

Electron Supplement Information to

Journal: RSC CrystEngCom

Alexander I. Loskutov, Boris V. Lokshin, Nellya M. Sazonova, Nestor Solis Pinargote, Vladimir V. Vysotskii and Sergei A. Loskutov

“Features of crystallization of multicomponent solutions: dipeptide, its salt and potassium carbonate”

TOC graphics to Electron Supplement Information (ESI)

ESI contains additional materials to the manuscript, which are divided into 4 sections.

1. Materials: figures S1, S2, S3, S4, S5

Figure S1. Structure of dipeptide molecule

Figure S2. AFM image of the surface of gold films, prepared by magnetron sputtering

Figure S3. ¹H NMR spectra (4.4 ppm-1.1 ppm region) DPT-0 (neutral molecule) (a), DPT-1 (salt form in carboxyl groups) (b)

Figure S4. ¹H NMR spectra (region of amide protons.) DPT-1 (salt form in carboxyl groups) (a), DPT-0 (neutral molecule) (b).

Figure S5. Structure of potassium salt of dipeptide molecule

2. Probe measurements: figures S 6, S 7, S 8, S 9, S 10, S 11, S 12, S 13, S14.

Figure S 6a. AFM-image of the surface of DPT-0 ultrathin layers on gold.

Figure S 6 b. Profiles of DPT-0 ultra-thin layers on gold - vertical (1) and horizontal (2)

Figure S 7. STM-image of the DPT-0 surface of thin layers on gold and corresponding profiles.

Figure S8. STM-image of the surface of ultra thin layers of DPT-0 on graphite and corresponding profile.

Figure S9a. STM-image of the surface of KHCO₃ thin layers on gold and the corresponding profiles.

Figure S9b. Increased STM-image of the surface of K₂CO₃ thin layers on gold and the corresponding profile

Figure S10. Increased STM-image of the surface of K₂CO₃ ultra thin layers on graphite and the corresponding profile.

Figure S11. STM-image of the surface of DPT-1 ultra thin layers on graphite and corresponding profiles

Figure S 12. STM-image of the surface of thin DPT-1 layers on graphite and corresponding profiles

Figure S13. AFM-image of the surface of ultra thin layers at the initial stage of DPT-1 growth on gold.

Figure S14. AFM -image of the surface of DPT-1 ultra thin layers at the subsequent stage of growth on gold on gold and the corresponding profile.

3. CVCs measurements: figures:, S15, S16, S17, S18.

Figure S15. LTCVCs at different points on the surface of DPT-1 thin layer on gold. Scan size 1.2x1.2 μm²

Fig. S 16. Cyclic measurements of LTCVCs at a given point on the DPT-1 surface on (a) gold and (b) graphite (30 cycles).

Figure S17. STM-image of the surface of a thin DPT-1 layer on graphite and corresponding LTCVCs measurements at different points on the surface of the layer

4. Processed IR spectra of dipeptide on gold and graphite: figures S18, S19, S20, S21

Figure S18. Transmission IR spectra of dipeptide: 1- DPT-0 (neutral molecule), 2- DPT-1 (potassium salt)

Figure S19. IR ATR spectra of dipeptide on gold: 1- DPT-0 (neutral molecule), 2- DPT-1 (potassium salt)

Figure S20. IR ATR spectra of dipeptide on graphite: 1- DPT-0 (neutral molecule), 2- DPT-1 (potassium salt)

Figure S21. Possible scheme of the orientation of the amine and carboxyl functional groups (peptide antennas) of DPT molecule in the adsorption layer on the surfaces of graphite, gold and mica.

1. Materials

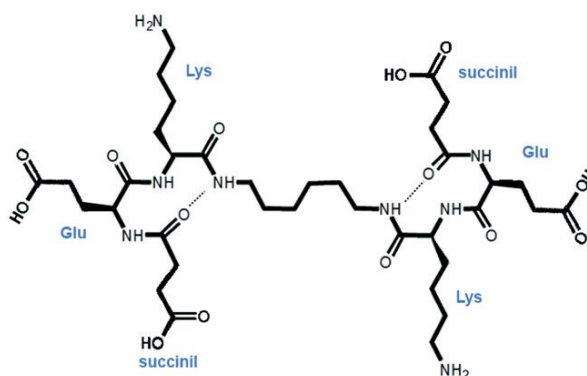


Figure S1. Structure of dipeptide molecule - hexamethylenediamide bis (N-monosuccinylglutamylsine).

The thickness of the gold layers, prepared by magnetron sputtering, was $\approx 0.5\text{--}1\ \mu\text{m}$. The surface roughness of the gold substrate was preliminarily estimated by AFM-STM (Fig.S 1). The lowest values were obtained in the case of STM measurements. The average surface roughness of the films, estimated by AFM, (S_a) was 7.8 nm and the root mean square roughness (S_q) 6.3 nm, the average size of rounded grains was 50 nm. The S_a and S_q values of graphite surfaces are almost an order of magnitude smaller. In this case, S_a and S_q of the DPT layers on gold substrates were always several times higher than the values of these parameters for the layers on the graphite surface, even at thicknesses equal to several hundred nanometers.

