



Supporting Information

for

Growth of a self-assembled monolayer decoupled from the substrate: nucleation on-command using buffer layers

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Beilstein J. Nanotechnol. **2020**, *11*, 1291–1302. [doi:10.3762/bjnano.11.113](https://doi.org/10.3762/bjnano.11.113)

Additional STM data

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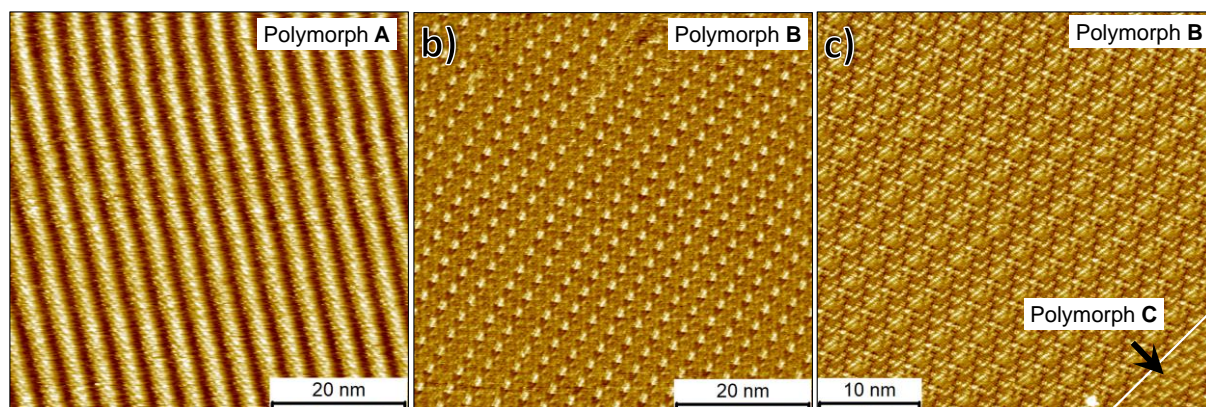


Figure S1: Additional large scale STM images of the three polymorphs of **BA-OC₁₄** observed at the 1-phenyloctane/HOPG interface. [**BA-OC₁₄**] = 9×10^{-5} M. Imaging conditions: (a) $I_{\text{set}} = 140$ pA, $V_{\text{bias}} = -0.7$ V. (b) $I_{\text{set}} = 160$ pA, $V_{\text{bias}} = -1.45$ V. (c) $I_{\text{set}} = 150$ pA, $V_{\text{bias}} = 0.55$ V.

