoscale columns, micron-scale stripes, and centimeter-scale monolayer. The column structure deforms under increasing load force, leading to a stepwise friction force curve and a transition among three friction states (ordered friction, collapsed friction, and worn friction). The structural deformation depends on both the order degree and anisotropic stiffness of columns. Columns in phthalocyanine SAMs show a larger stiffness when shearing against molecular plane than shearing along the molecular plane. The presented study on the interfacial structure and frictional mechanism promisingly supports the designing of novel boundary lubricants and their application in engineering.

Keywords: hierarchical assembly; molecular orientation; frictional mechanism; phthalocyanine

1 Introduction

With the micro-miniaturization of electromechanical devices, ultrathin organic films anchored on solid surface [1, 2] are regarded as promising boundary lubricants, which conquer the natural limits of bulk lubricants and show great compatibility with future nano-scale technologies. Self-assembled monolayers (SAMs) are ideal boundary lubricants and the molecular orientation and structure of SAMs have been proved to play a significant role in the frictional reducing process [3, 4]. Besides the friction reducing property, molecular orientation also relates with other attractive frictional properties of SAMs, including anisotropic friction [5], patterning friction [6], and stepwise friction [7, 8]. Despite the achieved progress, the studying objects are limited and the relationship between molecular structure of boundary lubricants and the frictional property is still ambiguous. More solid evidences of the interfacial structure and the structure variation under friction are needed to obtain a deeper insight into the molecular scale frictional mechanism.

Linear organic molecules, such as alkylsilane [9–12] and alkanethiol [13–15], are easily to self-assemble into ordered layers with brush-like configuration, which reduces friction by orienting along the shear direction [14, 16]. Comparing with linear molecules, two-dimensional [17–19] molecules keep good lubricity
with the introduction of alkyl side chains, and possess good rigidity and stability by the introduction of benzene groups. Phthalocyanines are typical two-dimensional molecules, which are widely used in the molecular and supramolecular assembly. Besides the application in catalyst [20], sensor [21], and electronic devices [22], phthalocyanines also show great potential as anti-friction [23] and anti-wear coatings [24]. Phthalocyanines can adopt different interfacial molecular orientations, including edge-on [25] (aromatic cores stand on the substrate) and face-on [26] (aromatic cores parallel to the substrate) orientations, which makes it a promising candidate to study the influence of molecular orientation on frictional properties.

Deformation [7] and desorption [27] of interfacial layers are common phenomena under friction, which can be ascribed to the variation of molecular structure and configuration. C–C bond of alkyl chains can rotate under friction and result in more excitation of defects and energy-dissipating modes [10]. An alkylsilane monolayer showed stepwise decreasing thickness under increasing load, which was interpreted by the tilting of alkyl chains [7]. However, solid evidences on the variation of interfacial molecular structure are still limited. Some in situ characterization techniques have been applied to study the molecular structure of the interfacial lubricant layer under macro friction, such as an in situ X-ray measurement system [28] and an in situ Raman microscopy system [29, 30]. Besides, atomic force microscopy (AFM) is a powerful tool for the study on nanofriction, which simultaneously gives the friction force and molecular arrangement with sub-molecular resolution [31]. By constructing a single-asperity contact between the AFM probe and interfacial layer, AFM is a promising method to simplify the realistic multi-asperity condition and reveal the nature of nano-friction [3].

In this work, the structure and frictional properties of 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine (PcOC₈, Fig. 1(a)), a two-dimensional molecule with an aromatic core and eight octyloxy chains, has been characterized by AFM. PcOC₈ molecules self-assemble into face-on and edge-on oriented monolayers by a droplet evaporation method. The edge-on monolayer is consisted of two sub-structures, which are nanoscale columns and micron-scale stripes. It has been proved that face-on oriented monolayer gives lower friction force and stronger wear resistance than edge-on oriented monolayer. The edge-on oriented monolayer also gives a stepwise friction force curve, which is due to the structural deformation of columns under friction. The application of in situ AFM provides robust evidences for the molecular structure and structural variation of PcOC₈ molecules under friction. The revealing of the molecular behavior under friction promotes a deep understanding of the nano-word and the future application in engineering.