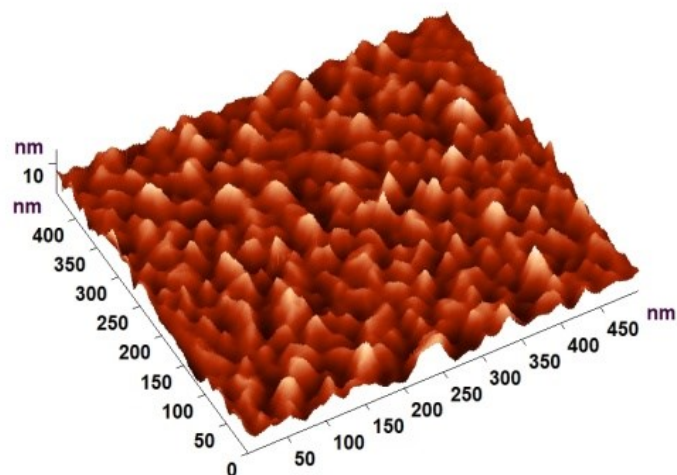


Figure S2. AFM image of the surface of gold films, prepared by magnetron sputtering

In each experiment, 10 ml of DPT or K_2CO_3 aqueous solution at different pH was deposited at room temperature on the surfaces of polycrystalline gold films and freshly prepared HOPG (ZYA, ZYH) (NT-MDT, Russia) surfaces. To increase the calculated layer thickness after complete evaporation of water, this procedure was carried out several times

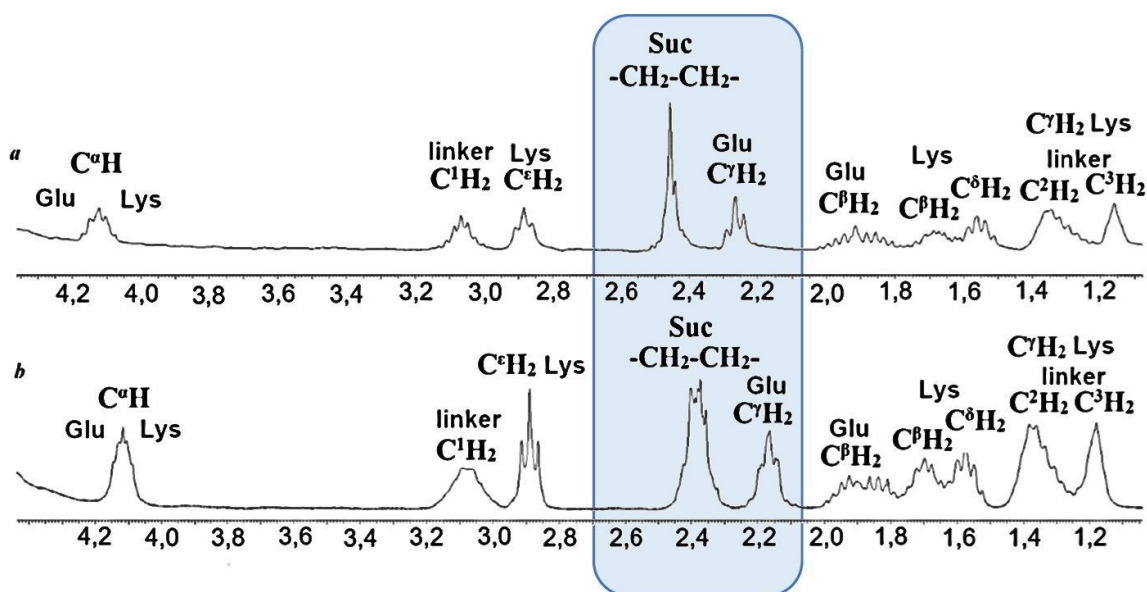


Figure S3. 1H NMR spectra (4.4 ppm-1.1 ppm region) DPT-0 (neutral molecule) (a), DPT-1 (salt form in carboxyl groups) (b)

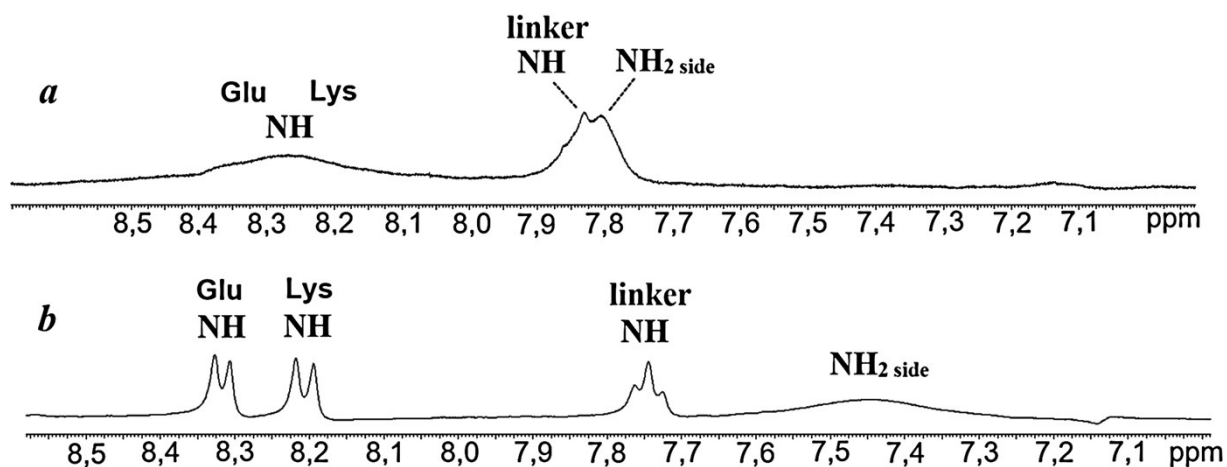


Figure S4. ^1H NMR spectra (region of amide protons.) DPT-1 (salt form in carboxyl groups) (a), DPT-0 (neutral molecule) (b).

