

Supporting Information

Forced to Align: Flow-Induced Long-Range Alignment of Hierarchical Molecular Assemblies from 2D to 3D

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Experimental Section:

STM experiments

All experiments were performed at room temperature (20–22°C) using a Multimode Nanoscope IIIa (Bruker) operating in constant-current mode at either the TCB/HOPG or air/HOPG interface. STM tips were prepared by mechanical cutting from Pt/Ir wire (80%/20%, diameter 0.25 mm). TCB (Sigma-Aldrich, ≥99%) was used as the solvent without further purification. Prior to imaging, solid HDI was dissolved in TCB and a droplet of this solution was applied onto a freshly cleaved surface of highly oriented pyrolytic graphite (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland, USA). The experiments were repeated in several sessions using different tips to check for reproducibility and to avoid experimental artifacts, if any. For analysis purposes, recording of a molecular image was followed by imaging the graphite substrate underneath it under the same experimental conditions, except for lowering the bias. Typical conditions used for STM imaging range from: substrate bias, $V_{\text{bias}} = 0.30$ V to 1.00 V and current set point $I_{\text{set}} = 50$ pA to 300 pA. The images were corrected for drift *via* Scanning Probe Image Processor (SPIP) software (Image Metrology ApS), using the recorded graphite images for calibration purposes, allowing a more accurate unit cell determination. The unit cell parameters were determined by examining at least 5 images and only the average values are reported. After the determination of the unit cell from the acquired STM images, a molecular model of the observed monolayer is constructed using HyperChemTM Professional 7.5 program. First, a molecular model for a single molecule is built, and then this model is duplicated. The model of the entire monolayer is constructed by placing the molecules in accordance with the intermolecular distances and angles obtained from the analysis of the calibrated STM images. The imaging parameters are indicated in the figure caption: tunneling current (I_{set}), and sample bias (V_{bias}).

The shear flow method

To induce large area assembly of HDI the flow was created as follows: Prior to applying the flow, the symmetry axes of the HOPG lattice were determined by STM. Upon the introduction of a 10- μ L droplet of sample solution on HOPG, a piece of lens tissue or Kimwipe was employed to absorb the solvent. The flow was applied along either the normal to the symmetry axes of HOPG lattice (*flow I*) or one of the main symmetry axes (*flow II*). The linear flow rate was *ca.* 0.5–0.6 mm/s. This procedure furnishes a steady laminar flow. A photograph below illustrates the shear flow treatment with a piece of paper.¹



Since the flow rate triggered by the adsorption *via* tissues is determined by the volume of the solution droplet on HOPG, a flow-driven molecular alignment will be successful only if a large enough volume is applied. For instance, a drop of 10- μ L solvent leads to a linear flow rate of *ca.* 0.5–0.6 mm/s, which is effective for the molecular alignment in the present study, whereas a solvent volume less than 3 μ L is unable to create an effective flow. Thus, an additional 10- μ L droplet of neat solvent (TCB) was applied on the surface prior to the generation of the second flow.

Histogram

Each histogram presented in the study showing the angle distribution of the molecules adsorbed in upper layers with respect to those in the lower layers was acquired from at least four 75 $\times$ 75-nm² STM images obtained within the active zone described in the main text. Representative STM images corresponding to histogram provided in Figure 1(e) in the main text were obtained on the surface formed upon simple drop casting. The representative STM image corresponding to the histogram after *flow I* treatment (Figure S3) was obtained from the area B in the cartoon of Figure S3 whereas the STM image corresponding to the

histogram obtained after *flow II* treatment (Figure 1f in main text) is from the B' area in the cartoon of Figure S4.

STS experiments

Tunneling spectroscopy measurements were performed at the TCB/HOPG interface with the feedback loop closed, thereby adjusting the tip-sample distance. Prior to recording of the I - V curves, the STM parameters were $V_{\text{bias}} = 0.75$ V and current setpoint $I_{\text{set}} = 100$ pA. The voltage was ramped between -1.5 and +1.5 V with a ramping rate of 1.64 Hz. The I - V curves were only considered for analysis provided: (1) The STM imaging was stable and basically provided identical images before and after spectroscopy measurements. (2) The forward and reversed traces (velocity: 9.85 V/s) of STS overlapped perfectly and passed through the setpoint of bias and current parameters. Due to the noise, *ca.* 15 % of the curves were discarded. To reduce thermal drift, prior to recording the I - V curves, we first scanned a large-area surface and then zoomed-in on a small area (3×3 – 5×5 nm²) including the selected points for STS measurements. This practice ensures that we can reliably record STS curves at specific locations, for example 1, 2, 3-layer structures of HDI within a film (e.g., Figure 3 in the main text). Thus, we can reduce the number of STS traces originating from alkyl parts of HDI. When taken randomly, the STS results included *ca.* 30% traces of lower conductance which may be contributed to the alkyl chains of HDI (e.g., Figure S15). The percentage of lower conductance is consistent with the surface coverage of alkyl chains. The protocol followed, i.e. zooming in, leads to an increase in the reliability and reproducibility of the measurements (e.g., Figure S16 showing the standard deviation of STS measurements).

The calculation of reduced band gap was carried out based on reference 27 in the main text. The reduced band gap in the present case refers to a difference in the values of band gap of molecular stack comprising a monolayer and three layers. Band gap of a molecule or a stack of molecules in an STS measurement is inferred from a small region around the HOPG Fermi level (baseline, 0 nA on Y axis) with suppressed detected tunneling current. The calculation of the reduced value of band gap (*ca.* 0.2 eV) in this study is derived by comparison of the band gap between monolayers and trilayers as shown by dashed lines in Figure 3b. An assumption here is that the LUMO values for all STS data (right side of tunneling currents in STS spectra) are either the same or the differences are small enough and thus can be ignored.

