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Supporting Information

for

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

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Additional STM data

Contents:

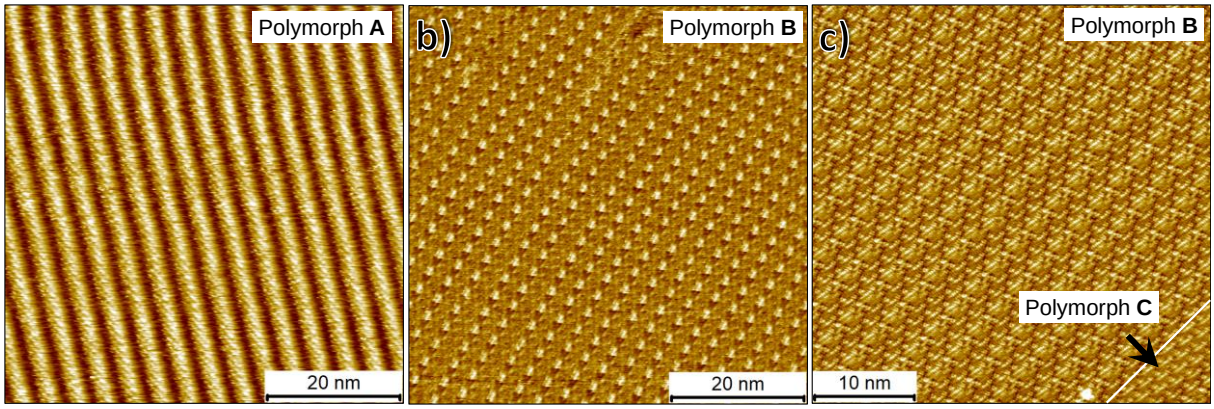

Figure S1: Additional large scale STM images of the three polymorphs of **BA-OC$_{14}$** observed at the 1-phenyloctane/HOPG interface. [**BA-OC$_{14}$**] = 9×10^{-5} M. Imaging conditions: (a) I_{set} = 140 pA, V_{bias} = -0.7 V. (b) I_{set} = 160 pA, V_{bias} = −1.45 V. (c) I_{set} = 150 pA, V_{bias} = 0.55 V.