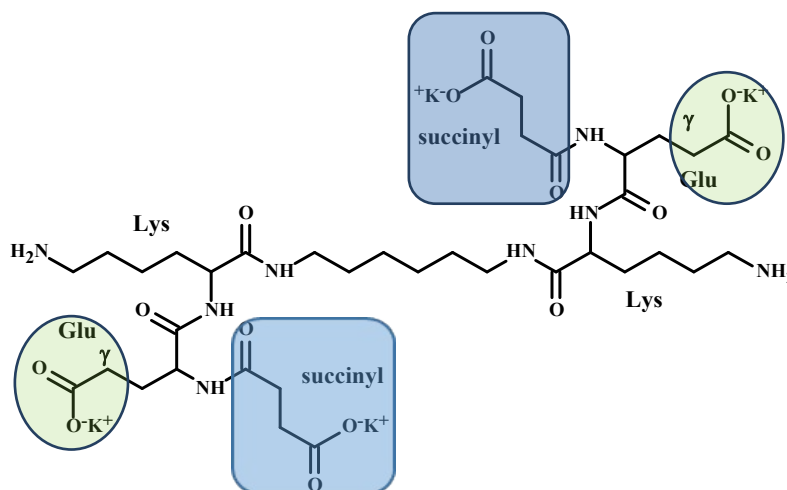


Figure S5. Structure of potassium salt of dipeptide molecule

2. Probe measurements.

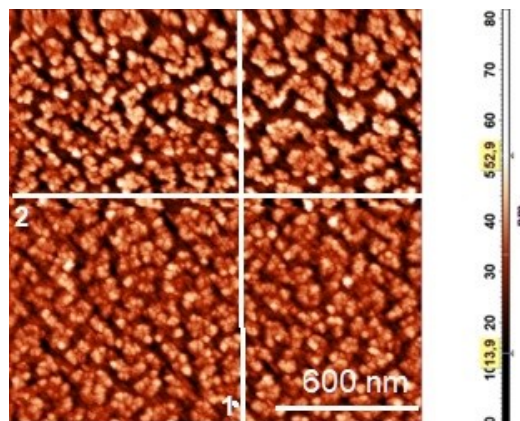


Figure S6a. AFM-image of the surface of DPT-0 ultra thin layers on gold (the white lines correspond to the profiles in Figure S6b).

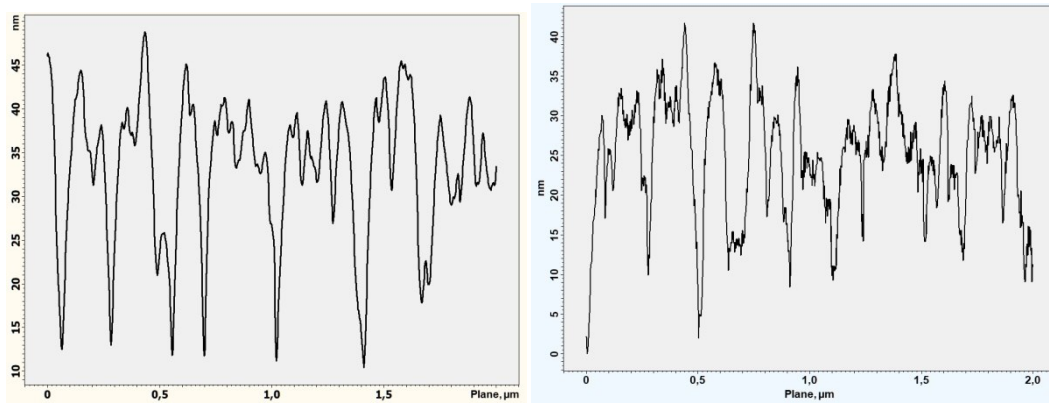


Figure S6b. Profiles of DPT-0 ultra thin layers on gold - vertical (1) and horizontal (2)

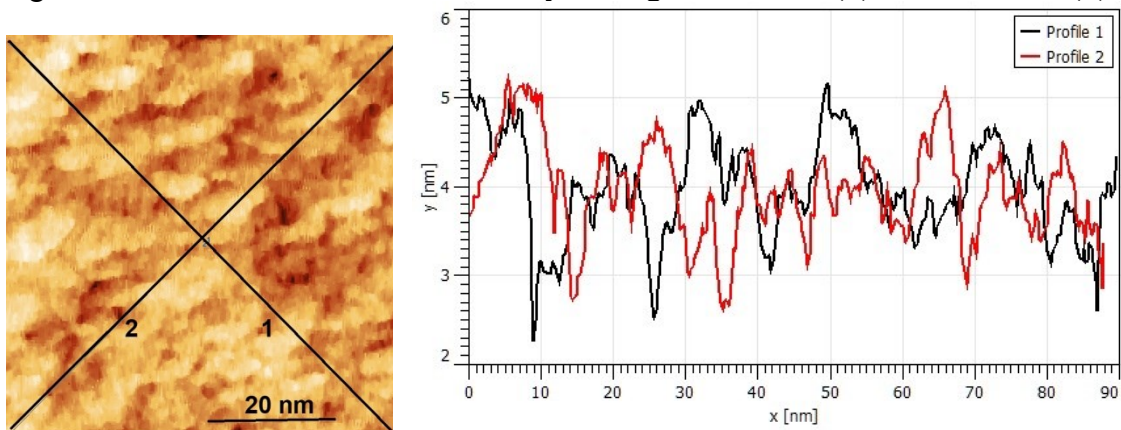


Figure S7. STM-image of the surface of thin layers of DPT-0 on gold and corresponding profiles.

