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Shear-Induced Uniaxial Assembly of Polyaromatic Monolayers*

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The control of spatial arrangements of molecular building blocks on surface opens the foundational step of the bottom-up approach toward future nanotechnologies. Contemporarily, the domain size of monolayers exhibiting crystallinity falls in the submicron scale. Developed herein is a method that allows the alignment of polyaromatics with one-single domain for as long as ∼7 mm. Even more exciting is the fact that the method is applicable to every laboratory with negligible cost. The monolayers are prepared simply by placing a piece of folded lens paper against the substrate and the deposition solution containing the compound of interest. The essence of the film preparation is similar to the Couette flow where the laminar flow takes place between two concentric walls, one of which rotates and creates viscous drag proven useful to align macromolecules. The method can induce an edge-on orientation for 3,6,11,14-tetradodecyloxydibenzo[g,p]chrysene (DBC-OC$_{12}$), hexakis-(4-dodecyl)-*peri*-hexabenzocoronene (HBC-C$_{12}$) and 3,6,12,15-tetrakis-(dodecyl)-tetra-benz[a,c,h,j]anthracene (TBA-C$_{12}$), which would otherwise adopt the face-on arrangement on graphite. [DOI: 10.1380/ejssnt.2009.157]

Keywords: scanning tunneling microscopy; monolayers; solid-liquid interface; self-assembly

I. INTRODUCTION

One of the main challenges and important goals in material science is the fabrication of well-defined periodic nanostructures [1–8] for applications involving the mobility of charges across electrodes, such as organic thin film transistors [9] and photovoltaic cells [10, 11]. The orientations and packing quality of the stacked molecules control the charge-carrier pathways and thus the performance of the molecule-based devices [12]. The alignment of polyaromatic or copolymeric thin films has been achieved by utilizing magnetic fields [13], electric fields [14, 15], Langmuir-Blodgett technique [16], zone-casting technique [17], and the phenomenon of dewetting [18–21]. Well-controlled dewetting such as dip-coating [18] can be used to align molecules of interest, simply by the rupture of solutions on a solid surface [22]. However, in most cases, the dewetting of a solution causes multi-rings with random sizes or amorphism [23]. Alternatively, shear flow [24–26] is recently applied to align macromolecules and inorganic materials such as lyotropic micelles, block copolymers, carbon nanotubes, and mesoporous silicates. Contrary to the aforementioned polymeric materials, reported herein is the monolayer assembly of relatively small aromatic compounds. The alignment is achieved by a simple shear force using a piece of cellulose paper, lens tissue, or Kimwipe, available to every laboratory. The shear changes molecular orientations from face-on to edge-on and confers one single domain for as long as ∼7 mm [27]. Other than the images acquired at the first monolayer from the substrate by STM (scanning tunneling microscopy), presented here includes images of AFM (atomic force microscopy), suggesting that the alignment extends multilayer thickness to the film-solvent interface.

II. EXPERIMENTAL

All chemicals were ACS grade. DBC-OC$_{12}$ (3,6,11,14-tetra-dodecyl oxydibenzo[g,p]chrysene) [28], TBA-C$_{12}$ (3,6,12,15-tetrakis(dodecyl)tetrabenz-[a,c,h,j]anthracene) [29], and HBC-C$_{12}$ (hexakis(4-dodecyl)-*peri*-hexabenzocoronene) [30] were synthesized based on literature reports. The deposition solutions for monolayer alignment contained 0.1-mM or saturated polyaromatics in phenyloctane, trichlorobenzene, dichlorobenzene, p-xylene, or toluene.

The monolayers were prepared with introducing an aliquot of 10-μL deposition solution on freshly cleaved HOPG (highly orientated pyrolytic graphite, ZYH grade, Advanced Ceramics, USA). A piece of cover glass was then placed against the sample solution and in parallel to the HOPG. A syringe pump or index finger were then pushing the cover glass at the fastest speed yet maintaining a great steadiness. Alternatively, the alignment was obtained by placing a piece of cellulose paper, lens tissue, or Kimwipe which absorbed and pulled the solvent for 8-10 sec. During this period, the solution flow drove a shear at the solid-liquid interface and dragged the molecules stacked.