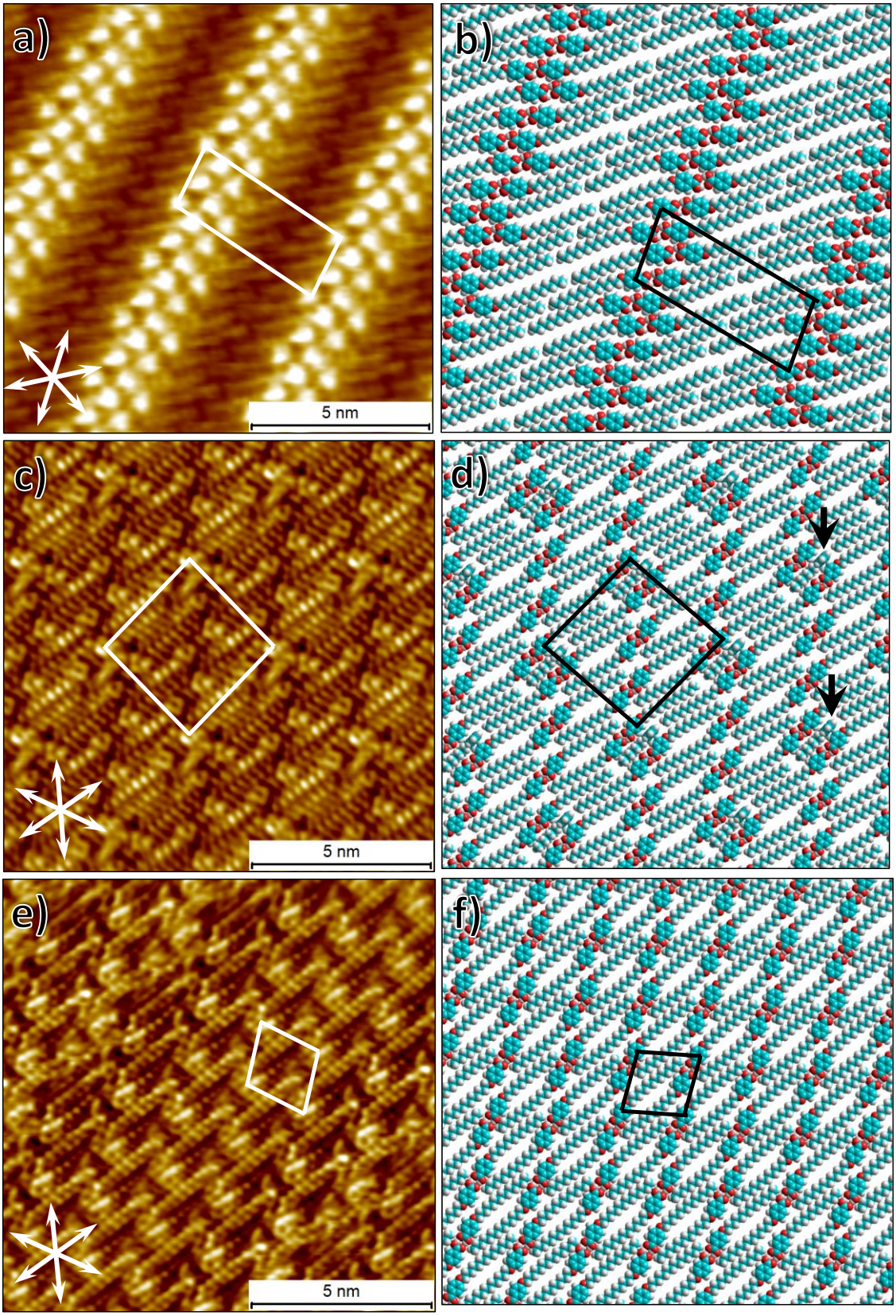

Figure S2: Magnified version of Figure 2 provided in the main text highlighting the high-resolution STM images and the corresponding molecular models.