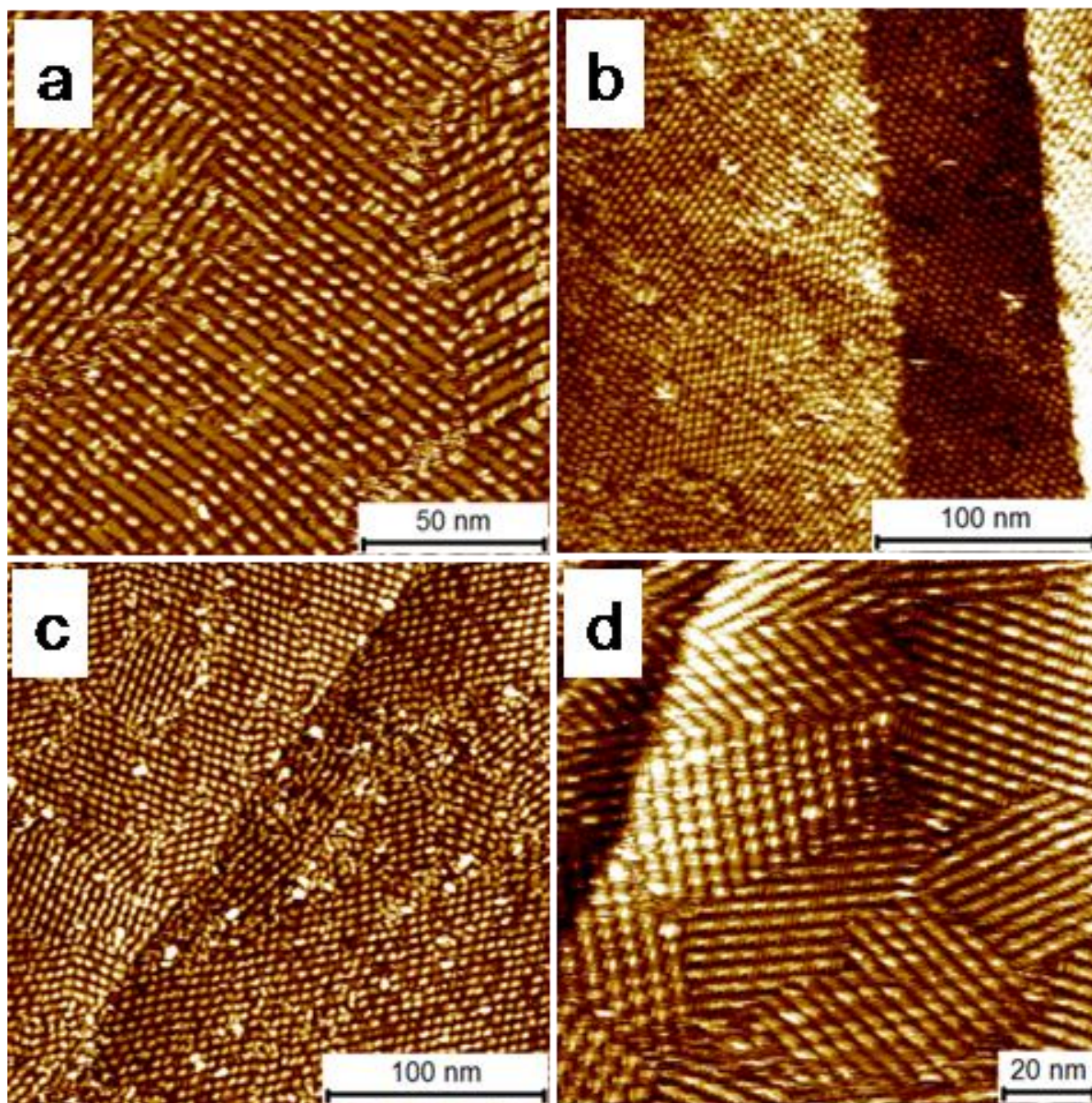


Figure S1. STM images showing spontaneously self-assembled network of HDI at the TCB/HOPG interface without any flow treatment. The surface morphology is dominated by multiple small domains (average domain size $\sim 60 \times 60 \text{ nm}^2$). Imaging conditions: $V_{\text{bias}} = 750 \text{ mV}$, $I_{\text{set}} = 100 \text{ pA}$.

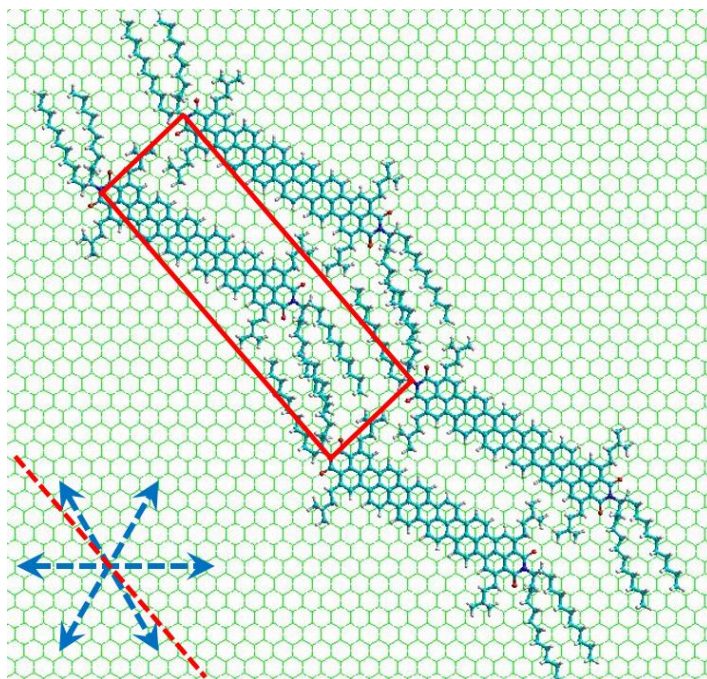


Figure S2. A molecular model showing the unit cell of HDI on HOPG lattice. It can be noticed that the aromatic backbone of the HDI molecule is adsorbed on the HOPG lattice in ABAB... type fashion that is typical for commensurate adsorption of polyaromatic molecules on graphite surface. This scheme further implies that although the HDI unit cell is oriented at a small (11°) angle with respect to the nearest lattice vector of HOPG, the molecular components of the adlayer are still commensurate with HOPG substrate.