STM and AFM imaging was carried out with a PicoScan (4500, Agilent Technologies) at room temperature. The STM probes were commercially available Pt/Ir tips (PT, Nanotips, Veeco Metrology Group/Digital Instruments, USA). Typical imaging conditions of bias voltage and tunneling current ranged from −0.10 to −1.40 V and from 10 to 100 pA, respectively. Images were acquired using a 10-μm scanner and monolithic silicon cantilevers (NCHR, NanoWorld, Neuchatel, Switzerland) whose force constant and the typical tip radius of curvature were 42 nN/m and 10 nm, respectively. All the presented images were subjected to a first-order flattening to minimize noise and without further processing. The lattice parameters of the adlattice with respect to those of the underlying HOPG were obtained at a relatively small impedance (E_{bias} −0.10 V, $I_{\text{tunneling}}$ 0.50 nA).

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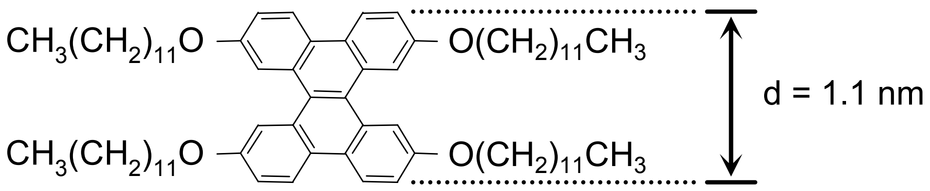

FIG. 1: Structure of DBC-OC$_{12}$.

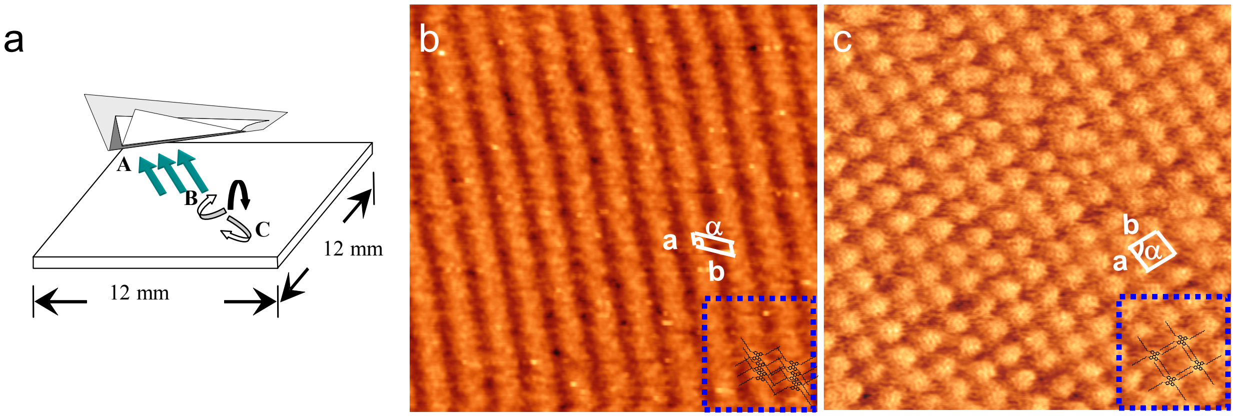

FIG. 2: (a) A scheme illustrating how the molecules are aligned after being subjected to flow treatment. STM image and model of (b) an edge-on and (c) a face-on orientation of DBC-OC$_{12}$. The E_{bias}, $I_{\text{tunneling}}$, and imaging sizes for Panels b and c are, −0.80 V, 36 pA, 30 × 30 nm and −0.80 V, 60 pA, 30 × 30 nm, respectively. The E_{bias} and $I_{\text{tunneling}}$ used to reveal the underlying HOPG were −0.10 V and 0.50 nA.