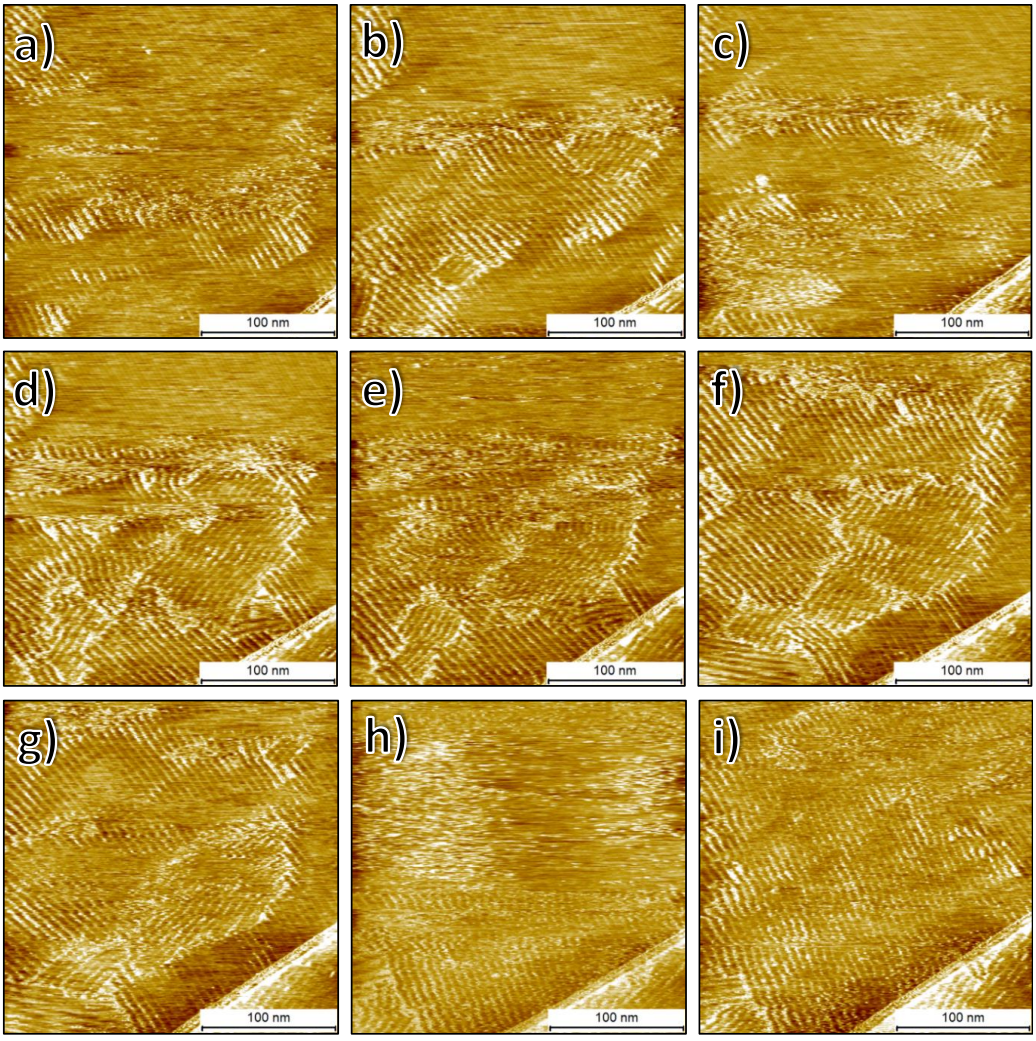

Figure S3: Sequential STM images showing the highly dynamic behavior of ***n*-C_{50}** at 7.0×10^{-6} M at the 1-phenyloctane–HOPG interface. With each scan significant rearrangement in the domain structure is visible. The sample was annealed at 50 °C for 15 min and afterwards rinsed with 1-phenyloctance.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