2 Experiment

2.1 Materials

In this study, 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine (PcOC₈, 98%), 2,3,9,10,16,17,23,24-octabutoxy-29H,31H-phthalocyanine (PcOC₄, 98%) and phthalocyanine (Pc, 98%) were purchased from Sigma-Aldrich (Shanghai, China). The chemical structure of the three phthalocyanine molecules are

Fig. 1 Chemical structures of (a) PcOC₈, (b) PcOC₄, and (c) Pc molecule.
shown in Fig. 1. Chloroform (98%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). All the materials were used without any further purification.

2.2 SAM preparation

The self-assembly process by droplet evaporation is as follows. Solutions with a concentration of $1 \times 10^{-4}$ M were prepared in glass containers by dissolving the solid-state phthalocyanine derivatives into chloroform, followed by an ultrasonic processing for 30 min. Afterward, a nearly 3 µL droplet of the solution was dropped on fresh mica by micro syringe. And then, the evaporation was conducted in a hood with a room temperature of 24 °C and an environment humidity of 10%. Finally, the SAMs were deposited on mica substrate after evaporation.

During the evaporation, the contact angles of the droplet were recorded by contact angle tester (Dataphysics OCA 25, Germany) and optical microscopy (OM, Olympus, Japan), respectively. All the tests were repeated at least three times.

2.3 Langmuir-Blodgett film preparation

The Langmuir-Blodgett (LB) film of PcOC₈ was prepared by a KSV 2000 Langmuir trough (KSV Instrument Ltd., Helsinki, Finland) equipped with a Wilhelmy plate. The trough and barriers were rinsed by ethanol and pure water for three times, respectively, before each experiment. After spreading 200 µL PcOC₈-chloroform solution with a concentration of $1 \times 10^{-4}$ M on water by a micro-syringe, the chloroform was evaporated and the PcOC₈ monolayer was left on the water-air interface. The surface pressure was adjusted by compressing the two barriers on the water surface with a speed of 5 mm/min. The surface pressure ($\pi$) versus area ($A$) isotherm was measured to evaluate the physical states and molecular orientation of the monolayer. LB films were prepared by compressing the two barriers until certain surface pressure was achieved and then the films were transferred onto freshly cleaved mica with an automatic dipper. The LB films were transferred at surface pressures of 6, 20, and 31 mN/m, which were used to obtain the thickness of the monolayer of PcOC₈ and evaluate the layer structure of PcOC₈ SAMs prepared by droplet evaporation.

2.4 STM measurement

Scanning tunnelling microscope (STM) was used to obtain molecular configuration of PcOC₈ SAMs prepared by droplet evaporation. The substrates for STM measurements were highly oriented pyrolytic graphite (HOPG, grade ZYA, NTMDT, Russia). The STM tips were Pt/Ir wires (80/20) prepared by mechanically cutting. STM experiments were performed using a Nanoscope IIIA system (Bruker, USA) under ambient conditions. The images were obtained in the constant-current mode, and specific tunneling conditions including tunneling current and bias were presented in the corresponding Figure captions.

2.5 AFM measurement

After the evaporation, the topography images of PcOC₈ SAMs were characterized by AFM (Dimension icon, Bruker, USA) under PeakForce Tapping mode. Triangular cantilevers with a nominal normal spring constant of 0.350 N·m⁻¹ and a tip radius of 2 nm (SNL-10, Bruker, USA) were used. The scan frequency was set to 1 Hz with an auto-optimization of gains and setpoint.