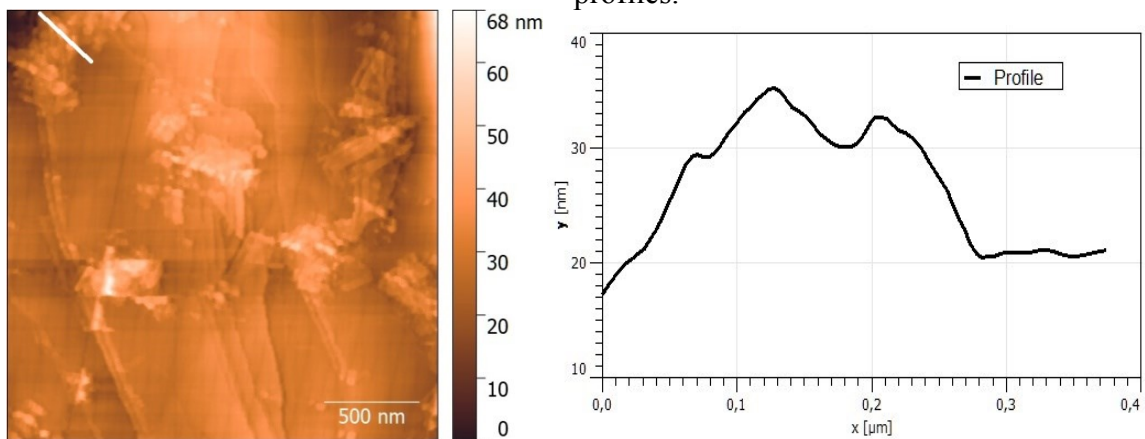


Figure S8. STM-image of the surface of ultra thin layers of DPT-0 on graphite and corresponding profile.

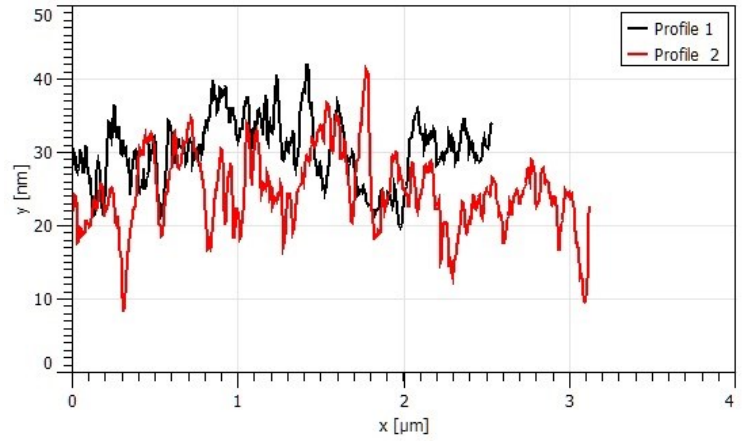
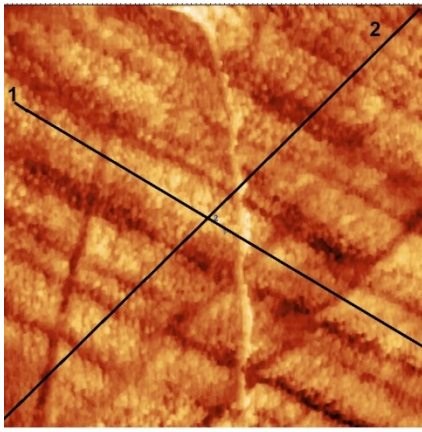


Figure S9a. STM-image of the surface of K_2CO_3 thin layers on gold and the corresponding profile.

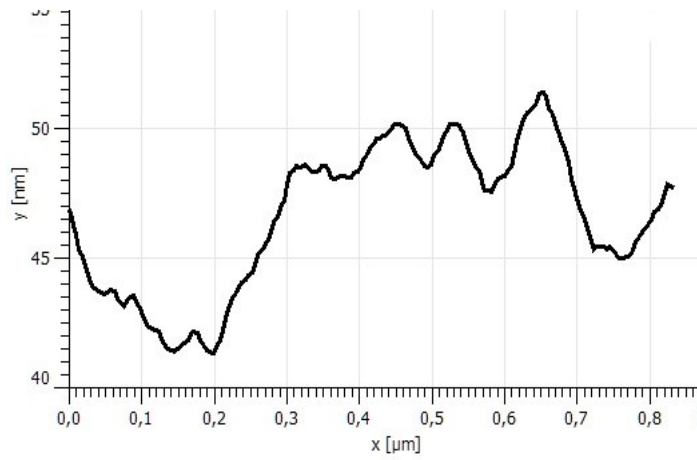
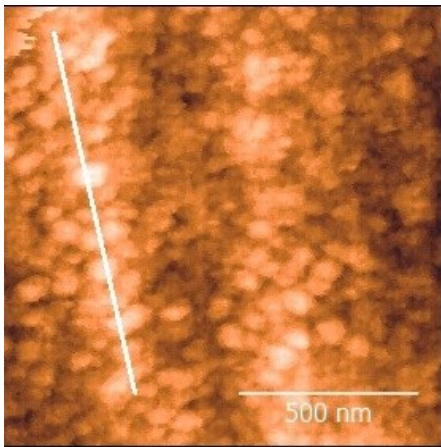


Figure S9b. Increased STM-image of the surface of K_2CO_3 thin layers on gold and the corresponding profile