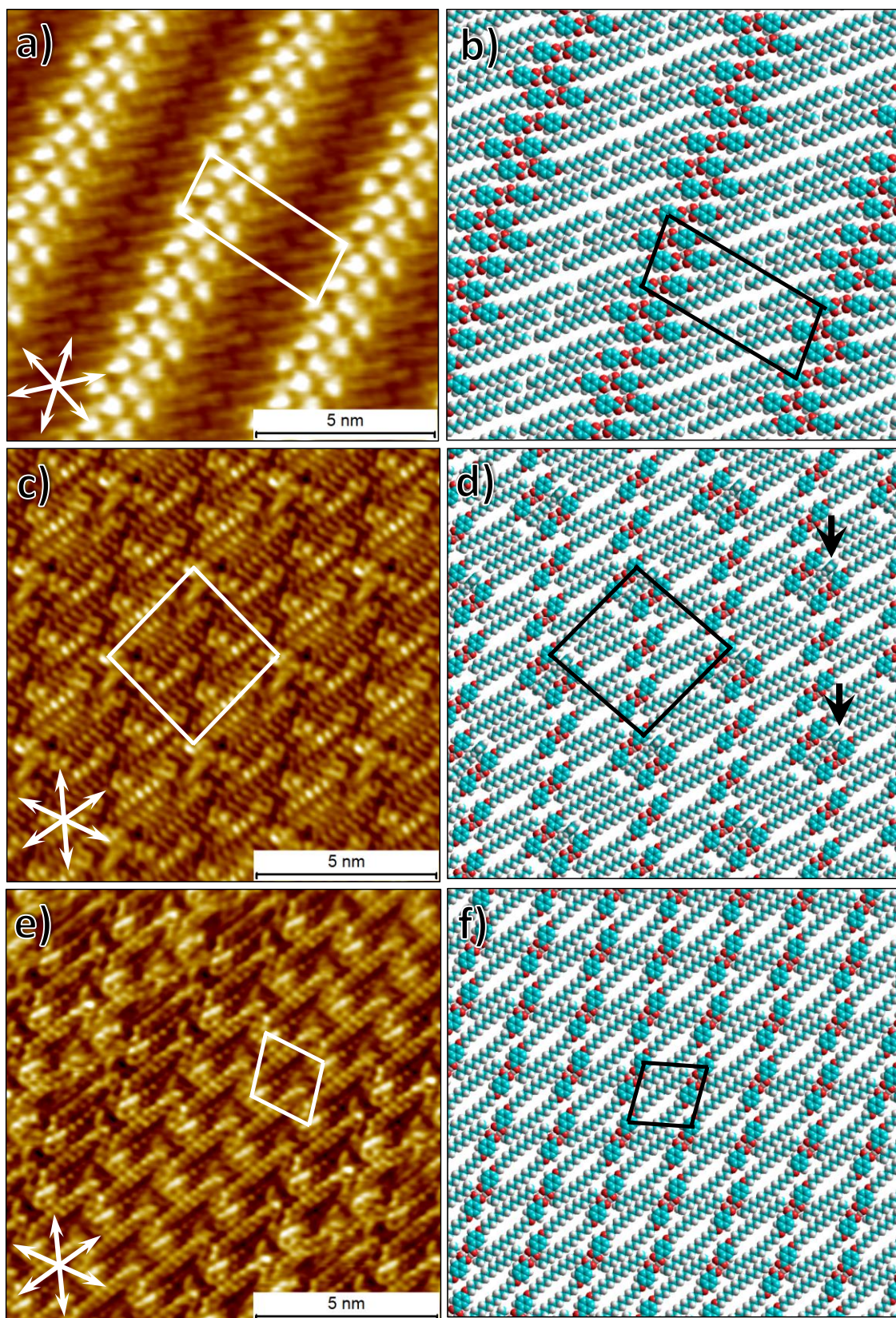


Figure S2: Magnified version of Figure 2 provided in the main text highlighting the high-resolution STM images and the corresponding molecular models.