The adhesion forces of PcOC₈ SAMs were mapped by AFM under PeakForce Quantitative Nanomechanical Property Mapping (QNM) mode with SNL-10 tips and a scan frequency of 1Hz. A normal factor of the tip, which was a product of the normal photodetector sensitivity and normal spring constant [24], was calibrated before the measurements. The normal photodetector sensitivity was calculated from the slope of the force-distance curve obtained by approaching against a hard substrate such as silicon wafer in air. The normal spring constant of the tip was estimated from the power spectral density of the thermal noise fluctuations in air [24, 25]. Adhesion forces were a product of the normal factor of the tip and the voltage signals from the AFM.

The friction forces of PcOC₈ SAMs were characterized by AFM under contact mode with SNL-10 tips. Besides the normal factor, a lateral factor of the tip was also calibrated by an improved wedge calibration [24, 26] and a commercially available TGF11 silicon grating (MikroMasch) [24]. The lateral force was a product of lateral deflection voltage and the lateral factor.
The friction force was determined by taking half of the difference between the left-to-right and right-to-left lateral deflection forces. Besides, the frictional topography, i.e., frictional force map measured under a soft load force, gives a molecular-scale resolution and reveals the real-time molecular structure and structural variation of SAMs under friction.

All the AFM measurements were repeated at least three times, under ambient conditions with a room temperature of 24 °C and an environment humidity of 10%.

3 Results and discussions

3.1 Droplet evaporation

Two-dimensional phthalocyanine molecules can form columnar stacks with the axis parallel or stand on the substrate [27], which makes it a promising candidate for the study on the frictional dependence on molecular orientation. As shown in Fig. 1(a), PcOC₈ with eight carbons in the side chains is chosen in this work, as the long alkyl chains strengthen the interchain Van der Waals force and enable an ordered molecular arrangement [28]. The side length of the aromatic ring is 1.2 nm and the thickness of aromatic ring is 0.35 nm [29]. The length of alkyl chain is 1.3 nm [30].

The contact angles of the evaporating droplet are given in Fig. 2(a). The evaporation process of the PcOC₈ chloroform droplet can be divided into a constant-contact-angle (CCA) regime and constant-contact-radius (CCR) regime. CCA and CCR evaporation regime results in different deposition states, respectively. As shown in Fig. 2(c), the evaporation process of the droplet was monitored by Optical Microscopy (OM). The shape of the droplet contact line keeps uniform and circular during evaporation. For CCA regime, there is no visible deposition remained on the substrate. For CCR regime, a green “ring” was deposited on substrate after evaporation, with a diameter of nearly 600 μm.

The topographies of the deposition of CCA and CCR regimes have been characterized by AFM, as shown in Fig. 2(d). Topography of region A shows that monolayers with a thickness of 1.0 nm and 1.8 nm are formed during CCA evaporation regime. The layer thickness greatly increases at the transition from CCA to CCR regime, as shown by the topography of region B. From the topography of region C at the “ring” deposition, the layer thickness reaches 30 nm, indicating a multilayer deposition under CCR evaporation regime. The layer thickness decreases when approaching to the center of deposition as shown by the topography of region D. All the deposition regions show uniform layer structure, indicating orderly self-assembly of PcOC₈ molecules. The droplet evaporation process and the deposition are illuminated in Fig. 2(b).

The mechanism of the formation of different layer thickness is thought to be induced by the fluid flow during evaporation. It has been proved that capillary force [31] would exert an outward flow and carry solute from the droplet center to the contact line in CCR regime. The capillary flow is determined by the nonuniform evaporative flux, which increases towards the contact line for contact angles < 90°. The above theory agrees with the formation of the green “ring” deposition of PcOC₈ on mica substrate. Nevertheless, the capillary force is only effective when the contact line is pinned. For the CCA regime, convective Marangoni flow [32] can circulate the solute in the droplet and generate residue with a uniform distribution [31]. The Marangoni flow is induced by surface tension gradient and the direction of the circulating flow in chloroform is upward from the contact line to the top of the droplet [33]. To sum up, the Marangoni flow in CCA regime promoted a uniform distribution of PcOC₈ molecules in the droplet and resulted in thin self-assembled layers with millimeter scale size. The capillary flow in CCR promoted the accumulation of PcOC₈ molecules near the contact line and resulted in the “ring” deposition.