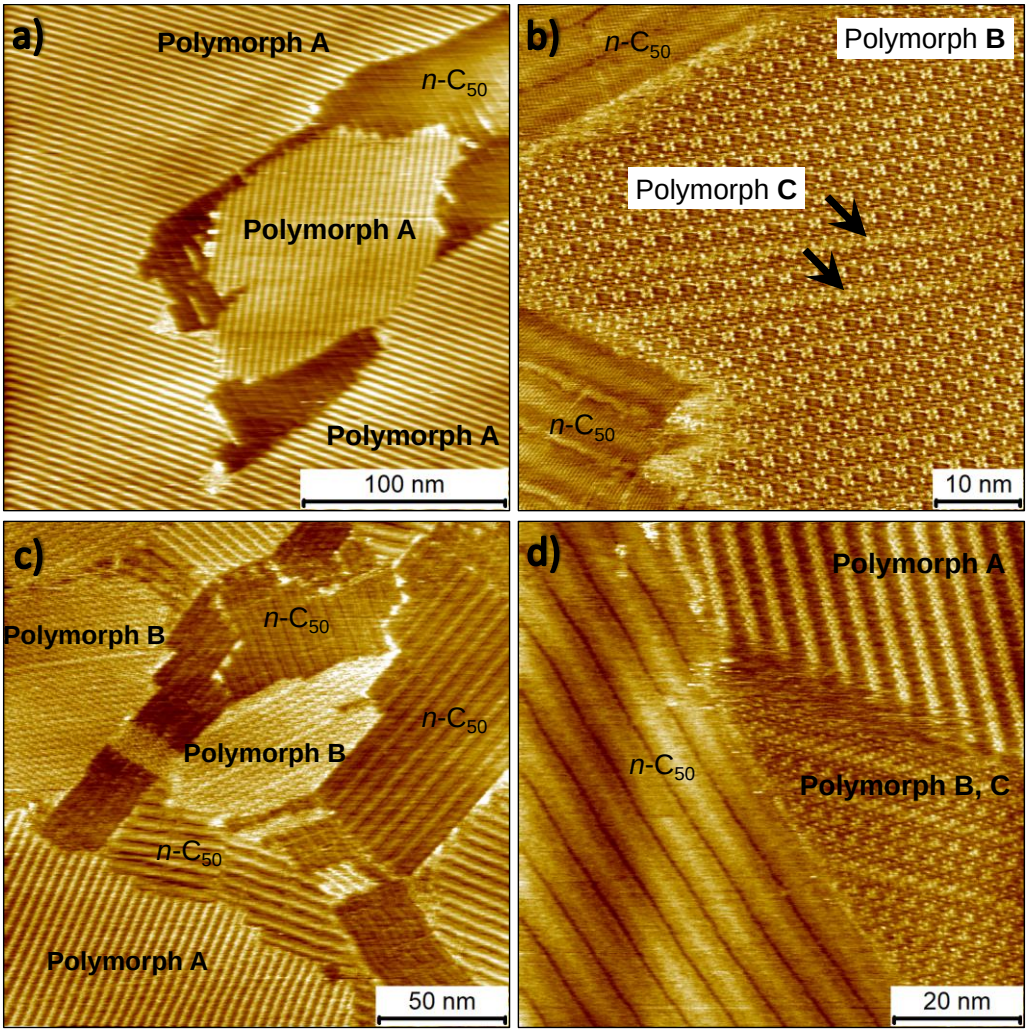

Figure S4: Additional STM images for the domains of polymorph **A, B** and **C** nucleated on top of the ***n*-C$_{50}$** buffer layer. Imaging conditions: (a) I_{set} = 130 pA, V_{bias} = −1.3 V. (b) I_{set} = 190 pA, V_{bias} = −0.4 V. (c) I_{set} = 140 pA, V_{bias} = −0.65 V. (d) I_{set} = 140 pA,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