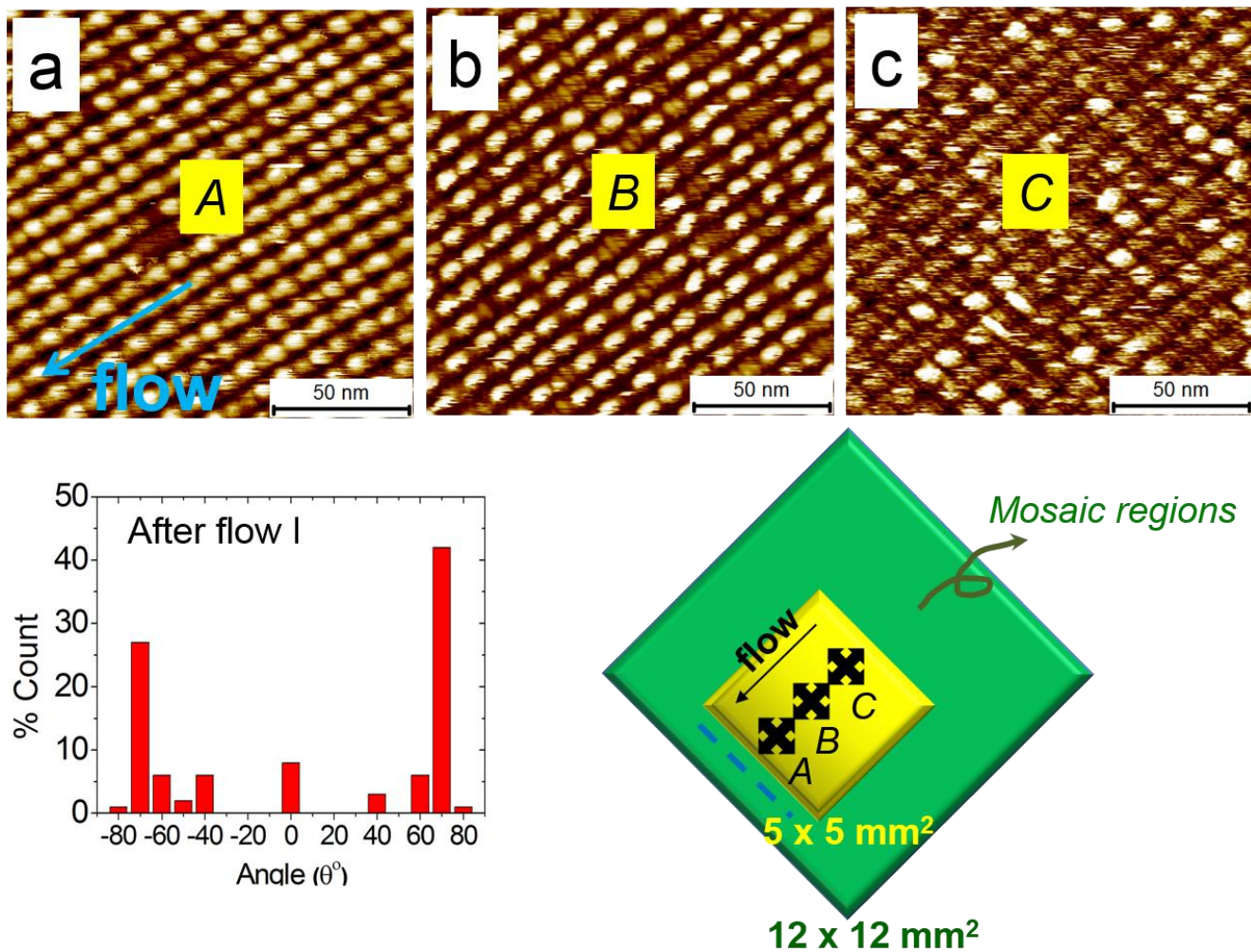


Figure S3. Change in the surface morphology after the first-step flow treatment. Large area patterning of HDI (5 × 5 mm²) was achieved by the first-step flow treatment. Panels (a), (b), and (c) were obtained from the locations A, B, and C, respectively, as indicated in the cartoon that represents the sample surface: the regions B and C are 2 mm and 4 mm away from region A, respectively. The blue dashed line represents the contact line where Kimwipe tissue was touched for generating the flow. The arrow in panel (a) indicates the direction of *flow I*. These STM images were obtained by moving the substrate in a direction parallel to the flow direction away from the contact line. Only in regions far away (*ca.* 6 mm or more) from the tissue contact line, the mosaics of HDI domains similar to those shown in Figure S1 are observed. Thus, the mosaic patterns are found in the region indicated by green color in the cartoon. The histogram shows the angle distribution of the molecules adsorbed in upper layers with respect to those in the lower layers after the *flow I*. Imaging conditions: $V_{\text{bias}} = 750$ mV, $I_{\text{set}} = 100$ pA.

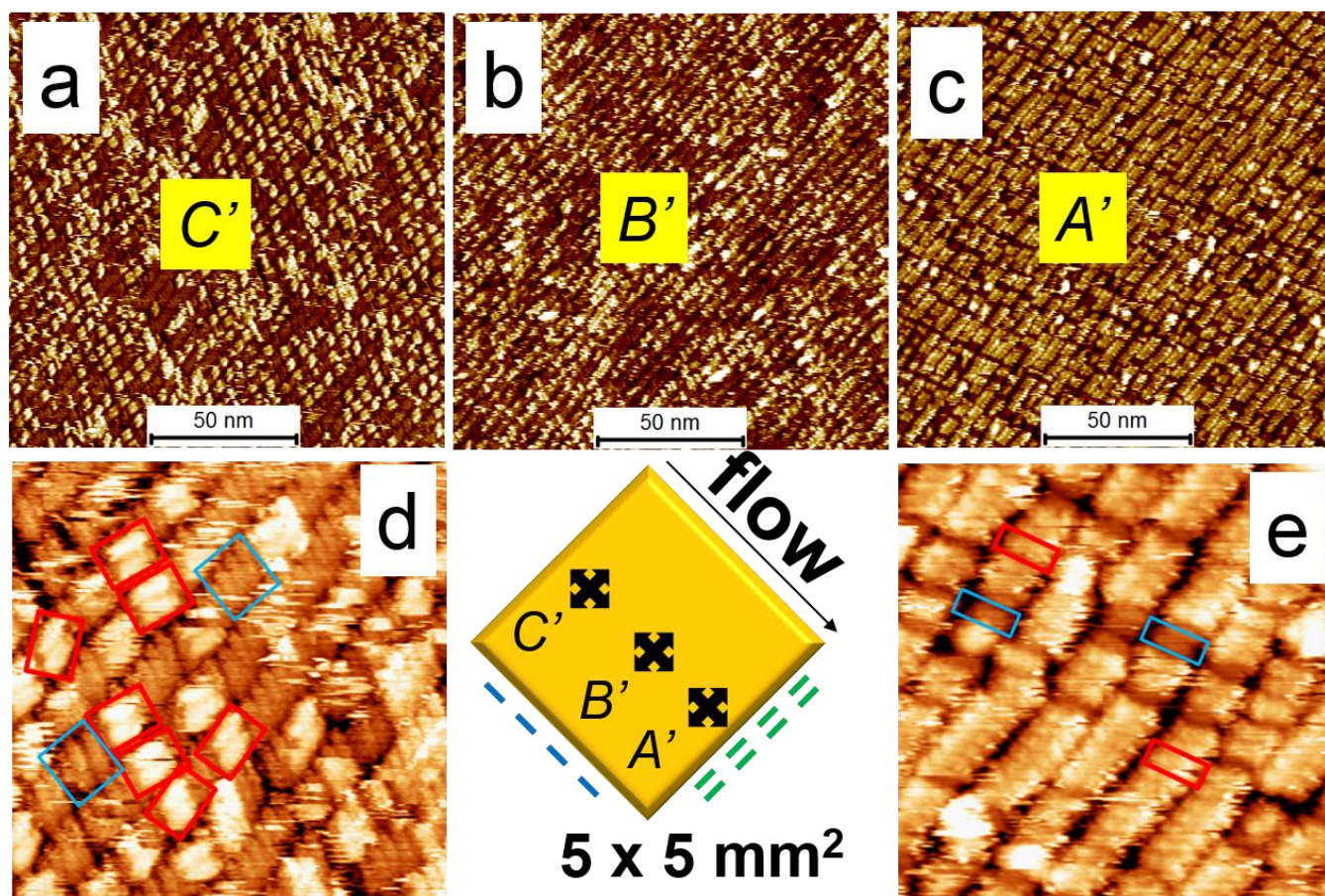


Figure S4. Change in the surface morphology after the second flow treatment. The STM images clearly show that the two-step flow treatment enables long-range collinear packing of HDI molecules. These STM images were obtained by moving the substrate in a direction parallel to the second flow direction moving away from the second contact line. The blue and green dashed lines indicate the contact lines of Kimwipe for generating the first-and the second-step flow, respectively. Additional measurements in the area between region A' and B' as well as B' and C' suggest that the alignment area of the collinear packing of HDI is as large as $2.5 \times 2.5 \text{ mm}^2$. The digital zooms provided in panels (d) and (e) correspond to the regions C' and A', respectively and highlight the difference in the alignment efficiency close to and away from the second contact line. The red and blue rectangles indicate the relative orientation of the molecules adsorbed in the upper-most and lower layers, respectively. These results have been reproduced several times. Imaging conditions: $V_{\text{bias}} = 750 \text{ mV}$, $I_{\text{set}} = 100 \text{ pA}$.

