

Shear-Induced Long-Range Uniaxial Assembly of Polyaromatic Monolayers at Molecular Resolution

Shern-Long Lee,[†] Cher-Yi Jason Chi,[†] Min-Jie Huang,[†] Chun-hsien Chen,^{*,†} Chia-Wen Li,[‡] Kamalkishore Pati,[‡] Rai-Shung Liu[‡]

[†]*Department of Chemistry, National Taiwan University, Taipei, Taiwan 10617, and* [‡]*Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043*

Experimental Methods

Method 1: shear treatment by a peristaltic pump.

Method 2: shear treatment by capillary force from a piece of lens paper.

Figure S1. Effect of the shear treatment of the monolayer structure of tetrabenz[*a,c,h,j*]anthracene (TBA-OC₁₂), hexa-*peri*-hexabenzocoronene (HBC-C₁₂), and coronene.

Figure S2. Images of 3,6,11,14-tetradodecyloxydibenzo[*g,p*]chrysene monolayers in phenyloctane.

Figure S3. Shear alignment using a peristaltic pump to generate Couette-like flow for 3,6,11,14-tetradodecyloxydibenzo[*g,p*]chrysene monolayer.

Experimental Method

The synthetic procedures for alkyl-derivatized polyaromatics [*i.e.*, DBC (3,6,11,14-tetradodecyloxydibenzo[*g,p*]chrysene),¹ TBA-OC₁₂ (3,6,12,15-tetrakis(dodecyloxy)tetrabenz[*a,c,h,j*]anthracene),² and HBC-C₁₂ (hexakis(4-dodecyl)-*peri*-hexabenzocoronene)³] were reported previously. Coronene was commercially available (TCI) and was used as received.

Deposition solutions. Prior to imaging, all compounds under investigation were dissolved in 1-phenyloctane or other solvents described in the text. The examined concentrations were 0.10 mg/mL, 0.15 mg/mL, 1.0 mg/mL, and at saturated level. The revealed lattice structures of edge-on DBC on HOPG (Advanced Ceramics, ZYH grade) appeared independent of the concentration used. The solutions of coronene and HBC-C₁₂ were subjected to ultrasonication or warmed up to improve the solubility.

Method 1: shear treatment by a peristaltic pump. Because of the difficulty in description, a video file was prepared in the Supporting Information for the demonstration of the process. A peristaltic pump and a glass slide were utilized to generate a plane Couette-like flow.

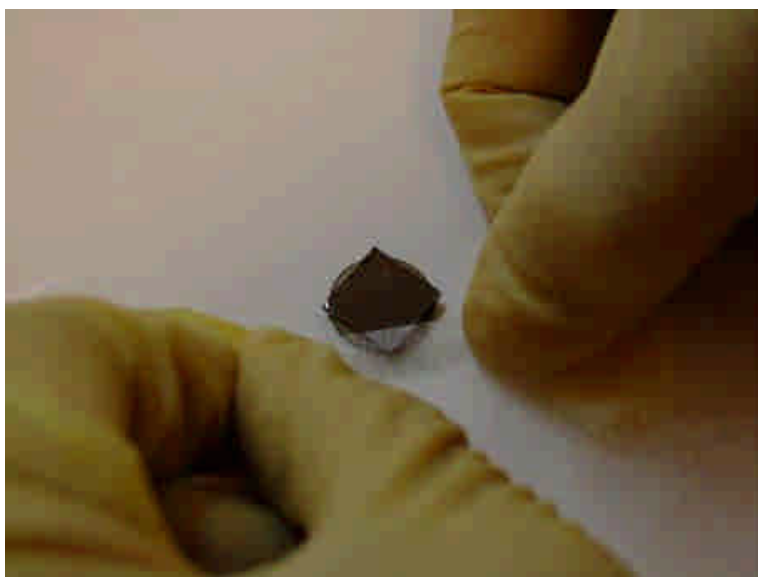
The preparation of the monolayers began with introducing on HOPG a 10-μL drop of sample which contained 0.10 mg/mL, 0.15 mg/mL, 1.0 mg/mL, or saturated polyaromatics in phenyloctane, trichlorobenzene, dichlorobenzene, or toluene. To mimic the plane Couette flow cell, a microscope glass slide was then placed against the sample solution and in parallel to the HOPG substrate via a spacer of about 1 mm that defined the solution thickness. Please see the following photo and the video file prepared for the Supporting Information. The spacing was defined by the distance between HOPG and the