III. RESULTS AND DISCUSSION

To illustrate this shear-induced alignment, DBC-OC$_{12}$ [28] (Fig. 1) was chosen as model system because of its relatively small number of aromatic rings and weaker intermolecular π-π attractions than most macrocyclic polyaromatics. The shear flow was driven by a piece of cellulose paper, lens tissue, or KimWipe which generated capillary force and a laminar flow upon contacting the solvent. The laminar flow (green arrows in Fig. 2(a)) orientated DBC molecules and carried them stacking along the flow direction. The [01$\bar{1}$0] direction of HOPG was pre-determined and was perpendicular to where the folded lens paper was placed against. To find out the linear flow rate, an oversaturated solution was prepared. The flow rate of colloidal precipitates was ca. 0.5-0.6 mm/s, clocked by an optical microscope. This procedure furnished the laminar flow with great steadiness.

Without being subjected to the shear treatment, molecules of DBC-OC$_{12}$ exhibited a face-on orientation on graphite (Fig. 2(c)), the same as other polyaromatics. Figure 2(b) shows that this shear treatment was strong enough to rearrange face-on molecules of DBC-OC$_{12}$ into striped features. The nearest neighbor spacing along $\vec{a}$ was reduced from 1.7 nm to 0.5 nm. The unit cell parameters of $|\vec{a}|$, $|\vec{b}|$, and α for images (b) and (c) were, respectively, 1.04 ± 0.09 nm, 3.06 ± 0.13 nm, $115° \pm 3°$, and 1.70 ± 0.11 nm, 1.92 ± 0.12 nm, $95° \pm 4°$. The lower right corners of Panels b and c illustrate the corresponding packing models. The detailed analysis of STM images was described in our recent report [27] which also demonstrated that the well defined packing feature exhibited a single domain with a size of 7 mm in parallel with the flow direction. If the alignment was performed deliberately off the [01$\bar{1}$0] direction of HOPG, it no longer showed the feature of one single domain, indicative of the influence of the substrate on the molecular packing [27].

The effect of solvent evaporation was a significant factor on the thin-film assembly [19, 31, 32] because evaporation generated unwanted turbulent flow and devastated the film quality. For solvents with a high boiling point such as phenyloctane, the influence of solvent evaporation was negligible and thus the domain size was very large. For solvents with a low boiling point such as *p*-xylene and toluene, the domain sizes were reduced to 2 mm from that of ∼ 7 mm in phenyloctance. At locations where the shear became less influential (e.g. location C in Fig. 2(a)), DBC-OC$_{12}$ adopted the face-on orientation (Fig. 2(c)).

The films were examined by TM-AFM (tapping mode atomic force microscopy) which revealed morphological features of the outermost layer, as opposed to the imaging mechanism of STM in which the tip penetrated into the film and the tunneling current unveiled the very first adsorbed layer on substrate. Panels (a) and (c) of Fig. 3 show images of films prepared by the shear treatment and by dropcasting, respectively. Figure 3(a) unveils packing stripes, consistent with the direction of the laminar flow, and thus demonstrates that the effect of the shear treatment was not limited to the first monolayer. Figure 3(b) displays a section profile, corresponding to the dotted line in Fig. 3(a). Other than the periodic modu-