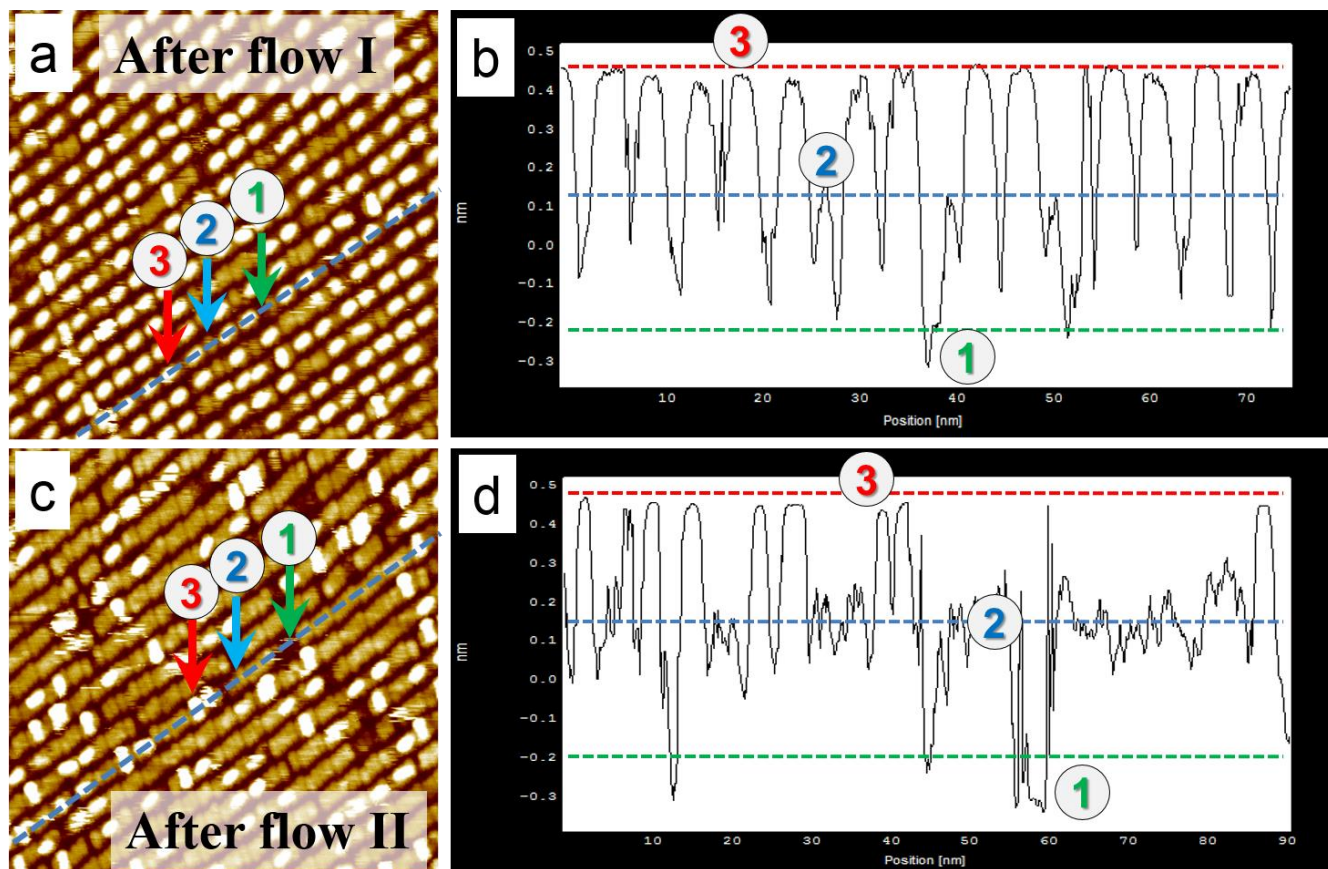


Figure S5. STM images together with corresponding line profiles along the column axis of HDI assemblies obtained after *flow I* (a, b) and *flow II* (c, d) treatment. The green, blue and red arrows indicate 1, 2 and 3 layers of HDI.