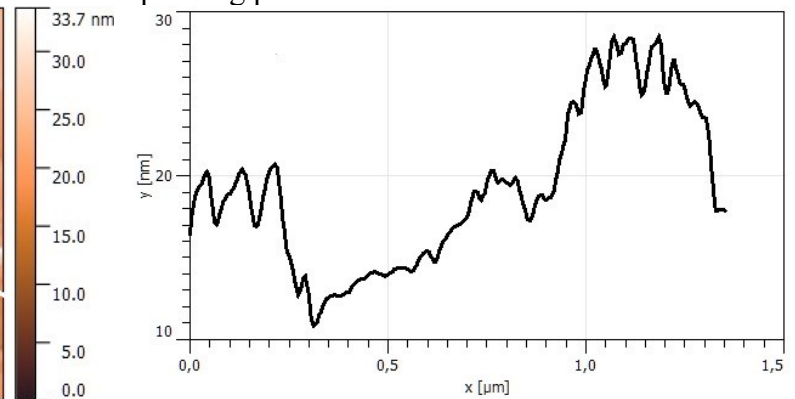
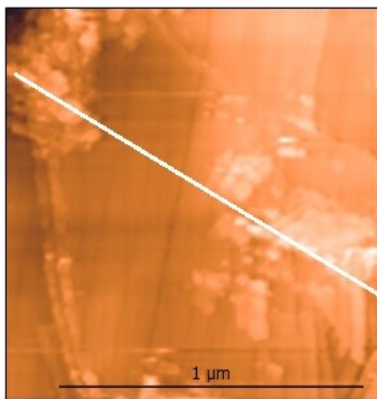


Figure S10. Increased STM-image of the surface of K_2CO_3 ultra thin layers on graphite and the corresponding profile.

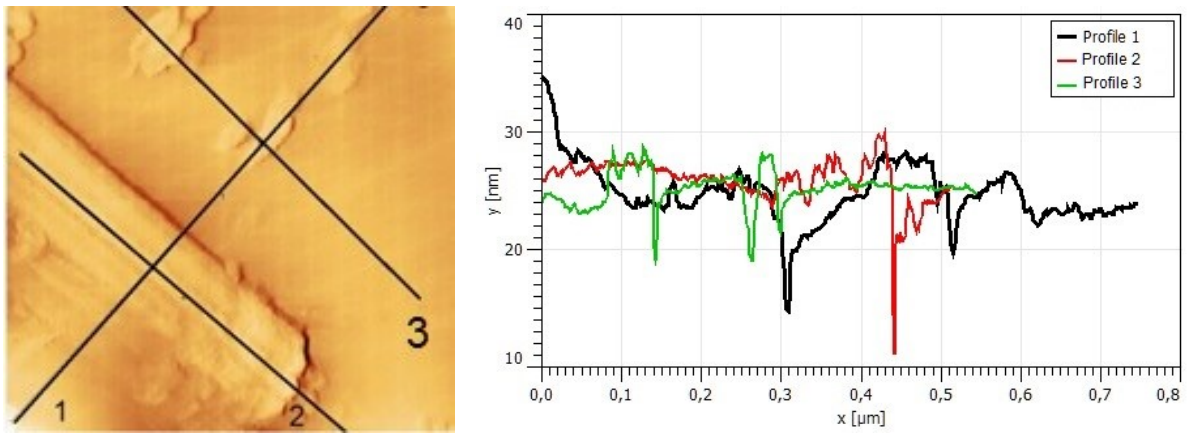


Figure S11. STM-image of the surface of DPT-1 ultra thin layers on graphite and corresponding profiles

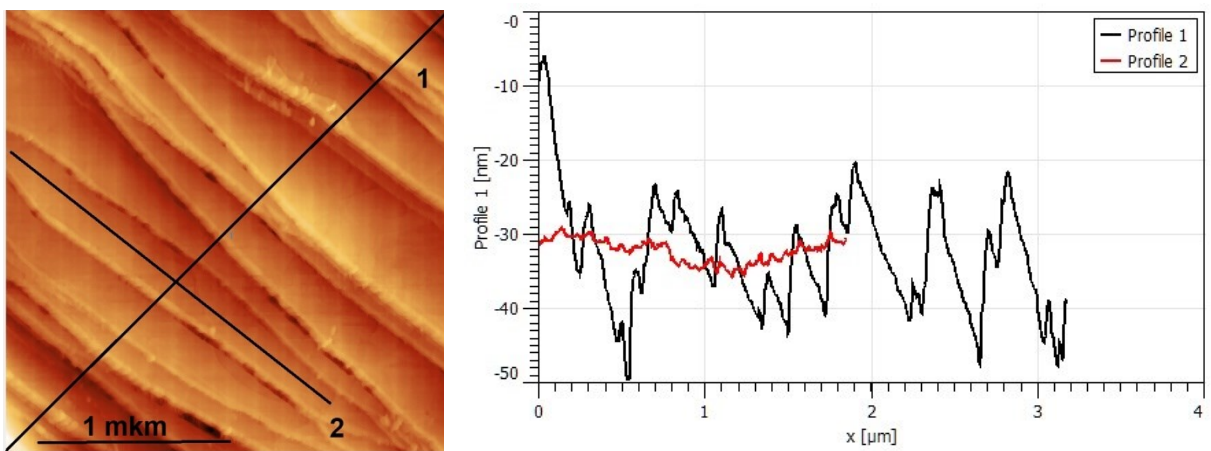


Figure S12. STM-image of the surface of thin DPT-1 layers on graphite and corresponding profiles.

In figures S13 and S14 consecutive stages of growth of DPT-1 ultra thin layers on gold are presented.