grooves or the tracks for the glass slide to glide over HOPG. Each groove was prepared by 3 pieces of 1"x3" glass slides glued together (see the following photo). HOPG, the substrate, was hold still by a magnet (see the following photo) while the shear force was applied by pushing the glass plate using a syringe pump or by pulling the glass plate using a peristaltic pump.



The molecules remained lying flat at a slow speed (≤ 0.2 mm/s) and became stacked when the glass moved faster than 8 mm/s, where the respective rates corresponded to the maximal speed of the syringe pump and the minimum of the peristaltic pump. The strong dependence of the molecular orientation on the moving speed of the cover glass manifests that certain strength of the shear at the liquid/solid interface was required to agitate the adsorbed molecules and to prompt the face-to-face packing arrangement. In fact, using the index finger to laterally glide the cover glass with sufficient momentum guaranteed the edge-on arrangement of DBC. The stripes appeared wavy (Figure S3) because, with our present device to generate the plane Couette flow, the mechanical movement of the glass slide was not perfectly smooth, linear, and parallel to the HOPG substrate. Hence, the flow likely carried pulsating unevenness and resulted in stacking faults here and there (Figure S3). The striped arrays were similar to, but not as ordered and uninterrupted as, those shown in Figure 2 which was typical from samples prepared by Method 2.

Method 2: shear treatment by capillary force from a piece of lens paper. After introducing a $\sim 10\text{-}\mu\text{L}$ drop of sample solution on HOPG, a piece of cellulose paper, lens tissue, or Kimwipe was employed to absorb, to pull the solvent, and thus to drag a shear at the surface for 8~10 sec. In the following photo, a piece of lens paper was used. The linear flow rate was ca. 0.5~0.6 mm/s. As described in the note of the main text, the flow rates were measured by oversaturated solutions. This procedure furnished the laminar flow with great steadiness. The striped arrays (*e.g.* Figure 2) were better aligned and less interrupted than those prepared by Method 1. Generally speaking, Method 1 confers longer striped features (*i.e.*, all over the substrate) while the packing quality for films prepared by Method 2 is better.



STM experiments. STM imaging was carried out with a PicoScan (Agilent Technologies) at room temperature and the liquid-solid interface. 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. All the presented images were subjected to a first-order flattening to minimize noise and without extending processing.

Determination of the unit cell vectors for the adlattice. The angles between the unit vectors of the adlattice relative to those of the underlying HOPG of which the lattice parameters were obtained at smaller impedance (E_{bias} 0.10 V, $I_{\text{tunneling}}$ 0.5 nA) and were utilized to calibrate the length of the unit cell vectors of the DBC adlattice.

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Effect of the shear treatment of the monolayer structure of unsubstituted coronene.

The motive to study unsubstituted coronene arises from the facts that it is analogous to HBC (hexabenzocoronene), a potentially important compound for molecular electronics,⁷⁻⁹ and that underivatized HBCs appear more difficult to adopt an edge-on orientation on surface than the alkyl derivatives. Molecules having π -electron-rich cores such as HBC⁶⁻¹⁰ and TTF (tetrathiafulvalene)⁹⁻¹¹ are candidates for fabricating nanometer-scale optoelectronics. A requirement for the molecules applicable in semiconductor devices is that the plane of HBC should stand vertically to the substrate and thus the electron-propagating pathway is parallel to the substrate. However, underivatized molecules have the tendency to form a monolayer with the π -electron-rich cores facing the surface of, for example, Au(111)⁵ or HOPG.⁶ Even with *n*-alkane-substituents, the molecules still adopt a face-on arrangement, instead of π - π stacking between the HBC planes. In addition, the current strategy to synthesize HBCs is difficult and the film preparation for the vertically-orientated molecular assembly needs special apparatus such as a Langmuir-Blodgett trough, a zone-casting equipment,⁷ and a so-called soft landing setup⁶ constituted with a laser to desorb HBCs and a low pressure chamber to place the substrate (similar to a mass spectrometer). Therefore, the edge-on orientation of coronene shown in Figure S1a (bottom row) demonstrates that this shear treatment is effective in the alignment of unsubstituted polyaromatics.