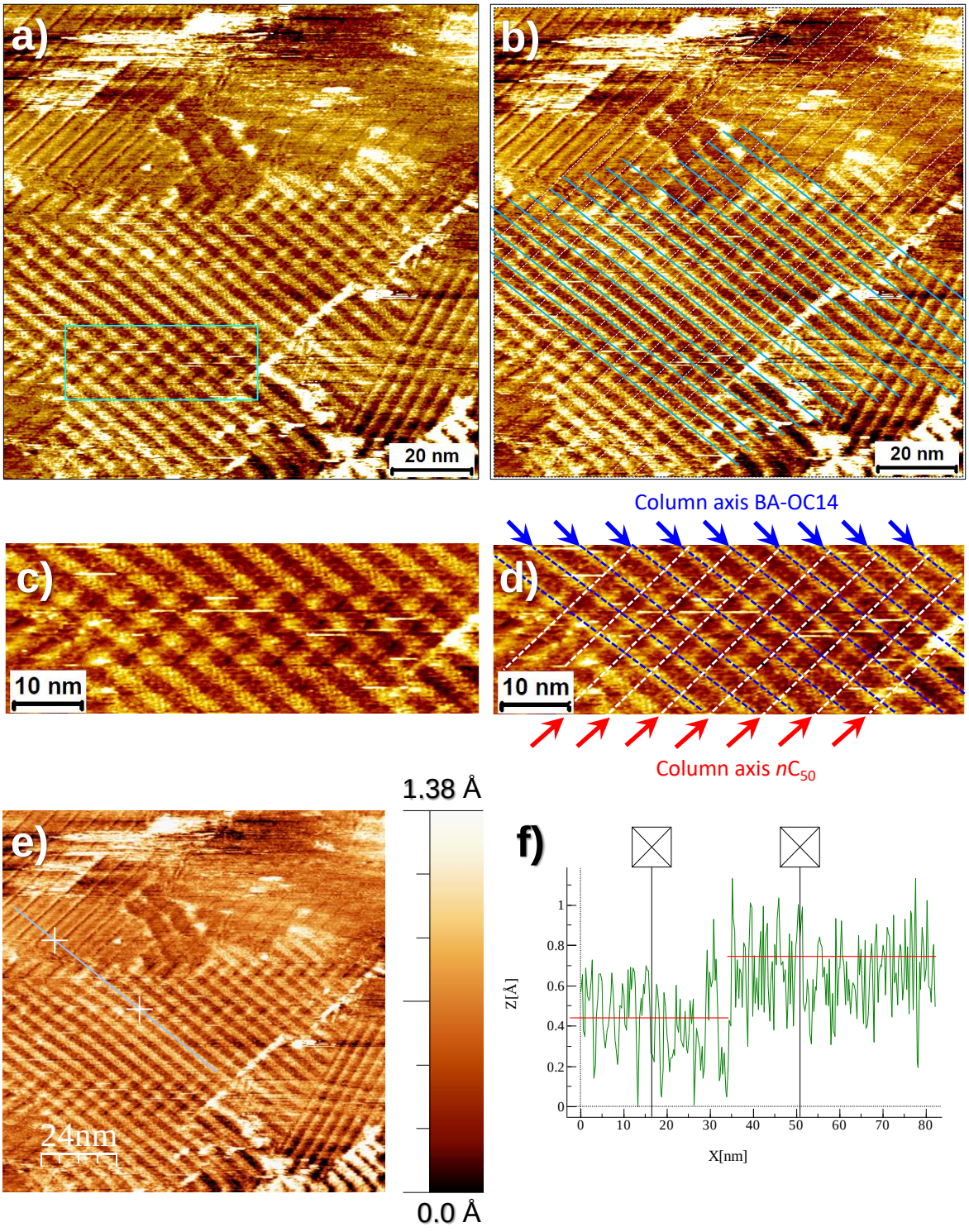

Figure S5: (a) Large scale STM image showing peculiar STM contrast that shows overlap of features of the columns of **BA-OC$_{14}$** and ***n*-C$_{50}$**. (b) Same STM image as in (a) but with overlaid colored markers for identifying the columns of **BA-OC$_{14}$** (light blue) and ***n*-C$_{50}$** (white). (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-OC$_{14}$** and ***n*-C$_{50}$**. Imaging conditions: I_{set} = 130 pA, V_{bias} = −0.65 V.

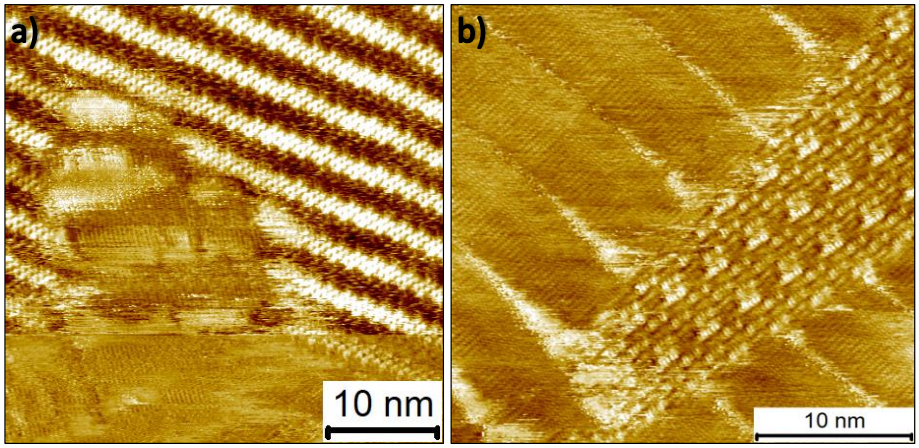

Figure S6: STM images showing the approximate alignment of the alkoxy chains of polymorphs A and B of **BA-OC$_{14}$** with the alkyl chains of ***n*-C$_{50}$** at the 1-phenyloctane–HOPG interface. Imaging conditions: (a) I_{set} = 90 pA, V_{bias} = –0.17 V. (b) I_{set} = 80 pA, V_{bias} = –0.95 V.