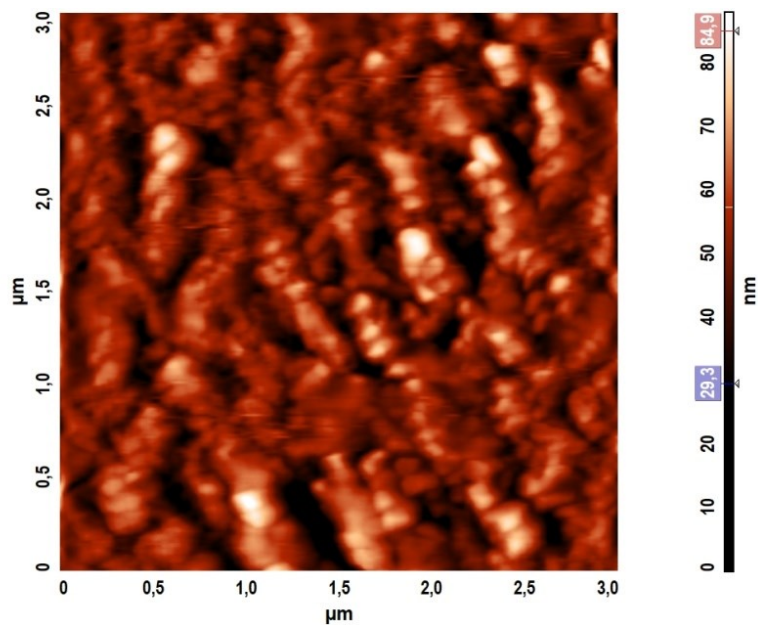


Figure S13. AFM-image of the surface of ultra thin layers at the initial stage of DPT-1 growth on gold.

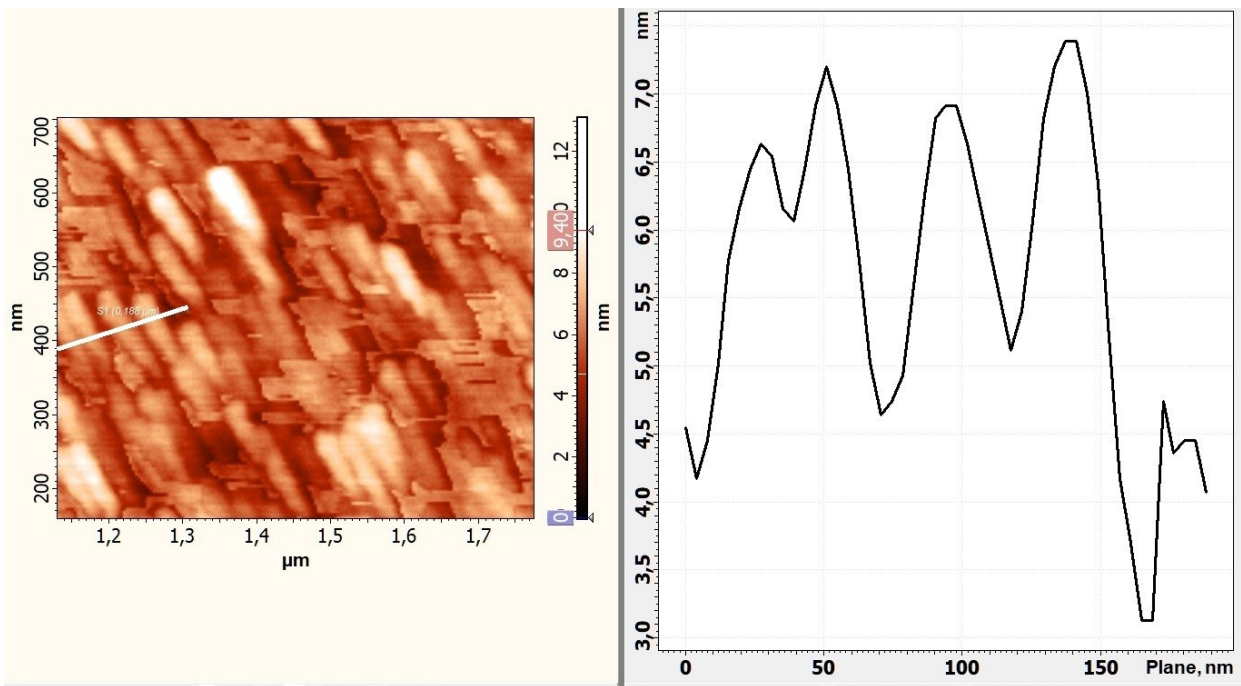
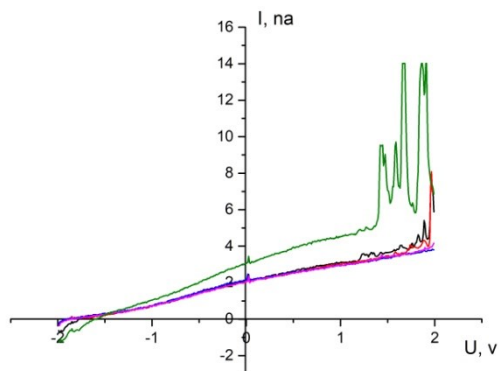
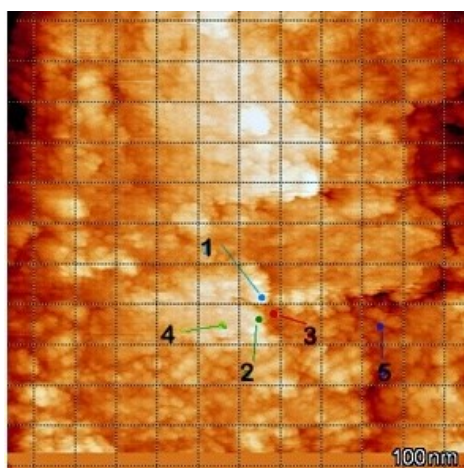


Figure S14. AFM -image of the surface of DPT-1 ultra thin layers at the subsequent stage of growth on gold on gold and the corresponding profile.

3. CVC measurements

When measuring CVCs at different points of the sample surface, the question arises about their reliability and reproducibility of the results obtained. The stability of Local Tunneling Current-Voltage Characteristics (LTCVCs) under multiple measurements at one point on the surface is also important for the practical use of this peptide.