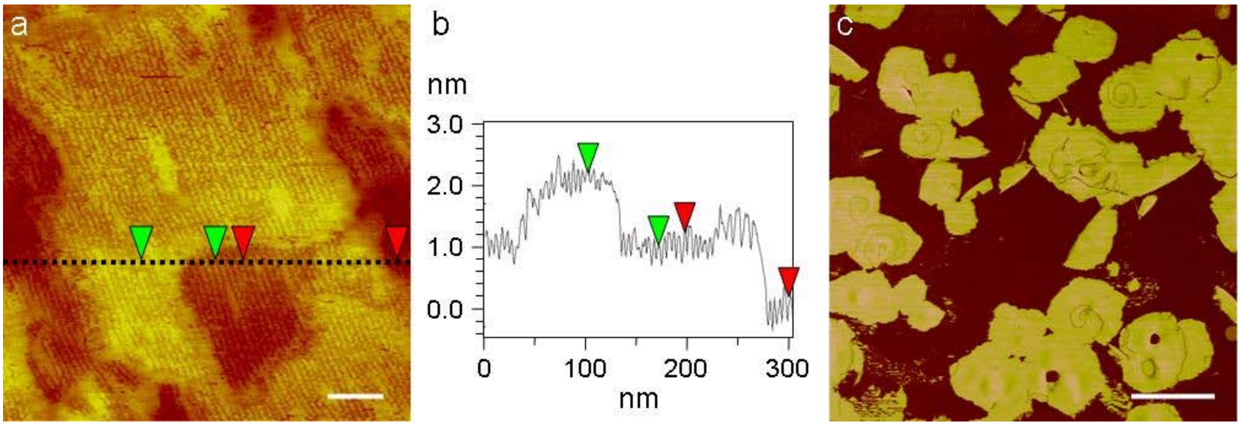

FIG. 3: Images of tapping mode AFM for films prepared by (a) the shear treatment and (c) dropcast on HOPG. Solvent: *p*-xylene. Image size: (a) 0.3 μm and (c) 5 μm. Scale bar: (a) 50 nm and (c) 1 μm.