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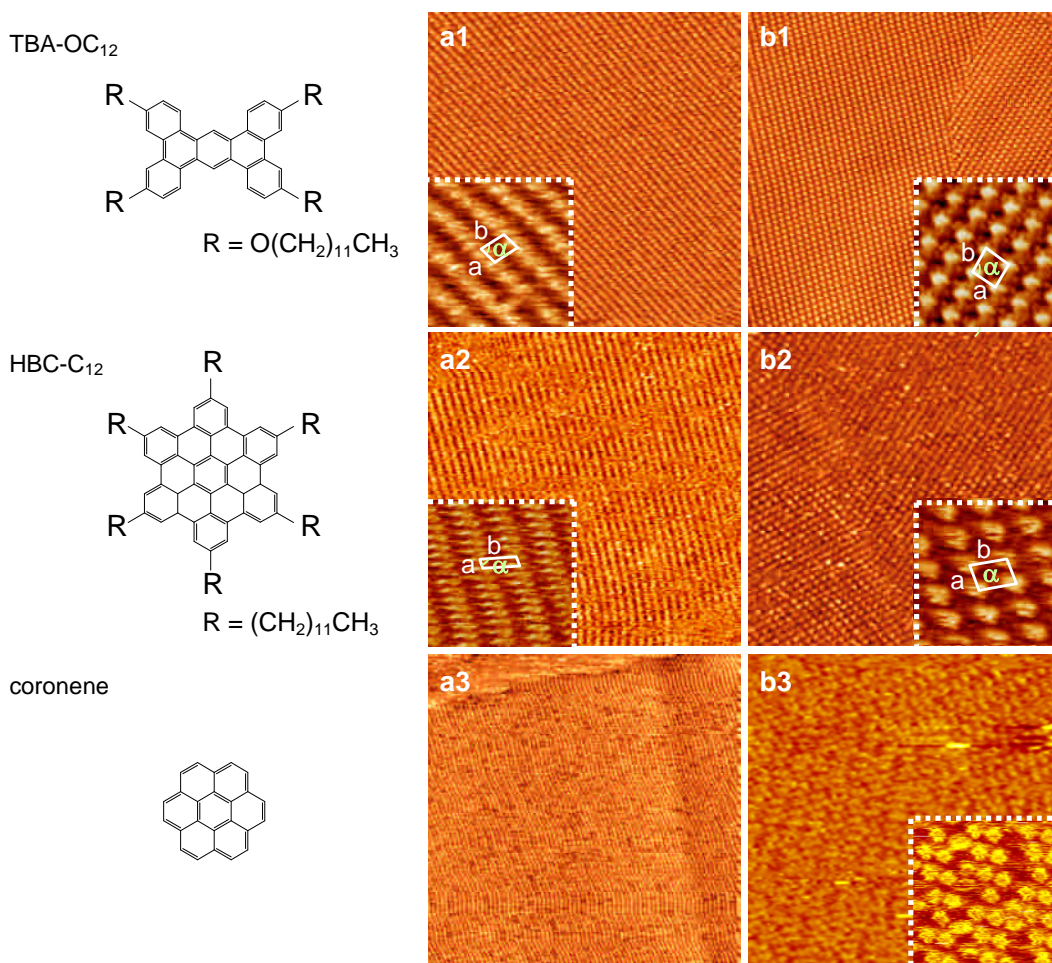