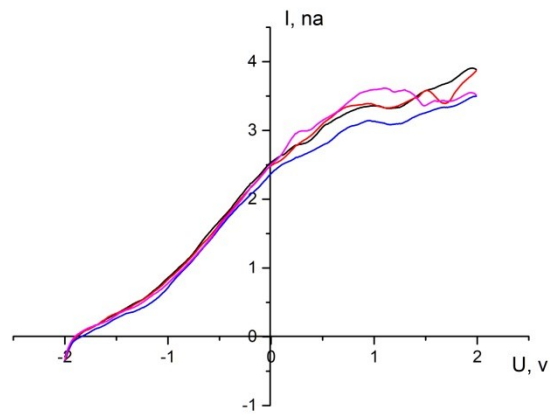
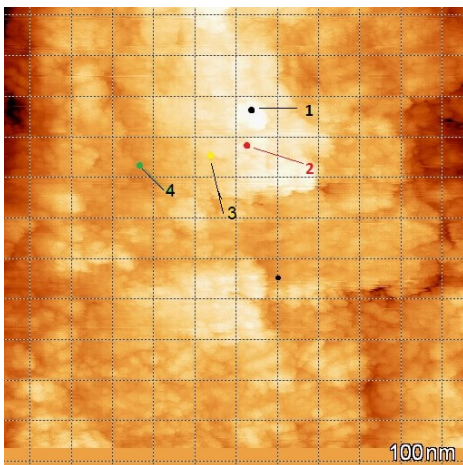
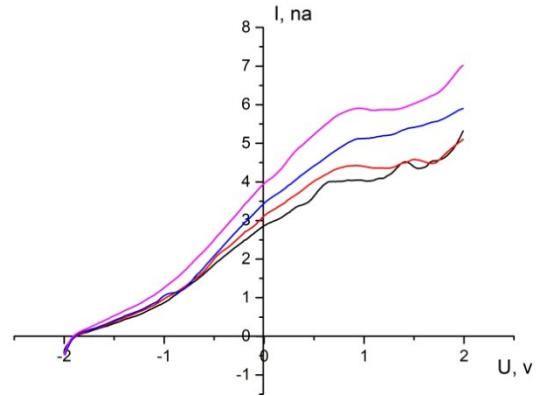
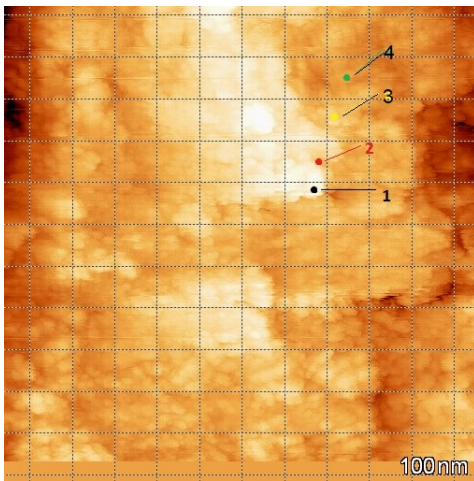


Figure S 15. LTCVCs at different points on the surface of DPT-1 thin layer on gold. Scan size $1.2 \times 1.2 \mu\text{m}^2$

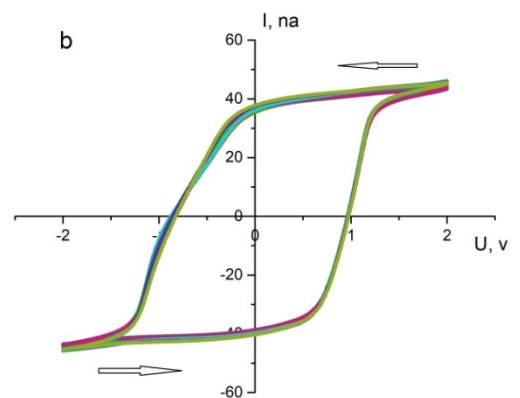
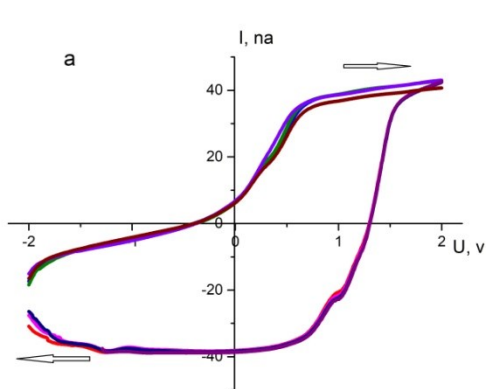


Fig. S 16. Cyclic measurements of LTCVCs at a given point on the DPT-1 surface on (a) gold and (b) graphite (30 cycles).

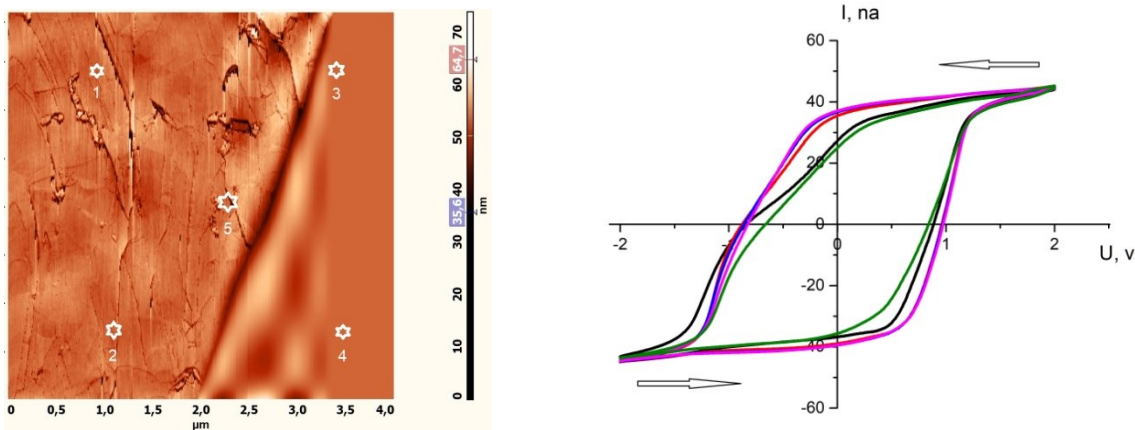


Figure S17. STM-image of the surface of a thin DPT-1 layer on graphite and corresponding LTCVCs measurements at different points on the surface of the layer