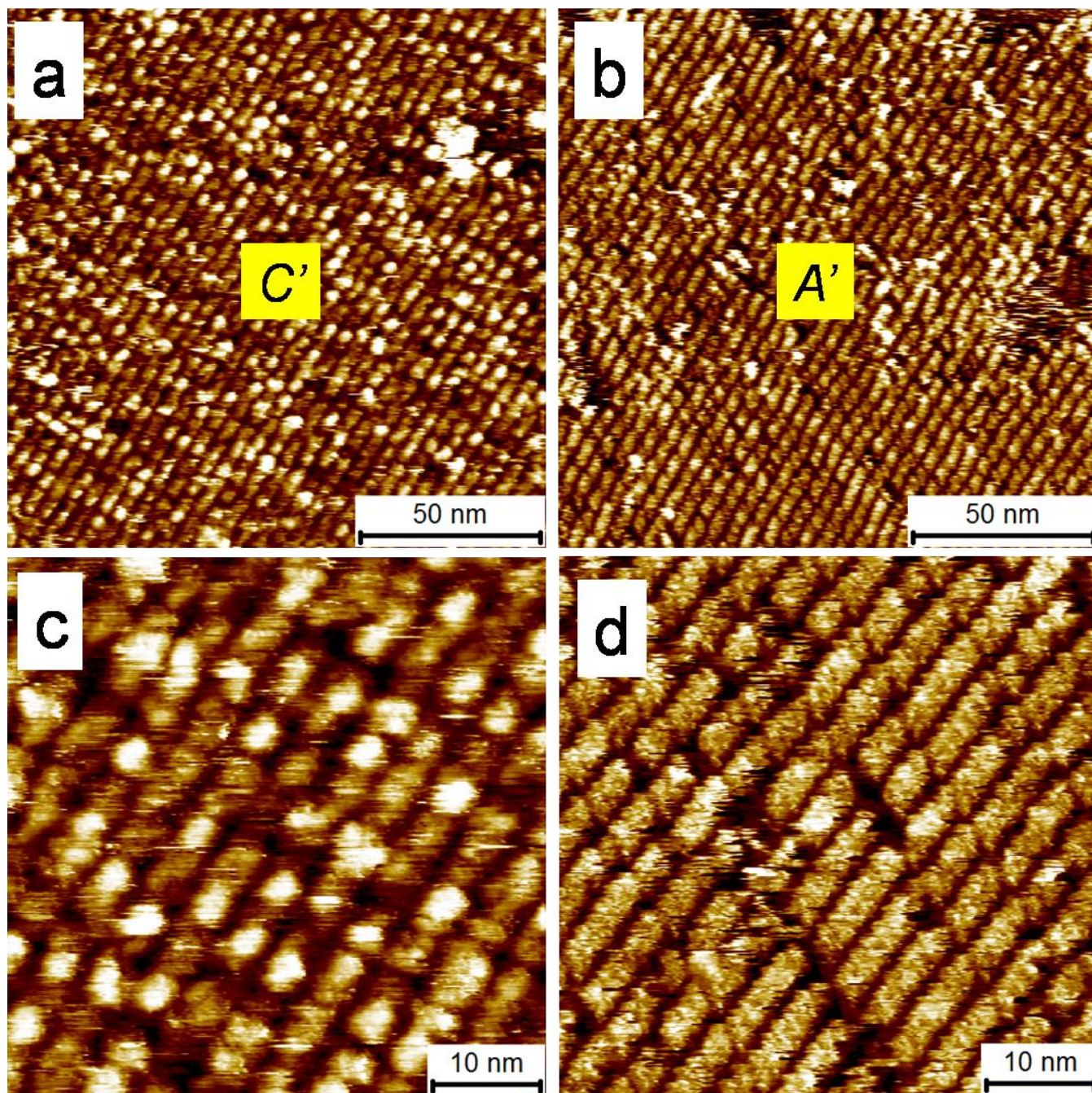


Figure S6. Surface pattern of a sample stored for 7 days under ambient conditions. Panels (a) and (b) were obtained near C' and A' region defined in Figure S4 and panels (c) and (d) are the small scale STM images, respectively. These images were obtained at the air/HOPG interface. Imaging conditions: $V_{\text{bias}} = 750 \text{ mV}$, $I_{\text{set}} = 100 \text{ pA}$.

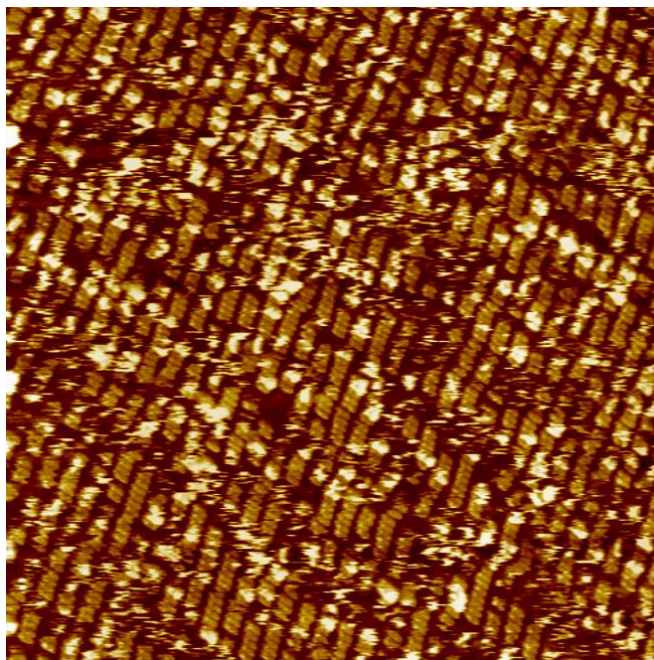


Figure S7. Representative STM image of the flow aligned surface subjected to annealing at 100°C for 30 minutes under ambient conditions. The large area domains as well as the long range alignment of the molecules adsorbed in subsequent layers remains virtually unchanged after the heat treatment demonstrating the stability of the thin films produced using flow treatment.

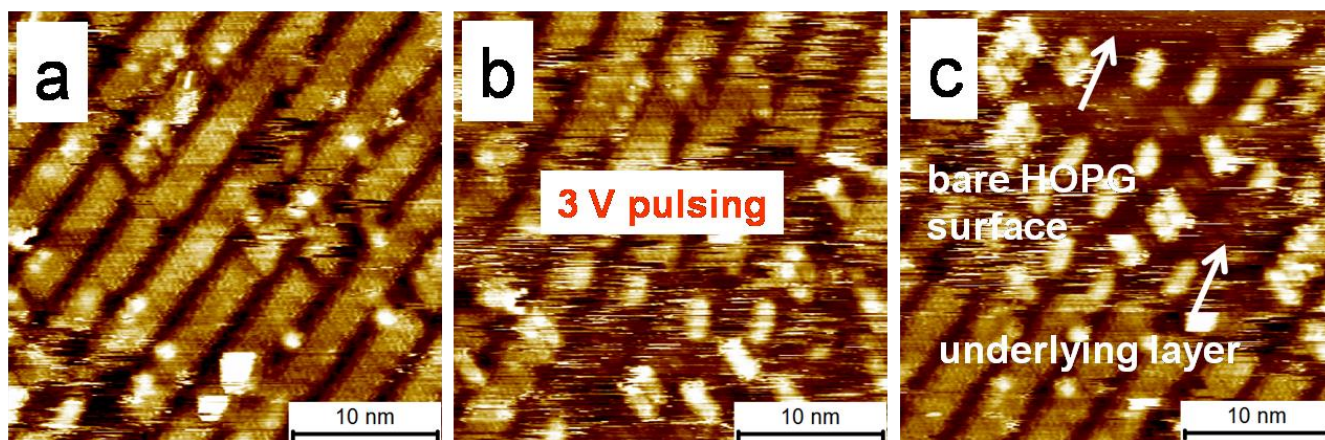


Figure S8. Generation of defects in the HDI layers for the accurate estimation of number of molecular layers in the film. STM images provided in panels (a) and (c) were recorded before and after a 3 V/100 ms pulse applied to the STM tip. After pulsing, a defect is created which unveils an underlying layer of HDI and the bare HOPG surface, indicating that the stable template layer of HDI is actually a bilayer. Imaging conditions: $V_{\text{bias}} = 750 \text{ mV}$, $I_{\text{set}} = 100 \text{ pA}$.

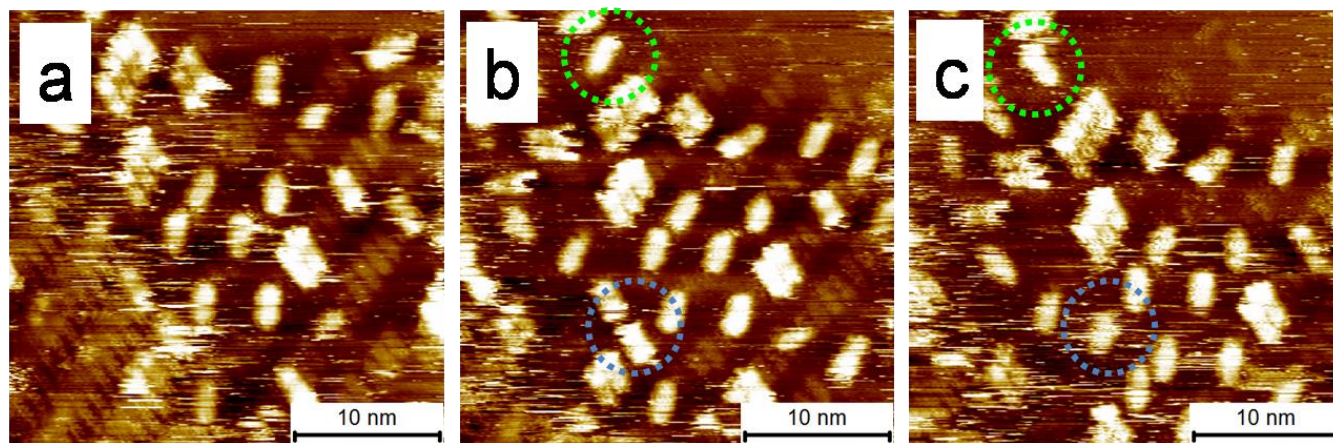


Figure S9. Sequential STM images obtained on the same surface depicting plausible scanning induced reorientation of HDI molecules adsorbed in the upper layers. These images help us discard the possibility of (large scale) collinear alignment of HDI molecules caused by the scanning STM tip. Continued scanning on the same surface as shown in Figure S8 in fact showed the effect of scanning is minimal and as highlighted by green and blue dotted circles. This effect is very localized and random (green: non-collinear to collinear alignment and blue: collinear to non-collinear alignment). Imaging conditions: $V_{\text{bias}} = 750 \text{ mV}$, $I_{\text{set}} = 100 \text{ pA}$.