Figure S1. Effect of the shear treatment of the monolayer structure of tetrabenz[*a,c,h,j*]anthracene (TBA-OC₁₂, upper row), hexa-*peri*-hexabenzocoronene (HBC-C₁₂, middle row), and coronene. Images of monolayers prepared by (a) Couette-like shear treatment and by (b) placing a drop of the sample solution on HOPG. The results demonstrate that, other than the square-like DBC-OC₁₂ discussed in the main text, the shear treatment can reorient polyaromatics of rectangular and discotic shapes, as well as polyaromatics without alkyl derivatives (e.g., coronene). Note that without such shear treatment, these polyaromatics all adopt a face-on orientation on graphite surface. Inset size: 10x10 nm. The unit cell parameters, *a*, *b*, and α , in the insets: (a1) 0.81 ± 0.12 nm, 1.86 ± 0.17 nm, $72^\circ \pm 3^\circ$; (b1) 2.05 ± 0.11 nm, 1.97 ± 0.14 nm, $96^\circ \pm 2^\circ$; (a2) 0.63 ± 0.17 nm, 2.53 ± 0.19 nm, $86^\circ \pm 4^\circ$; (b2) 1.93 ± 0.12 nm, 2.62 ± 0.15 nm, $80^\circ \pm 3^\circ$. Conditions of E_{bias} , $I_{\text{tunneling}}$, and frame size: (a1) -0.90 V, 17 pA, 100x100 nm; (b1) -0.90 V, 50 pA, 100x100 nm; (a2) -1.40 V, 127 pA, 100x100 nm; (b2) -1.40 V, 60 pA, 100x100 nm; (a3) -0.90 V, 30 pA, 200x200 nm; (b3) -0.90 V, 100 pA, 60x60 nm. Concentration of sample solutions: 0.1 mg/mL; solvent: TBA-OC₁₂ in trichlorobenzene, HBC-C₁₂ dissolved in warm trichlorobenzene, coronene in phenyloctane.

Long-range alignment of DBC films. The images of Figure 2 (main text) were acquired at the Location b, near the center of the HOPG. The striped patterns had the same orientation as that close to the lens tissue at Location a and as other images between the two points (Figure S2). The STM was equipped with a 2- μm tube scanner which made it impracticable to track the length of the stripes without repositioning the scanner head. Hence, in addition to the randomly picked sites in between Locations a and b, we inspected Location b firstly with the maximal scanning area of 2x2 μm which was obviously too large to resolve the stripe pattern and was subsequently scrutinized with 5 images of 0.4- μm zones frame by frame as the drawing in Figure 2 (main text). The orientation of the arrays in the 5 images was essentially the same and coverage of ~5% was found for stripes adopting other directions and for regions lack of distinct stripes. Figure S2a^o was obtained on where the lens paper was placed and exhibited multilayer features. Between Locations a and b', the images showed stripes with the same direction. If the shear-drag direction deviated considerably from $[01\bar{1}0]$ of HOPG, *e.g.* Figure S2d^o, the molecular assembly became no longer a single domain.