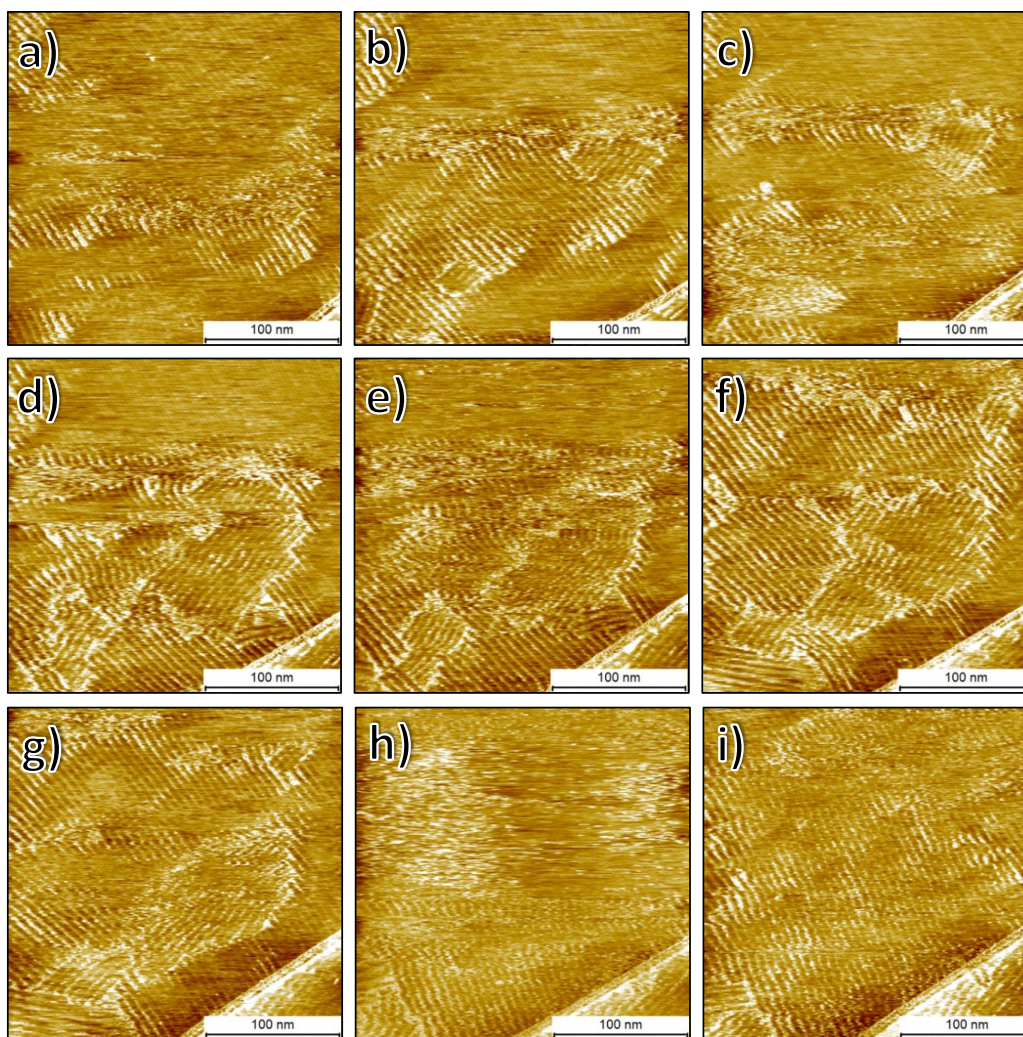


Figure S3: Sequential STM images showing the highly dynamic behavior of $n\text{-C}_{50}$ at 7.0×10^{-6} M at the 1-phenyloctane-HOPG interface. With each scan significant rearrangement in the domain structure is visible. The sample was annealed at 50 °C for 15 min and afterwards rinsed with 1-phenyloctance. Imaging conditions: $I_{\text{set}} = 160$ pA, $V_{\text{bias}} = -0.7$ V.