The length of side alkyl chains, which determines the Van der Waals interactions between phthalocyanine molecules, is a key factor to determine the self-assembly process and the final deposition. Figures 1(b) and 1(c) and Fig. 3 give the chemical structure and evaporation process of Pc without side chain and PcOC₄ with four carbon atoms in the side chains. Pc molecules aggregate into rod-like crystals, which distribute randomly on the footprint of the contact line. PcOC₄ molecules self-assemble into inhomogeneous
islands. For PcOC₈ with eight carbon atoms in the side chains, uniform monolayer structure as shown in Fig. 2(d) can be formed. The longer the side chain, the stronger the Van der Waals interaction [34], which induces a more uniformly distributed layer structure.

3.2 Molecular orientation and hierarchical structure of PcOC₈ SAMs

The self-assembled monolayers from CCA evaporation regime give two specific layers, with thicknesses of 1.8 nm and 1.0 nm, respectively. The two layers show different adhesion force, as shown in Fig. 4(b), indicating different molecular configurations inside the layer. Considering the 1.0 nm layer is even thinner than the side length of the aromatic core (1.2 nm), it can be easily concluded that the 1.0 nm layer adopts a face-on orientation, with the aromatic core of PcOC₈ lying on the substrate and the side alkyl chains stands perpendicular to the aromatic core. The molecular configuration in face-on oriented PcOC₈ SAMs is similar as a porphyrin derivative, whose alkyl chains also adopt a standing geometry [35] revealed by previous STM researches. The 1.8 nm layer is too thick for face-on orientation and corresponds to an edge-on orientation.

The single layer structure of the 1.0 nm layer and 1.8 nm layer is confirmed by comparing with the layer thickness of PcOC₈ LB monolayer. The π–A isotherm
in Fig. 5(a) shows that there is a state transition around 15 mN/m. The AFM topographies of PcOC₈ LB films transferred at 6, 20, and 31 mN/m are shown in Figs. 5(b), 5(c), and 5(d). It is clearly shown that the LB layer at 6 mN/m keeps the single layer structure. But the LB layers at 20 and 31 mN/m are corrupted into multilayer aggregates, which matches with the π-A isotherm. As shown in Fig. 5(b), the PcOC₈ LB monolayers transferred at 6 mN/m have two specific thicknesses, which are around 1.8 nm and 1.0 nm. Thus, the 1.8 nm and 1.0 nm SAMs prepared by droplet evaporation also have single layer structure. The π-A isotherm shows that the average projection area for one single PcOC₈ molecule is smaller than 100 Å². Considering that the side size of the aromatic core is around 12 Å and the area of aromatic core is 144 Å², most of the PcOC₈ molecules should adopt an edge-on orientation. Thus, the 1.8 nm monolayer, which covers most of the substrate, adopts an edge-on orientation. The 1.0 nm layer adopts a face-on orientation. The single layer structure of the 1.0 nm PcOC₈ layer also matches with the previous reported results. It is reported that a Zn phthalocyanine [36] with side chains formed a 1.1 nm monolayer on mica and the Zn phthalocyanine molecule is thought to lie flat on the surface, with a bucking of the core and flexible side chain. The sizes of the aromatic core and side chain of the above Zn phthalocyanine are similar to those of PcOC₈ molecule. Thus, the possibility that the 1.0 nm PcOC₈ layer is composed of a few PcOC₈ molecules layer with a thickness of 0.35 nm is excluded.

For the edge-on oriented PcOC₈ SAMs, the PcOC₈ molecule stands on the mica surface with a hydrogen bonding [37] between the ether oxygen of PcOC₈ and the hydroxyl groups of mica. Thus, the alkyl chains at the lower part of the aromatic core should lie on the substrate, and the alkyl chains at the upper part of the aromatic core should stand perpendicular to the substrate plane or slightly tilt. The configuration of the edge-on oriented PcOC₈ molecule matches with other reported [38] two-dimensional molecules.
with rigid aromatic core and flexible side chains. For the face-on oriented PcOC₈ SAMs, the aromatic core of PcOC₈ lying on the substrate and the side alkyl chains stands perpendicular to the aromatic core. The configuration of the face-on and edge-on oriented SAMs are illustrated in Fig. 5(b).