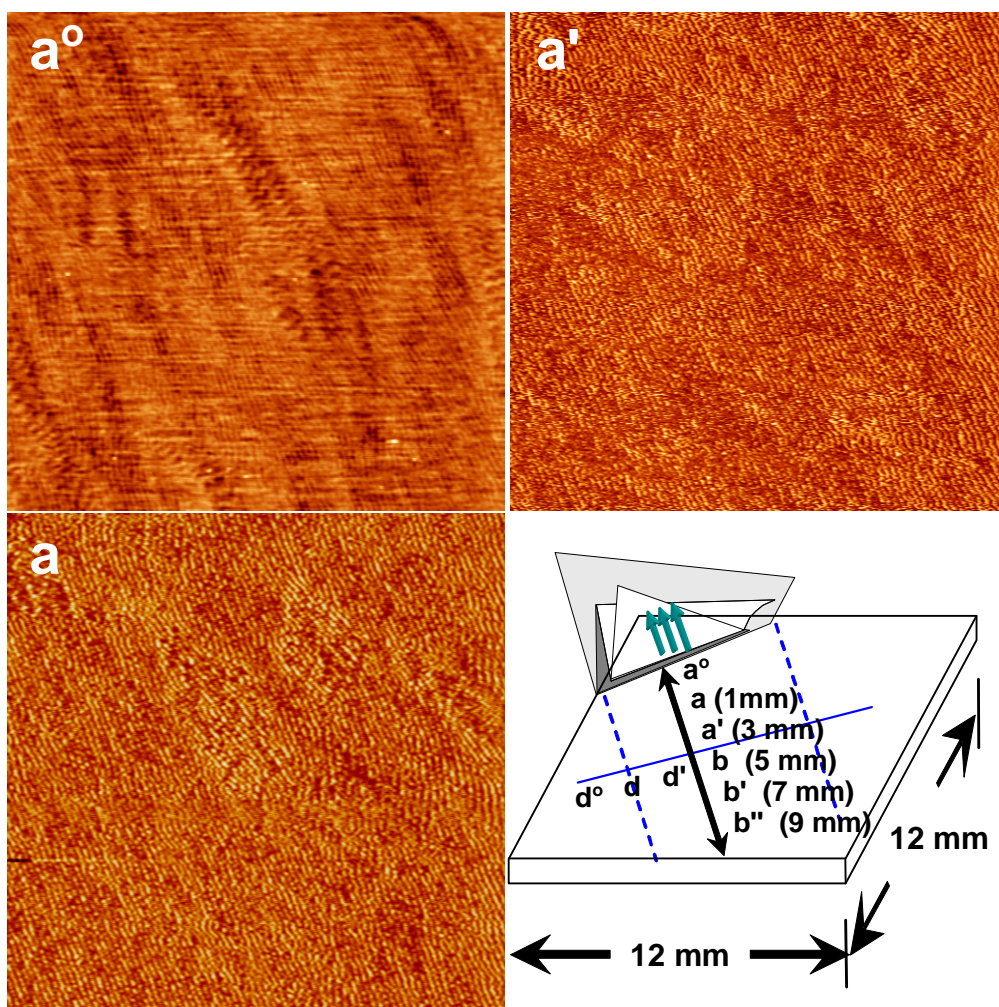
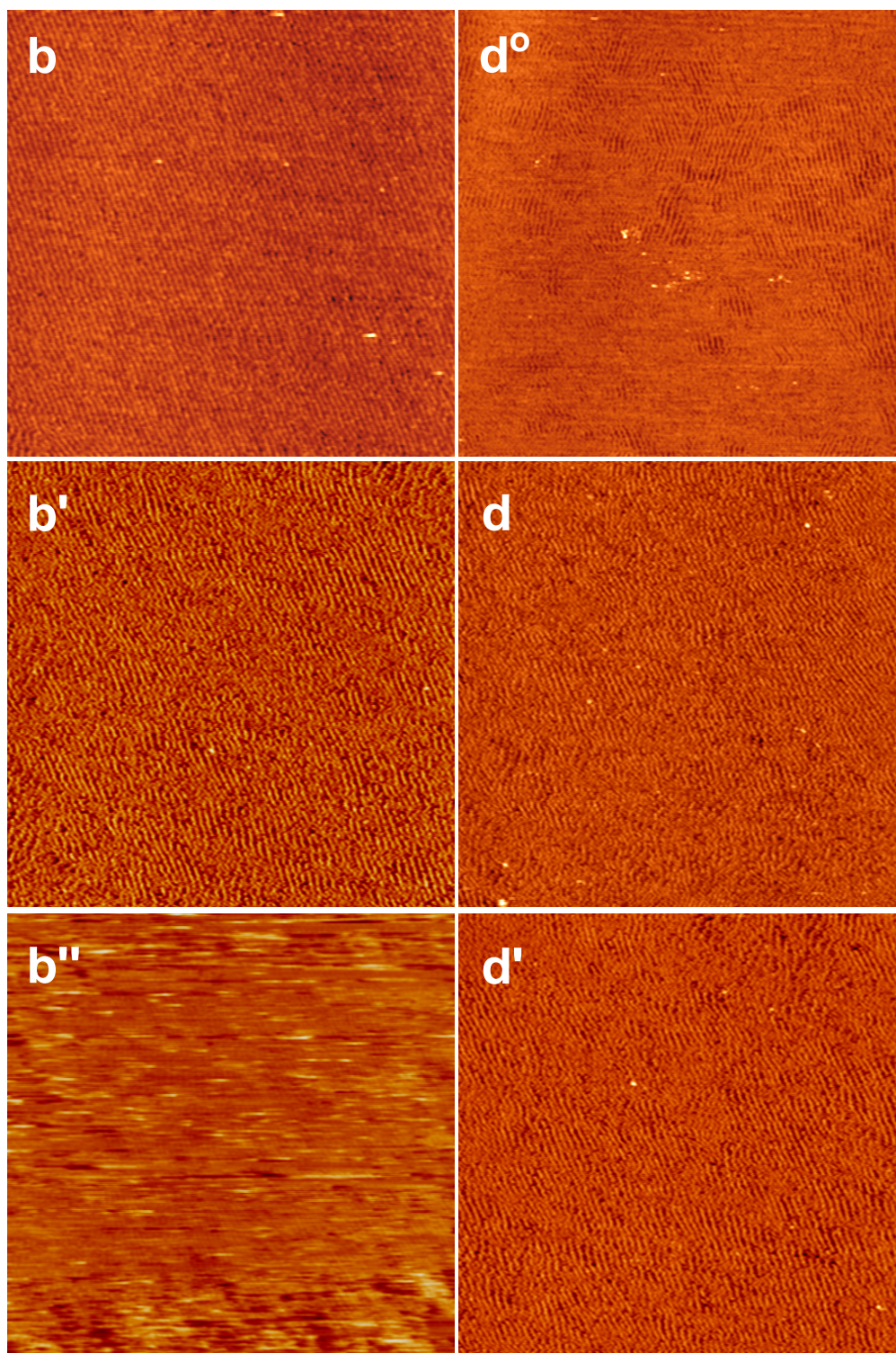