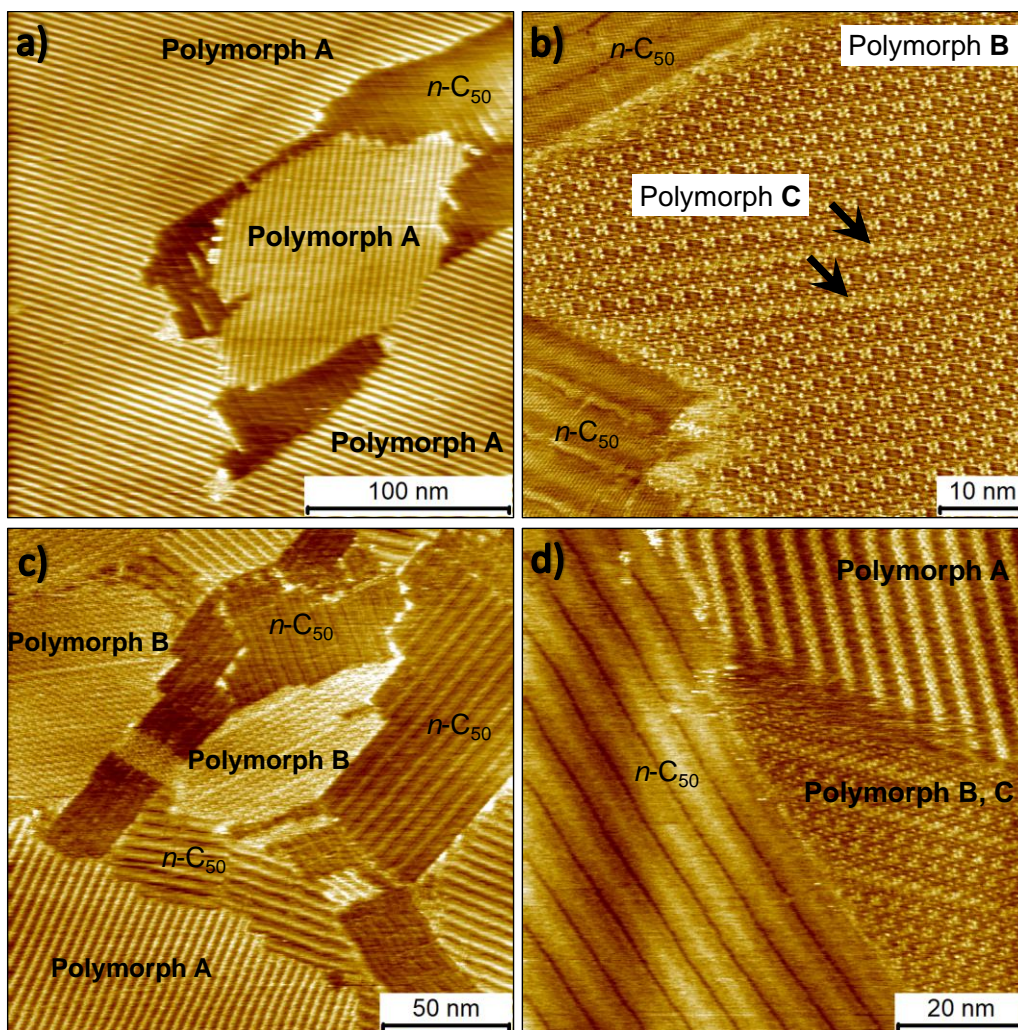


Figure S4: Additional STM images for the domains of polymorph **A**, **B** and **C** nucleated on top of the $n\text{-C}_{50}$ buffer layer. Imaging conditions: (a) $I_{\text{set}} = 130 \text{ pA}$, $V_{\text{bias}} = -1.3 \text{ V}$. (b) $I_{\text{set}} = 190 \text{ pA}$, $V_{\text{bias}} = -0.4 \text{ V}$. (c) $I_{\text{set}} = 140 \text{ pA}$, $V_{\text{bias}} = -0.65 \text{ V}$. (d) $I_{\text{set}} = 140 \text{ pA}$, $V_{\text{bias}} = -0.45 \text{ V}$.