The frictional topography of edge-on oriented SAMs reveals a hierarchical self-assembly structure and gives detailed evidence for the edge-on orientation. As shown in Figs. 4(c) and 4(d), periodic stripes with a
width of 38.0 nm and length of micron scale can be clearly discovered. Periodic columns with a width of 2.2 nm and length of tens of nanometer scale have been found inside the stripe structure, as shown in Fig. 4(e). Thus, the hierarchical self-assembly structure of edge-on oriented PcOC₈ molecules is consisted of nanoscale columns, micro-scale stripes, and centimeter-scale monolayers. The direction of the stripe is always perpendicular to the edge of the monolayer, as marked in Fig. 4(c), which is supposed to be induced by the evaporation flow. The nanoscale columns in the frictional topography correspond to the stick-Slip behavior when AFM tip slides over periodic edge-on oriented PcOC₈ columns.

STM measurement reveals the detailed molecular configuration of the edge-on oriented PcOC₈ SAMs. Although the STM measurements were conducted on HOPG, it still provides a good reference for the structure of PcOC₈ SAMs on mica. The edge-on oriented PcOC₈ SAMs give a double herringbone pattern in Fig. 4(f), indicating a co-facial stacking of PcOC₈ molecules, whose aromatic core stands on the substrate. Edge-on orientation is common for two-dimensional molecules, such as phthalocyanine [25] and porphyrin [32]. A similar double herringbone pattern of edge-on oriented naphthalene-1,5-diamine and 9-fluorenone [33] has also been revealed by STM. The double herringbone pattern of PcOC₈ molecules is resulted from the π‒π interaction between aromatic cores and the Van der Waals interaction between alkyl chains. A twist between the plane of aromatic core and plane of alkyl chains can be clearly seen in Fig. 4(f), which has also been observed in the self-assembly of a porphyrin derivative [32] with edge-on arrangement. The twist between aromatic core and alkyl chains promotes the formation of micro-scale stripes. The width of the double herringbone pattern is 6.6 nm, which is three times of the width of column in frictional topography, as shown in Figs. 4(e) and 4(f). The PcOC₈ molecules are supposed to overlap with each other in a manner shown by the molecular model in Fig. 4(e). The overlapping is driven by the Van der Waals interaction between the alkyl chains. The interlocking between alkyl chains and the π‒π interaction between aromatic cores help the forming of the SAMs structure.

The orientation of PcOC₈ molecules is determined by the competition of the substrate-molecule interaction (hydrogen bond and potassium ion adsorption interaction), and the intermolecular interaction (π‒π interaction and Van der Waals’ force). Hydrogen bond [34] between the ether oxygen of PcOC₈ and hydroxyl groups on mica surface, and adsorption interaction [35] between the ether oxygen of PcOC₈ and potassium ions on mica surface tend to confine the aromatic cores of PcOC₈ on the substrate surface and induce a face-on orientation. The π‒π interaction between aromatic cores tends to induce columns with axis parallel to the surface. The Van der Waals’ force from the interdigitation of alkyl chains [36] induces a uniformly lamellar self-assembled structure. The edge-on oriented PcOC₈ SAMs are formed under a dominance of intermolecular interaction while face-on orientation is formed under a dominance of substrate-molecule interaction.

3.3 Frictional response of face-on and edge-on oriented SAMs

The frictional measurements were performed in ambient air condition. Although it has been reported that long time exposure to ambient air can oxidize the gold-thiolate bond in thiol SAMs [37, 38], induce a losing of the ordered structure, and increase the friction coefficient [39], the effect of ambient exposure has been roughly eliminated by using freshly prepared SAMs and carefully chosen SAMs with ordered structure in this work. Without the oxidation of gold-thiolate bond, the PcOC₈ SAMs were assumed to keep stable for several days [40]. All the used PcOC₈ SAMs were freshly prepared and tested in several hours.