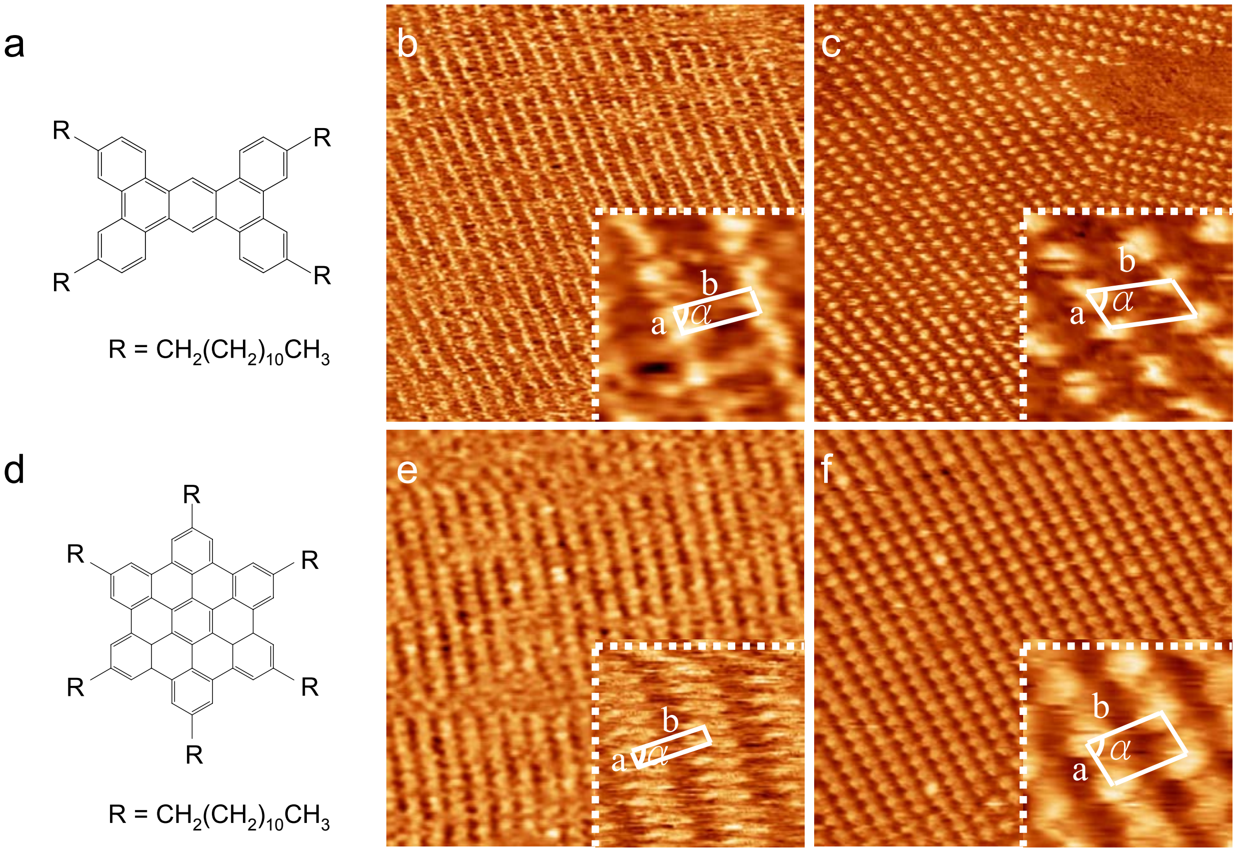

FIG. 4: The effect of the shear treatment on the reorientation and alignment of polyaromatics (a-c) TBA-C_{12} and (d-f) HBC-C_{12}. STM images after the films were prepared by (b, e) the shear treatment and by (c, f) dropcast. Imaging conditions of E_{bias}, $I_{\mathrm{tunneling}}$, and image sizes for (b), (c), (e), and (f) are, respectively, -0.9 V, 60 pA, 56×56 nm, and -0.9 V, 100 pA, 56×56 nm, and -1.0 V, 60 pA, 50×50 nm, and -1.0 V, 100 pA, 50×50 nm. Inset size: 7×7 nm. Unit cell parameters: $|\vec{a}|$, $|\vec{b}|$, and α for (b) 0.94 ± 0.36 nm, 2.64 ± 0.21 nm, $88^\circ \pm 4^\circ$; (c) 1.71 ± 0.15 nm, 2.46 ± 0.19 nm, $73^\circ \pm 3^\circ$; (e) 0.63 ± 0.17 nm, 2.53 ± 0.19 nm, $86^\circ \pm 4^\circ$; (f) 1.93 ± 0.12 nm, 2.62 ± 0.15 nm, $80^\circ \pm 3^\circ$.

lation arising from the striped feature, the trace showed plateau and discontinuity, indicative of a layered morphology. The plateaus were equally spaced and the difference in height between layers was found ca. 1 nm, equivalent to that of an edge-on DBC-OC_{12} molecule. Hence, the alignment of multilayers was achieved by the shear treatment. Such stripes were not found for dropcast films (images not shown) which instead had characteristics of islands with swirled terraces (Fig. 3(b)), particularly pronounced for low boiling point solvents such as *p*-xylene. Also noticed was the fluctuation in height for the aligned and dropcast films varies, respectively, within 2 nm and larger than 20 nm, suggesting that the shear was allowed to prepare relatively uniform films.

To demonstrate the generality of the method, TBA-C_{12} and HBC-C_{12} (Fig. 4) were synthesized and were subjected to the shear treatment. Panels b and e demonstrate that both molecules adopted the edge-on orientation and were well-aligned due to the laminar flow generated by a piece of folded lens paper. Note that without such treatment, both polyaromatics adopted a face-on orientation on graphite surface. Therefore, this shear treatment effectively reoriented and aligned a variety of molecular shapes, including square-like DBC-OC_{12}, rectangular TBA-C_{12}, and discotic HBC-C_{12}.

IV. CONCLUSIONS

The results presented here show STM images with spatial resolution at the molecular level which demonstrate polyaromatic compounds can be aligned in one single domain by a very simple shear treatment. The laminar flow creates hierarchical control to construct a high quality alignment of polyaromatics. The topography obtained by AFM reveals that the alignment extends to the outermost layer. This methodology costs negligibly and is readily available to laboratories that are interested in preparation of high-orderly organic thin films.

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