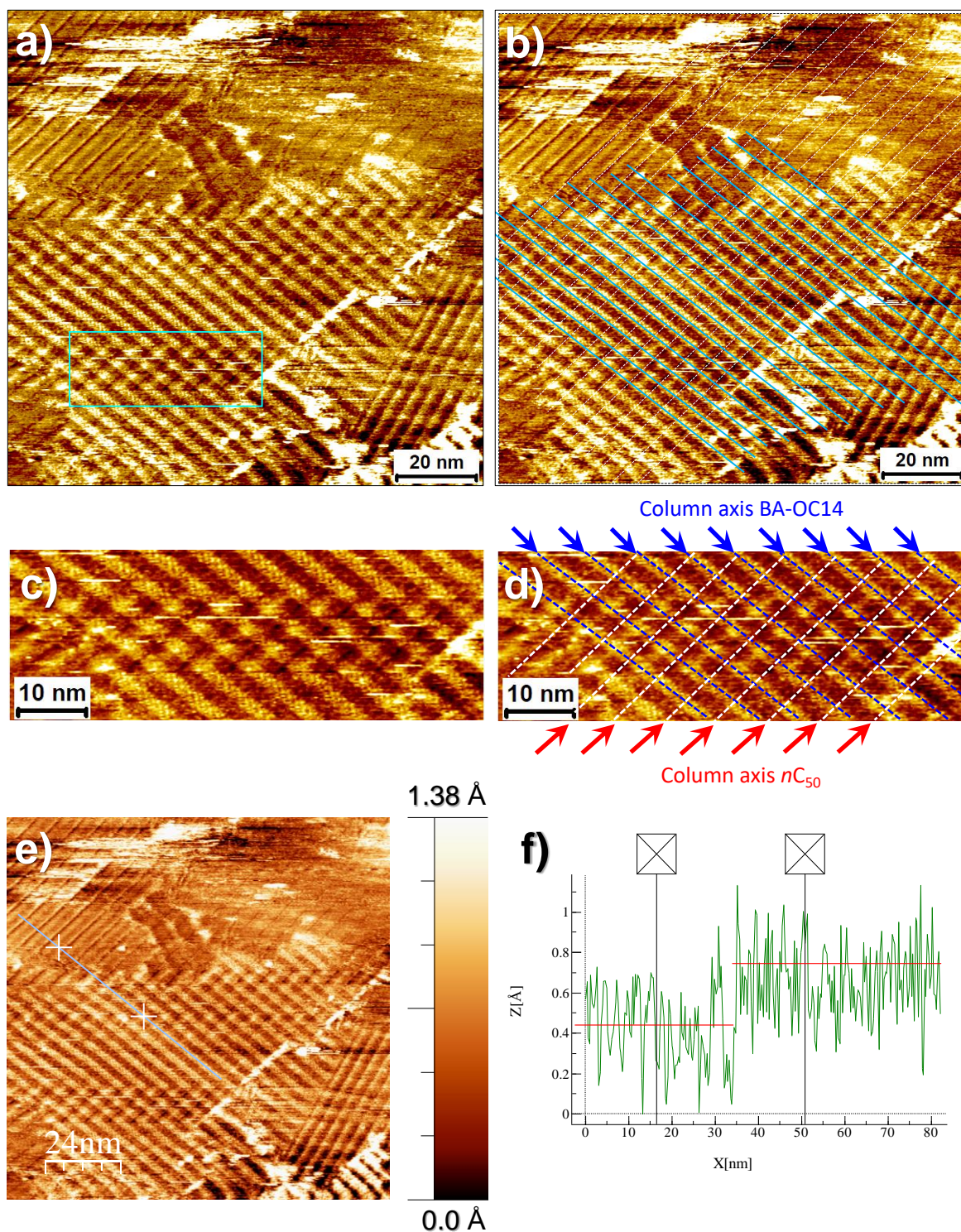


Figure S5: (a) Large scale STM image showing peculiar STM contrast that shows overlap of features of the columns of **BA-OC₁₄** and **n-C₅₀**. (b) Same STM image as in (a) but with overlaid colored markers for identifying the columns of **BA-OC₁₄** (light blue) and **n-C₅₀** (white). (c) Digital zoom of the area marked by cyan rectangle in (a). (d) The same zoom with overlaid markers. (e, f) Line profile across the molecular columns of **BA-OC₁₄** and **n-C₅₀**. Imaging conditions: $I_{\text{set}} = 130$ pA, $V_{\text{bias}} = -0.65$ V.

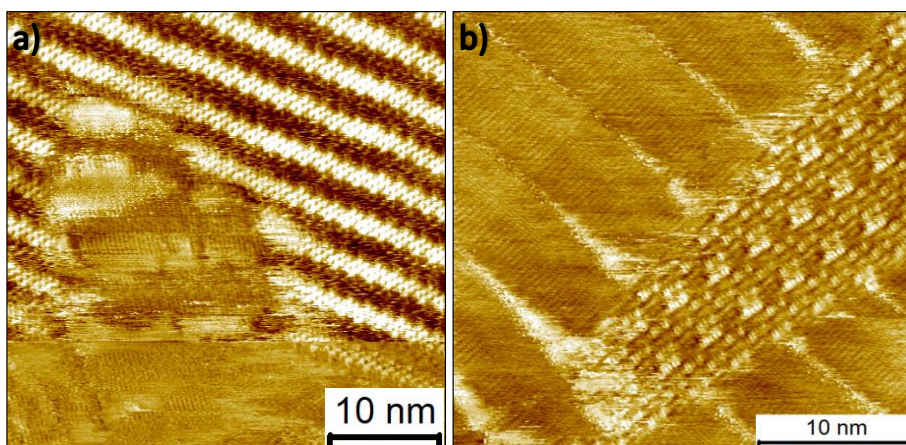


Figure S6: STM images showing the approximate alignment of the alkoxy chains of polymorphs A and B of **BA-OC₁₄** with the alkyl chains of ***n*-C₅₀** at the 1-phenyloctane-HOPG interface. Imaging conditions: (a) $I_{\text{set}} = 90 \text{ pA}$, $V_{\text{bias}} = -0.17 \text{ V}$. (b) $I_{\text{set}} = 80 \text{ pA}$, $V_{\text{bias}} = -0.95 \text{ V}$.