The orientation dependence of the frictional properties of PcOC₈ monolayer is explored by comparing the frictional response of face-on (1.0 nm) and edge-on (1.8 nm) oriented monolayers. Since the width of the stripe in edge-on layers is around 38 nm, all the frictional measurements were performed under a scan size of 20 nm × 20 nm. As shown in Fig. 6(a), edge-on (blue line) and face-on (green line) oriented layers both exhibit lower friction force and friction coefficient than fresh mica (black line). More specifically, the face-on oriented layer shows the greatest friction-reducing effect.
Fig. 6  (a) Friction-load curve of the PcOC₈ monolayer with edge-on and face-on orientation, and mica surface, which were measured under a scan size of 20 nm × 20 nm. (b) Initial topography of PcOC₈ SAMs before friction. (c) Worn topography after a frictional scan under a high load force of 80 nN.

The great friction-reducing effect of face-on oriented layer may be originated from a low packing density and high-order arrangement. The terminal groups of face-on and edge-on oriented SAMs are alkyls but face-on oriented SAMs have a significantly lower packing density than edge-on SAMs. The lower packing density of face-on oriented SAMs results in less interaction sites with AFM probe and lower adhesion force than edge-on oriented SAMs. Low adhesion force helps reduce the friction force. Besides, monolayers with lower packing density tend to have lower lateral stiffness [41]. The terminal alkyl chains in face-on oriented SAMs with a sparse packing density and low lateral stiffness can be reoriented along the sliding direction of AFM probe, which prevents the direct contact of asperities and reduces the friction force. Thus, low packing density of face-on oriented SAMs may help reduce friction force and friction coefficient. On the other hand, the degree of order arrangement is another crucial factor to determine the friction force. Less ordered arrangement induces more defects, such as gauche defect [10] and more excitation mode, which result in larger energy dissipation and friction force. The double herringbone pattern of edge-on oriented SAMs is much more complex than the structure of face-on oriented SAMs, which may induce more defects and larger friction.

Face-on oriented SAMs also has a stronger wear resistance than edge-on oriented SAMs. As shown in Figs. 6(b) and 6(c), the edge-on layers have been totally removed under a load force of 80 nN while the face-on layers remain unchanged. The main substrate-molecule interactions are the hydrogen bond between the ether oxygen of PcOC₈ and the hydroxy group of mica, and the interaction between the ether oxygen of PcOC₈ and potassium ions on mica surface. Face-on oriented PcOC₈ SAMs have more interaction sites and subsequently stronger interaction with the substrate than edge-on layer. Thus, the face-on oriented SAMs have a decreased freedom to be displaced and a stronger wear resistance. It has been proved that the tribological performance at both nano-scale and macro-scale depends on ordered molecular arrangement [29, 42, 43] and nanomechanical properties [44]. The exploration of the effect of molecular orientation on friction here furtherly helps to develop novel lubricants with controlled molecular orientation.

3.4 Structural variation of the edge-on oriented SAMs under friction

The structure of edge-on (1.8 nm) oriented PcOC₈ monolayer varies with increasing load force and shows a stepwise friction force curve. Three edge-on oriented SAMs with similar column direction (the angles between the column direction and shear direction of AFM probe (horizontal direction) of the three SAMs are 96°, 86°, and 105°, respectively) but different order degrees have been characterized. The “high-ordered SAMs” in Fig. 7(a) have the highest order degree of molecular arrangement, with clear and continuous column pattern and uniform column direction. The “medium-ordered SAMs” in Fig. 7(b) have a less order degree, with discontinuous column pattern but uniform column direction. The “low-ordered SAMs” in Fig. 7(c) have the lowest order degree, with discontinuous columns and nonuniform column direction. The initial frictional topographies were measured under a low load force around 30 nN. Then, friction scans under increasing loads were performed and the in situ frictional topography reveals the structural variation of columns. The gray maps on the right give the load range and critical loads of structural variation are marked by red line. The above three kind of SAMs with different order degree coexist in the edge-on oriented PcOC₈ monolayer and can be reproduced in different measurements. The
comparation among the three SAMs helps reveal the effect of order degree on frictional properties.