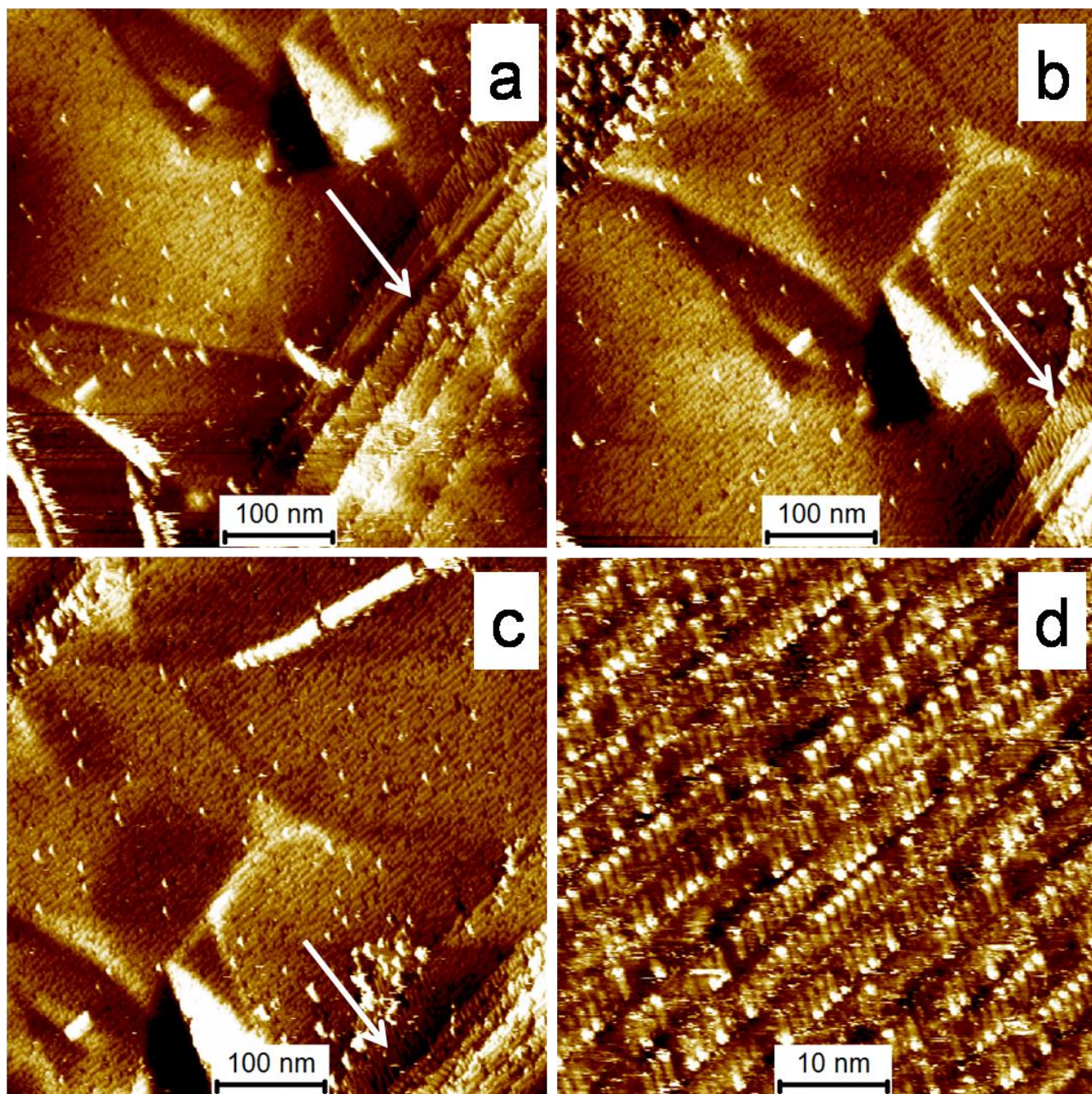


Figure S10. Large area STM images (a-c) showing the well-aligned multilayered organization of HDI prepared by two-step flow method. These images also demonstrate that long-range alignment is hardly affected by step edges on the HOPG surface as indicated by arrows. (d) A small scale STM image showing the detailed molecular arrangement. Imaging conditions: $V_{\text{bias}} = 750 \text{ mV}$, $I_{\text{set}} = 100 \text{ pA}$.

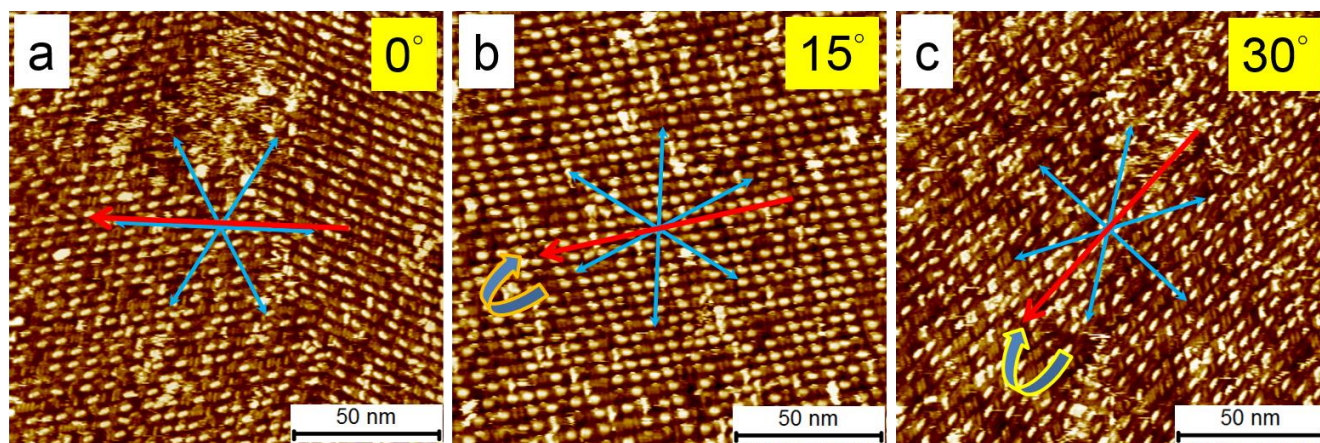


Figure S11. Dependence of applied *flow I* direction on the morphology of the substrate. The STM images reveal that when the flow is applied along the main symmetry axis of the HOPG lattice, the alignment process is inefficient. The efficiency is significantly improved when the flow direction is maintained at 15° or 30° with respect to the main symmetry axis. The increase in the efficiency of the uniaxial alignment process of the first layer(s) at these angles is related to the propensity of the HDI molecular rows to spontaneously crystallize nearly ($\pm 11^\circ$) along the normal to the main symmetry axis.