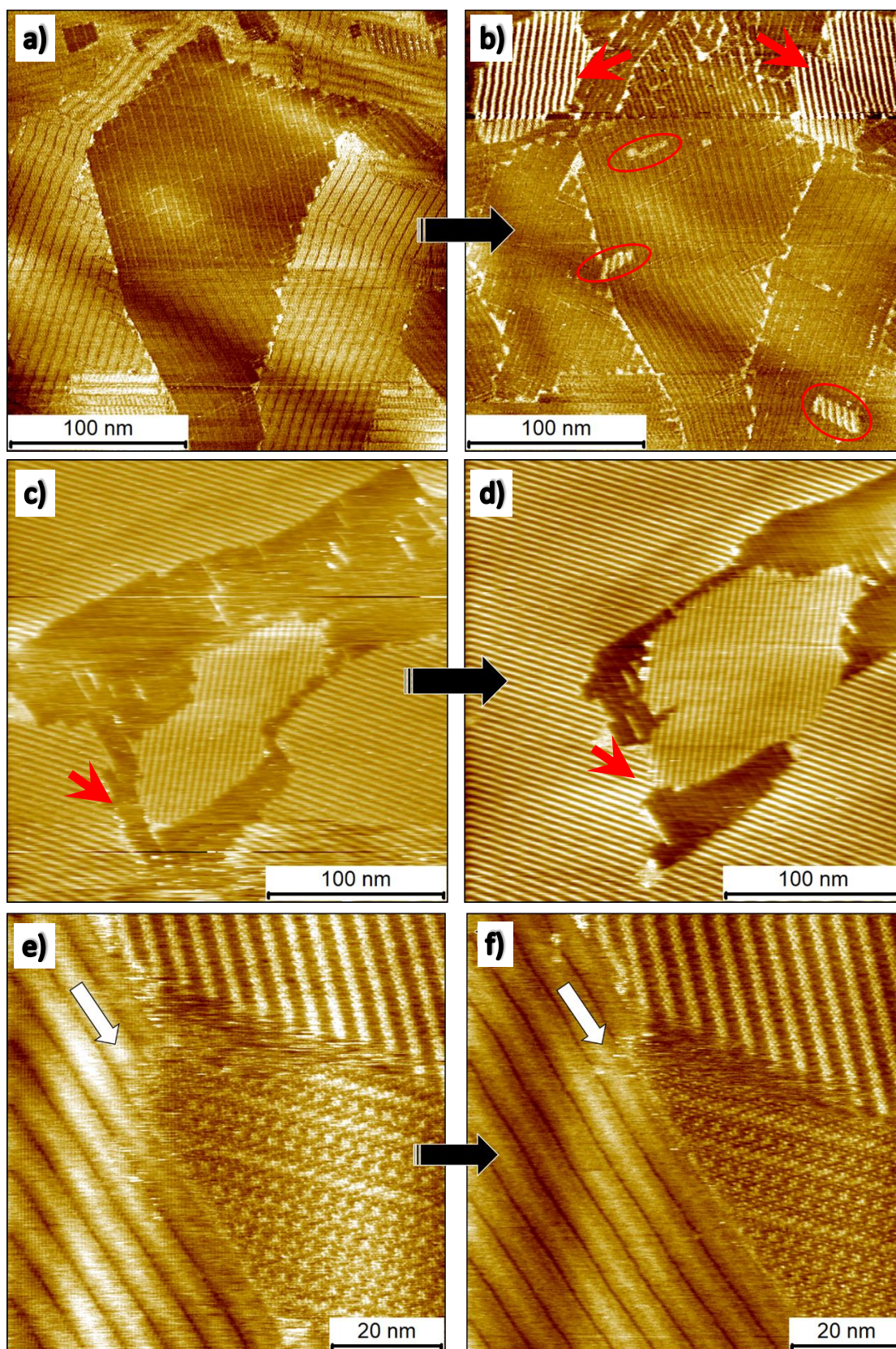


Figure S7: STM images showing the nucleation (a,b), growth (c,d) and desorption (e,f) of BA-OC₁₄ on top of the *n*-C₅₀ buffer layer at the 1-phenyloctane–HOPG interface. (a,b) $I_{\text{set}} = 130 \text{ pA}$, $V_{\text{bias}} = -0.85 \text{ V}$ (c,d) $I_{\text{set}} = 130 \text{ pA}$, $V_{\text{bias}} = -1.3 \text{ V}$. (e,f) $I_{\text{set}} = 140 \text{ pA}$, $V_{\text{bias}} = -0.45 \text{ V}$.