For the High-ordered SAMs with the highest order degree in Fig. 7(a), the direction and integrity of the columns remain unchanged when the load force is below 47 nN, indicating a stable structure under friction. When the load force is larger than 47 nN, the columns get distorted, indicating a weak deformation of the terminal alkyl chains on SAMs. Despite the weak structural deformation under high loads, the ordered SAMs still give an approximately linear friction force curve, which belongs to an “ordered friction” state, as shown in Fig. 7(d).

For the medium-ordered SAMs with less order degree and discontinuous columns, two transitions are occurred at load force of 47 nN and 55 nN, as shown in Fig. 7(b). When the load force is lower than 47 nN, the direction and integrity of the columns remain unchanged. As the load force increases and exceeds 47 nN, the columns disappear and the frictional topography becomes flat without any periodic features, indicating a collapse of the terminal alkyl chains called “collapsed column”. The structural transition from ordered column to collapsed column corresponds to a stepwise frictional increase, as shown by the magenta curve in Fig. 7(d). The stepwise friction originates from the deformation and collapse of the alkyl chains, which provides solid evidence for Barrena’s [7] and Mowery’s hypothesis [8]. The friction state of the collapsed columns is called “collapsed friction”. When the load force is even larger than 55 nN, the frictional topography gets ununiform and sharply fluctuated, accompanied by a sharp increase of the friction force curve, indicating a worn state of the columns. The high friction state after the wear of the edge-on SAMs is called “worn friction”.

For the low-ordered SAMs with the lowest order degree and discontinuous and nonuniform columns, as shown in Fig. 7(c), the columns disappear and the frictional topography gets sharply fluctuated when the load force is beyond 47 nN. The friction force curve transits from ordered friction to worn friction directly, as shown in Fig. 7(d). Collapsed column structure was not formed during the frictional shear, which should be due to that the initial structure with low order degree easily induces large frictional shear and wear of the SAMs. More than three times of measurements were performed on different medium-ordered SAMs and low-ordered SAMs, the reproducible results confirmed the effect of order degree on the frictional response of PcOC₈ SAMs.

Thus, the edge-on oriented PcOC₈ SAMs transit among three structure states under frictional shear, which are ordered column, collapsed column, and worn column. The structural transitions are accompanied by friction force transitions among three

\[ \text{Friction} \text{ 11}(3): 354–368 (2023) \]

Frictional topography (Initial) In situ frictional topography

(a) High-ordered SAMs

(b) Medium-ordered SAMs

(c) Low-ordered SAMs

(d) Friction-load curves of the three edge-on oriented SAMs. Three friction states (ordered friction, collapsed friction, and worn friction) are divided by the friction force and structural variation of columns.

Fig. 7  (a–c) In situ structural variation of the column structure of three edge-on oriented PcOC₈ SAMs with different order degree under friction. (d) Friction-load curves of the three edge-on oriented SAMs. Three friction states (ordered friction, collapsed friction, and worn friction) are divided by the friction force and structural variation of columns.

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frictional states, which are ordered friction, collapsed friction, and worn friction, respectively. There are two critical loads for the structural transition of PcOC₈ SAMs. The first critical load is around 47 nN, beyond which the structure transits from ordered column to collapsed column, accompanied by a collapse of the terminal alkyl chains of SAMs under frictional shear. The second critical load is around 55 nN, beyond which the structure transits from collapsed column to worn column, accompanied by wear of the SAMs under frictional shear. Sharp and stepwise friction force increase is induced by the structural transition. The initial order degree of the column structure can affect the critical load. For columns with high order degree, the column deformation gets weak and slow, with an increased first critical load. For columns with low order degree, the column is rapidly collapsed and worn under frictional shear, with a directly transition from ordered friction to worn friction.