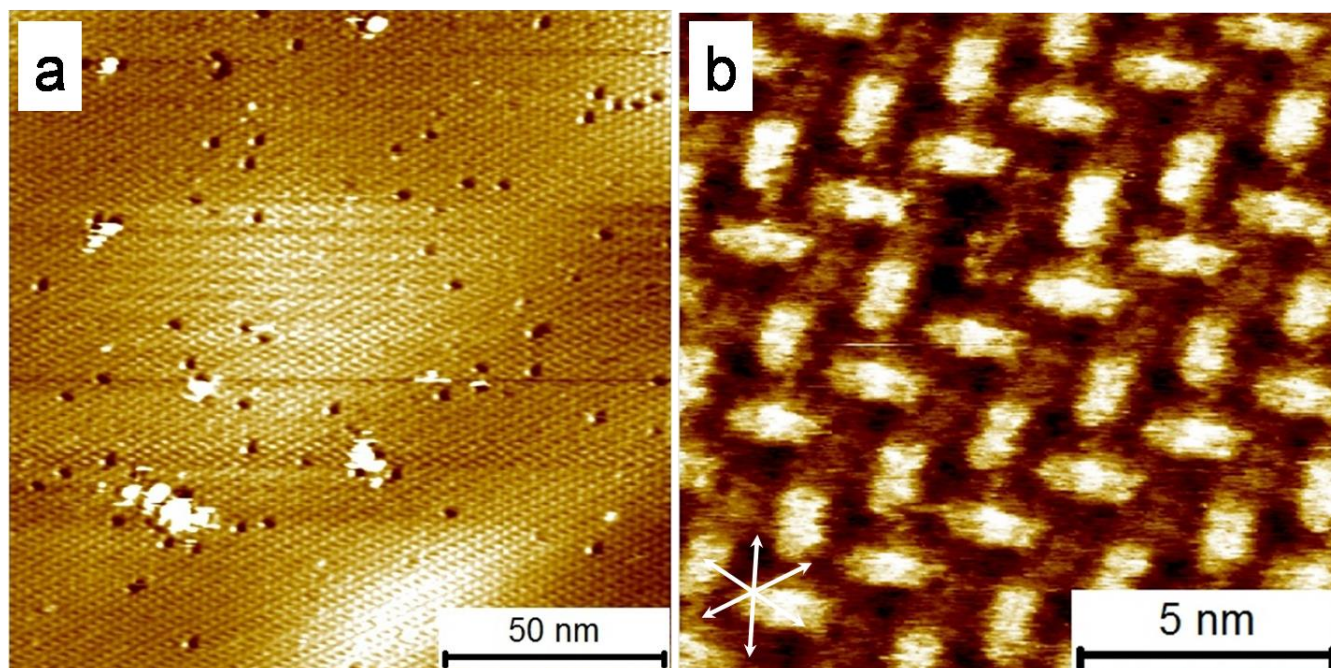


Figure S12. Impact of solution concentration on the flow-induced alignment of HDI on HOPG surface. (a) Large-scale and (b) HR STM images of the herringbone-type pattern of HDI. A flow treatment along one of the main symmetry axes of HOPG on a low concentration sample of HDI (2.5×10^{-7} M) leads to an alignment of the herringbone-type pattern. This packing-type is a concentration-dependent polymorphism that we have reported recently.²

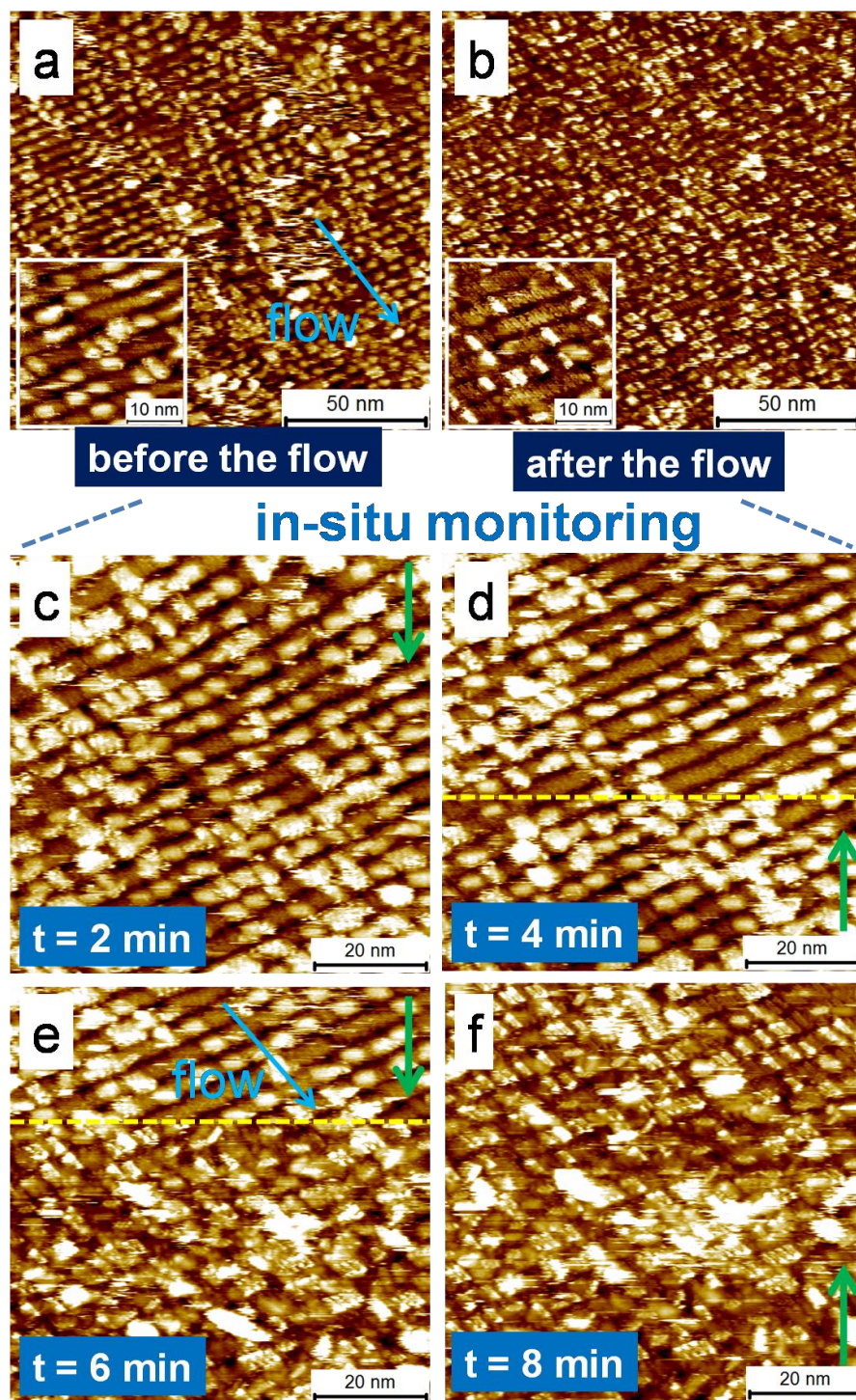


Figure S13. Real-time STM visualization of the multilayer packing state of HDI before (a) and after (b) the in-situ second-step flow treatment. The surface in (a) was prepared by the first-step flow. The surface in (b) is the result after the second-step flow treatment. The small-scale STM images in the lower left corner of (a) and (b) show the non-collinear and collinear packing of upper layer HDI, respectively. During the sequence of scans shown in panels (c-f), the scanning was continued as *flow II* was applied to