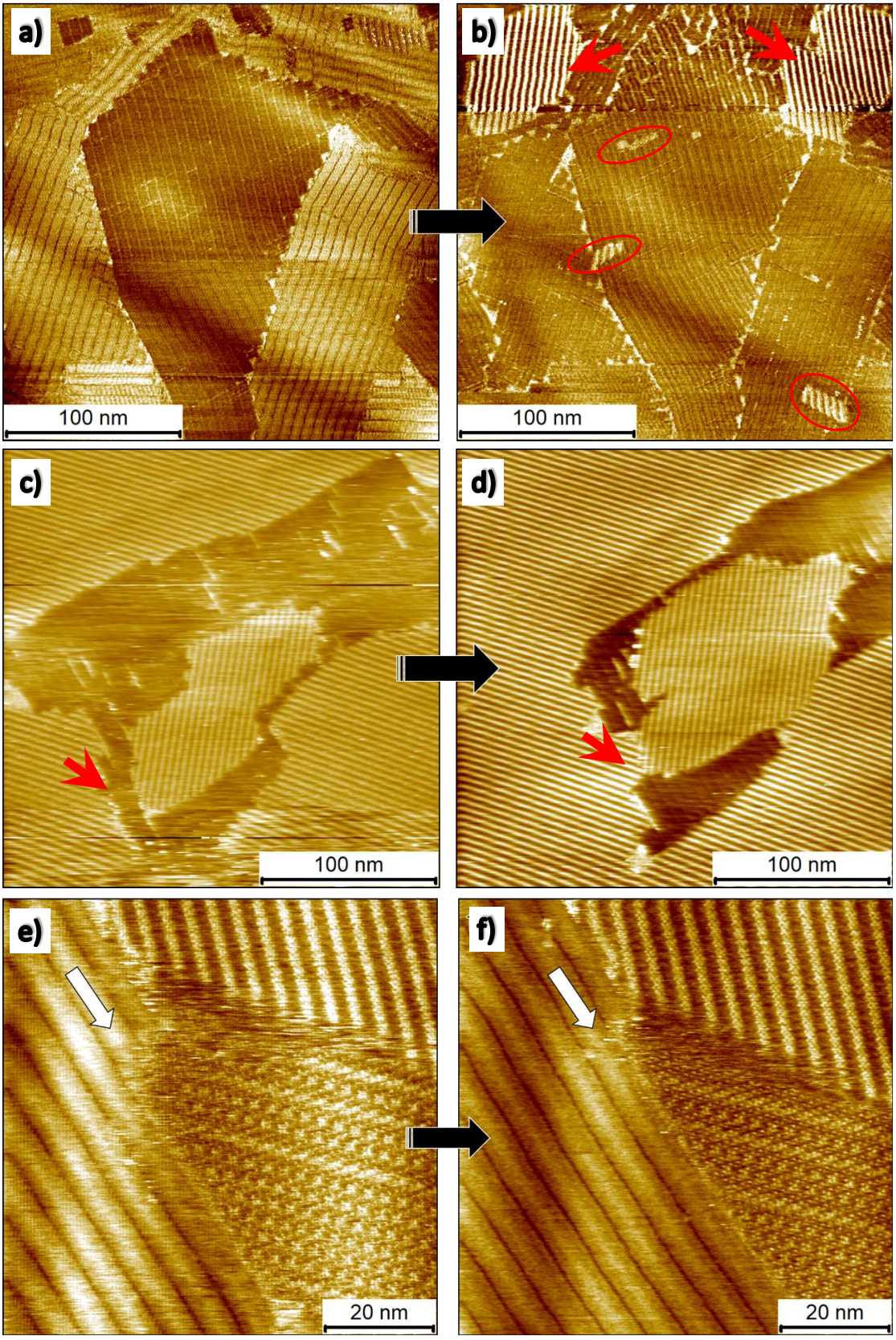

Figure S7: STM images showing the nucleation (a,b), growth (c,d) and desorption (e,f) of **BA-OC$_{14}$** on top of the ***n*-C$_{50}$** buffer layer at the 1-phenyloctane–HOPG interface. (a,b) I_{set} = 130 pA, V_{bias} = −0.85 V (c,d) I_{set} = 130 pA, V_{bias} = −1.3 V. (e,f) I_{set} = 140 pA, V_{bias} = −0.45 V.