Figure S2. Images of 3,6,11,14-tetradodecyloxydibenzo[*g,p*]chrysene monolayers in phenyloctane. The letters at the upper left corner correspond to the location that depicted in the Scheme. E_{bias} , $I_{\text{tunneling}}$, and imaging size are, respectively, -0.80 V, 60 pA, and 300×300 nm for each image.

Figure S2-2 (continued):



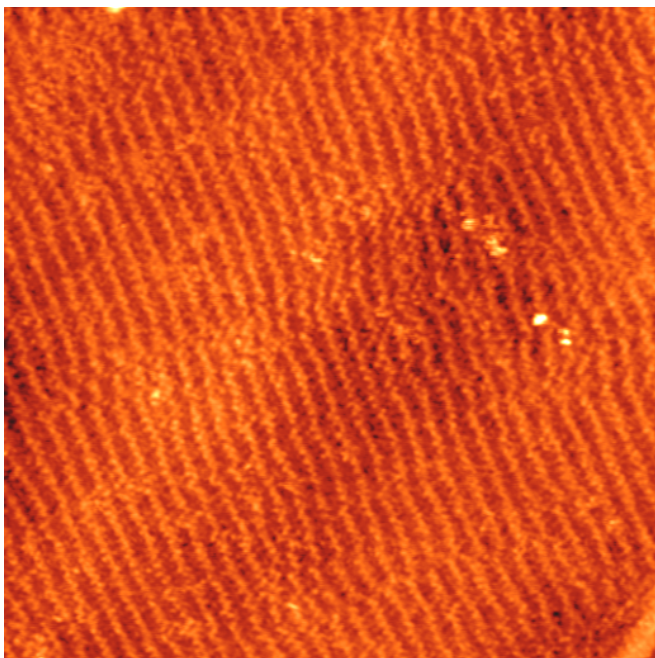


Figure S3. Image of 3,6,11,14-tetradodecyloxydibenzo[*g,p*]chrysene monolayers prepared by a peristaltic pump (i.e., Method 1). The image was obtained when the sample was placed on HOPG and covered by a glass side. The stacked stripes appear wavy, demonstrating the importance of a steady flow in preparing smooth arrays. E_{bias} , $I_{\text{tunneling}}$, and the imaging size are -0.80 V, 60 pA, 100×100 nm, respectively.