The used mica in this work gives a linear friction-load curve under a load range of 15–95 nN (not shown here), indicating that the wear of mica occurs under loads above 95 nN, which matches with the previous reported results [45]. The wear of mica occurs under a higher load than the wear of PcOC₈ monolayer, which has negligible effect on the structure dynamic of PcOC₈ molecules.

3.5 Structural anisotropy of the edge-on oriented SAMs

The first critical load of structural transition of edge-on (1.8 nm) oriented PcOC₈ monolayer shows an angular dependence on the column direction. The shear direction of the AFM probe is along the horizontal direction. The angle θ between shear direction of AFM probe and the column axis is illuminated in Fig. 8(a), which is measured by a NanoScope Analysis software with a resolution of 0.1°. Additionally, the uniformity of the column direction and the column width induce errors in the angle measurement. The columns are not perfectly uniform, which result in a slightly difference between the direction of different columns. And manually drawn solid line on the column during the angle measurement cannot perfectly match the column axis because the column has a width. The standard deviation of the angle measurement was evaluated to be ±1° by tens of measurements.

Since the column axis forms an angle of 57° with molecule plane from the STM measurement shown in Fig. 4(f), three specific θ angles are illuminated, in which the AFM probe shears against the molecular plane, along the molecular plane and along the column axis. The variation of critical load with angle θ is given in Fig. 8(b). A dotted trendline is qualitatively given to describe the anisotropic critical load. There is a minimum critical load at θ≈27° and a maximum critical load at θ≈57°, which approximately match with that the AFM probe shears against and along the molecule plane, respectively. There is an angle error between the measured θ (27°) for minimum critical load and the theoretical θ (33°) for a shear direction against molecular plane. The angle error may origin from the imperfect unidirectional arrangement of the columns in edge-on oriented PcOC₈ SAMs. The critical load reflects the resistance to structural deformation, which is stiffness. Thus, the edge-on oriented PcOC₈ SAMs show a small stiffness when shearing against the molecule plane and a large stiffness when shearing along the molecule plane. Considering the rotational symmetry, it is reasonable to have another minimum critical load at θ≈140° and maximum critical load at θ≈110°. Besides, the trendline gives a local minimum critical load at
$\theta \approx 86^\circ$, which is close to $90^\circ$ and may origin from a low stiffness of edge-on oriented SAMs when shearing against the column axis.

Thus, the order degree mentioned in the preceding section and the anisotropic stiffness of the column are two factors to determine the critical load of the structural deformation of PcOC$_8$ SAMs. Columns in PcOC$_8$ SAMs with higher order degree tend to show a larger critical load. Columns in PcOC$_8$ SAMs show a larger stiffness and critical load when shearing along the molecular plane, and a lower stiffness and critical load when shearing against the molecular plane.

4 Conclusions

In summary, two-dimensional phthalocyanine molecules were introduced into the study on the dependence of frictional property on molecular orientation and structure. Face-on and edge-on oriented PcOC$_8$ SAMs were assembled by a droplet evaporation method. Face-on oriented PcOC$_8$ SAMs show lower adhesion and friction, which may be due to lower packing density and higher arrangement order, comparing with that of edge-on oriented SAMs. Hierarchical assembly structure inside the edge-on oriented SAMs has been revealed by frictional topography. The centimeter-scale edge-on oriented monolayer is consisted of micron-scale stripes and nanoscale columns. The ordered columns can deform under increasing load, which gives a stepwise friction increase. Three friction states can be easily distinguished, which are “ordered friction”, “collapsed friction”, and “worn friction”. The structural deformation of column structure depends on the order degree of molecular arrangement and the anisotropic stiffness of columns. The in situ structural variation of the column under friction has been revealed by AFM, which provides robust evidence on the relationship between molecular structure and frictional response and gives a deep insight into the nano-scale frictional mechanism.

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