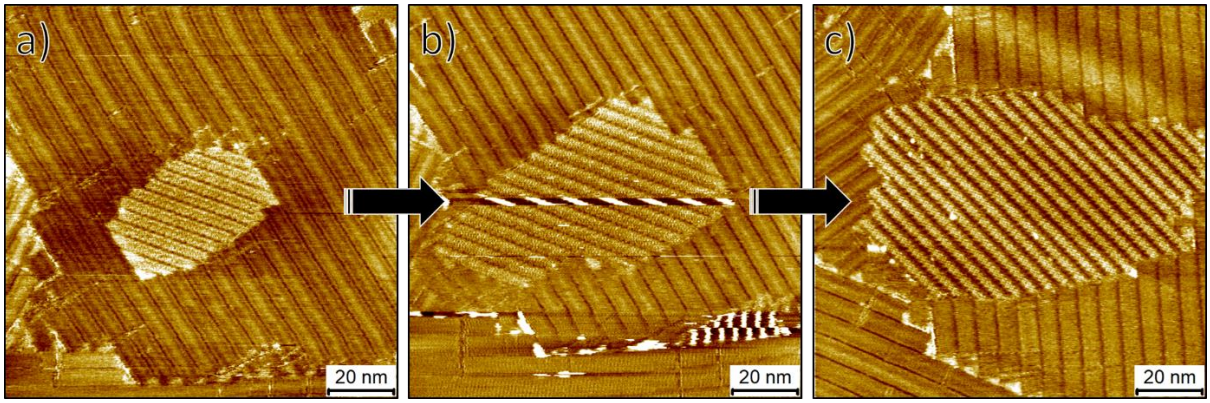

Figure S8: Rapid growth of **BA-OC$_{14}$** domain on top of the ***n*-C$_{50}$** buffer layer at the 1-phenyloctance–HOPG interface after nanoshaving-induced nucleation.(a) I_{set} = 140 pA, V_{bias} = -0.7 V (b) I_{set} = 170 pA, V_{bias} = -0.55 V (c) I_{set} = 90 pA, V_{bias} = -0.55 V.

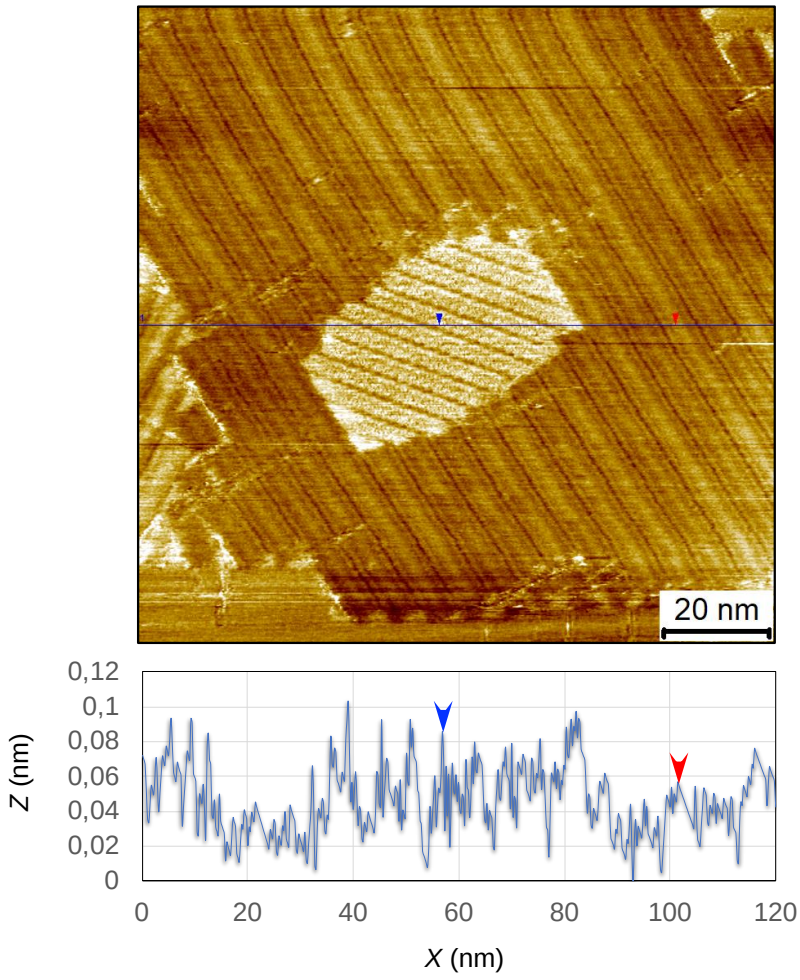

Figure S9: STM image showing an island of **BA-OC$_{14}$** monolayer formed on top of the buffer layer with a line profile across the island. Note that height in STM images is relative (thus the *Y* axis does not represent absolute numbers) and is a convolution of electronic and topographic effects. This image is the same as the one presented in Figure 6g in the main text.