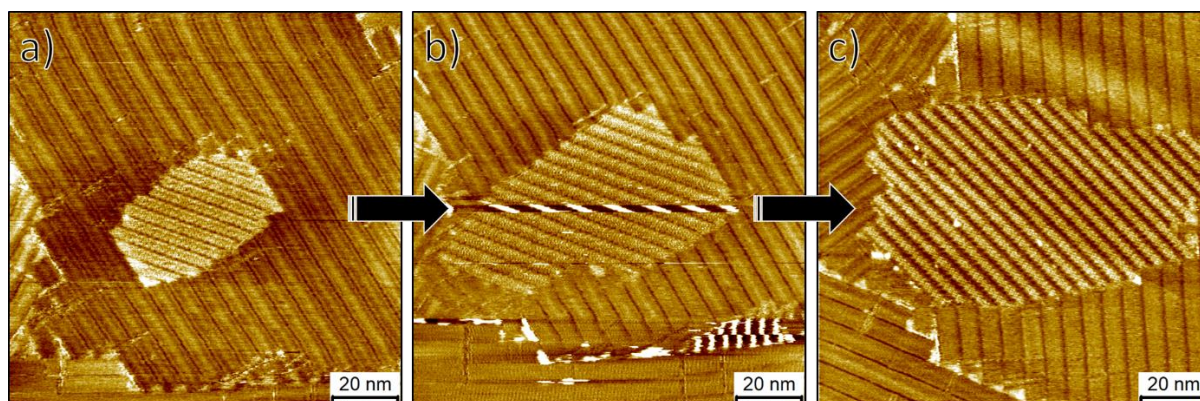


Figure S8: Rapid growth of **BA-OC₁₄** domain on top of the **n-C₅₀** buffer layer at the 1-phenyloctance–HOPG interface after nanoshaving-induced nucleation. (a) $I_{\text{set}} = 140 \text{ pA}$, $V_{\text{bias}} = -0.7 \text{ V}$ (b) $I_{\text{set}} = 170 \text{ pA}$, $V_{\text{bias}} = -0.55 \text{ V}$ (c) $I_{\text{set}} = 90 \text{ pA}$, $V_{\text{bias}} = -0.55 \text{ V}$.

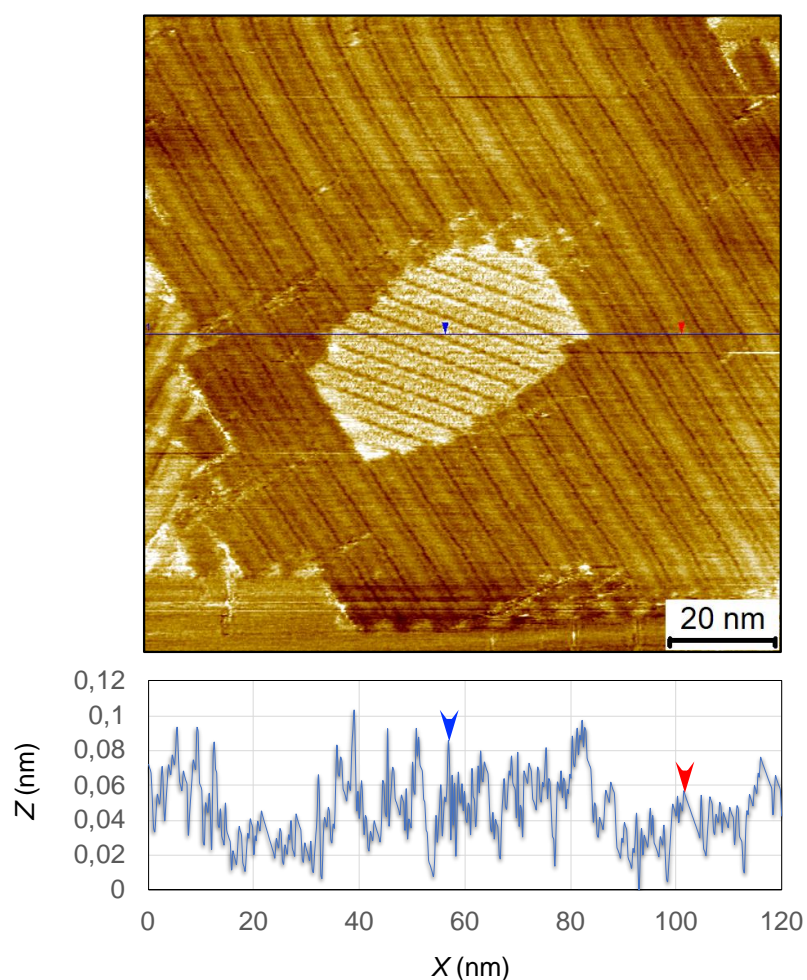


Figure S9: STM image showing an island of **BA-OC₁₄** monolayer formed on top of the buffer layer with a line profile across the island. Note that height in STM images is relative (thus the Y axis does not represent absolute numbers) and is a convolution of electronic and topographic effects. This image is the same as the one presented in Figure 6g in the main text.