the sample. These consecutive STM scans (c-f) reveal the alignment process of the HDI molecules adsorbed in upper layers in real time. The yellow dashed lines in (d) and (e) indicate the timing of the application of a 10- μ L droplet of neat TCB and the application of a flow on the surface during consecutive STM scans, respectively. The blue arrows in panel (a) and (e) indicate the flow direction. The green arrows in the panel (c-f) indicate the STM scan directions. Although after the application of a droplet of neat solvent, some of the HDI molecules originally adsorbed in the upper layer get dissolved into supernatant liquid (compare panel c with panel d), the upper layer HDI molecules that remain adsorbed show no change in their orientation with respect to the HDI monolayer underneath until the flow is applied. After the application of the flow, the forced alignment that is the reorientation from the non-collinear packing to the collinear one of HDI takes place (panel e). Imaging conditions: $V_{\text{bias}} = 750$ mV, $I_{\text{set}} = 100$ pA.

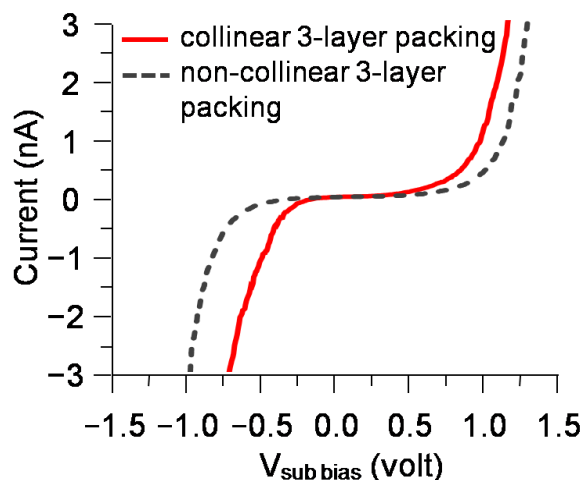


Figure S14. Comparison of tunneling spectra of collinear and non-collinear 3-layer packing structures of HDI. Each I - V curve was averaged from, respectively, 64 and 74 curves for collinear 3-layer and non-collinear 3-layer packing structures of HDI. Imaging conditions: $V_{\text{bias}} = 750$ mV, $I_{\text{set}} = 100$ pA. Setpoint for STS measurements: $V_{\text{bias}} = 750$ mV, $I_{\text{set}} = 100$ pA. The appreciable tunneling current for the non-collinear packing multilayers of HDI also suggests that there are partial π - π interactions among HDI

molecules and the tunneling current also undergoes ‘through-space’ electron transport within the non-collinear packing multilayers of HDI.³

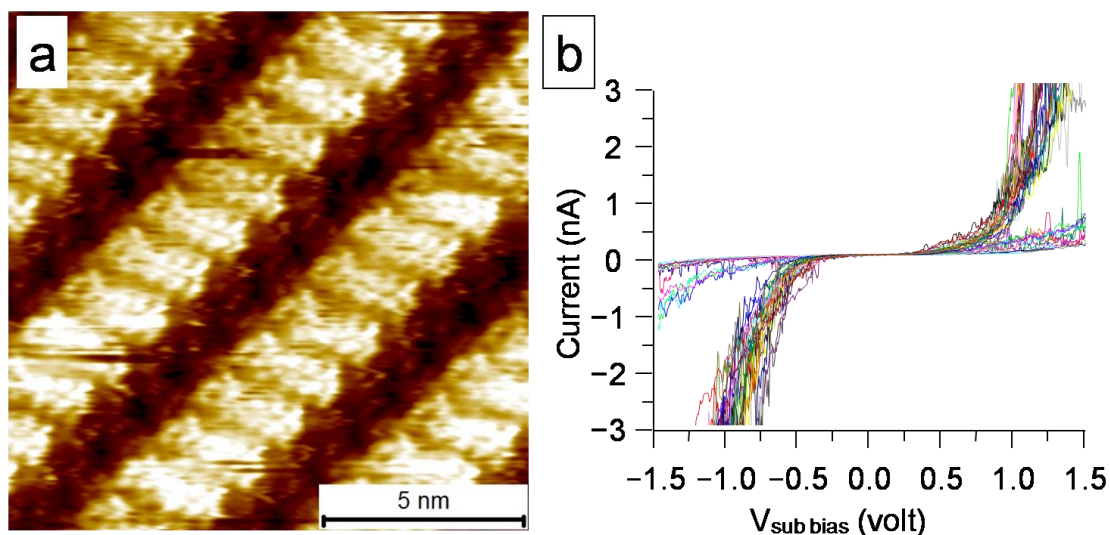


Figure S15. STS spectra recorded randomly on the bilayers of HDI. When taken randomly, the STS results included *ca.* 30% traces of the lower conductance which may be contributed by the alkyl chains of HDI. The percentage of lower conductance is approximately consistent with that of the surface coverage of alkyl chains in the STM image provided in panel (a). Panel (b) shows 40 curves from one experimental session. Setpoint for STS measurements: $V_{\text{bias}} = 750$ mV, $I_{\text{set}} = 100$ pA.

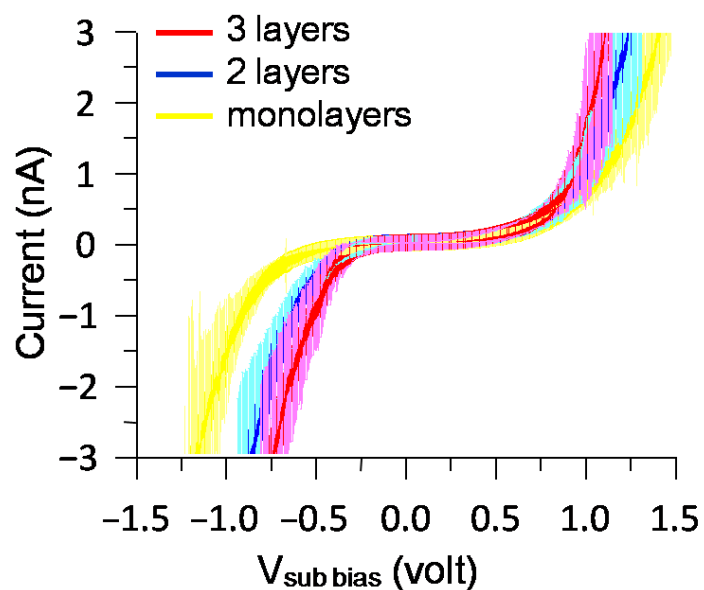


Figure S16. Stability of the tunneling spectra. The differences in STS results obtained on monolayer, bilayer and three layered packings of HDI are clearly distinguishable within the experimental standard deviation from this figure. Setpoint for STS measurements: $V_{\text{bias}} = 750 \text{ mV}$, $I_{\text{set}} = 100 \text{ pA}$.

References

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