4. Processed IR spectra of dipeptide on gold and graphite surfaces.

For a more detailed analysis of the IR spectra and determination of the secondary structure of the peptide and its potassium salt, we used their mathematical processing (differentiation or fitting of peacs). The software used MATLAB or Origin Pro 9.1.

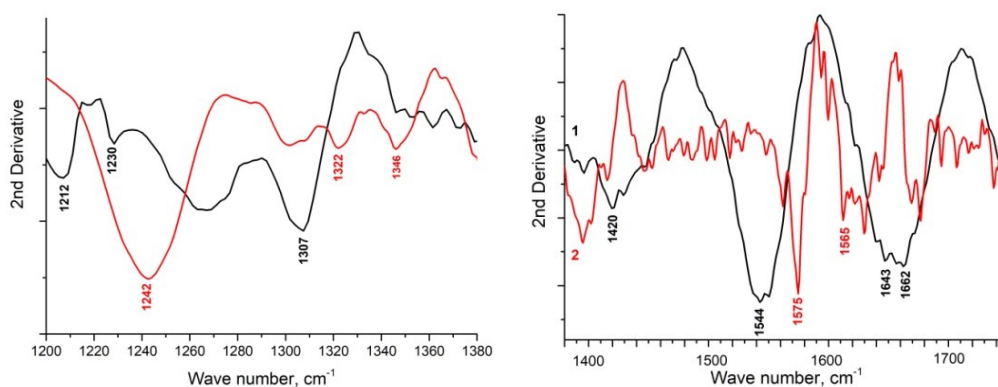


Figure S18. Transmission IR spectra of dipeptide: 1- DPT-0 (neutral molecule), 2- DPT-1 (potassium salt)

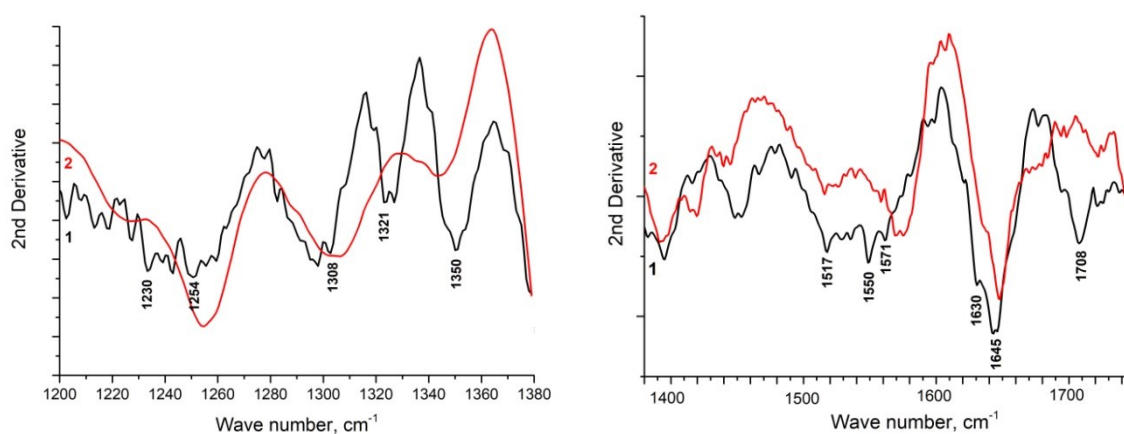


Figure S19. IR ATR spectra of dipeptide on gold: 1- DPT-0 (neutral molecule), 2- DPT-1 (potassium salt)

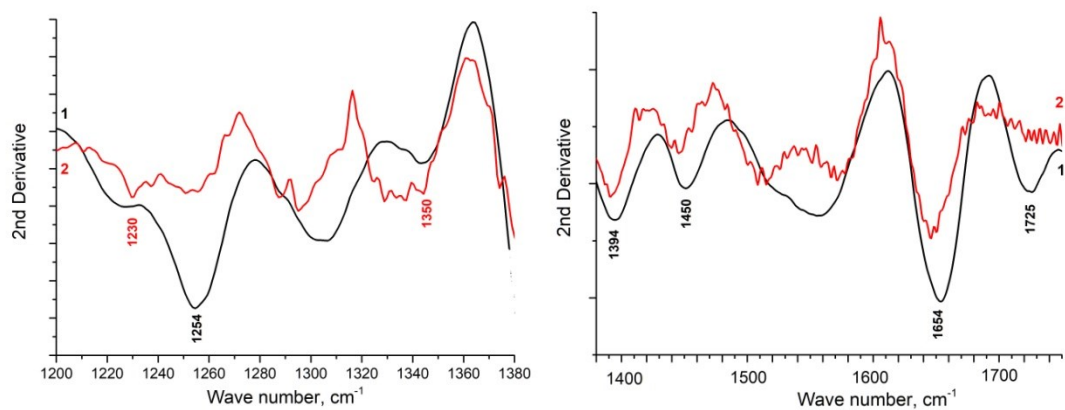


Figure. S20. IR ATR spectra of dipeptide on graphite: 1- DPT-0 (neutral molecule), 2- DPT-1 (potassium salt)

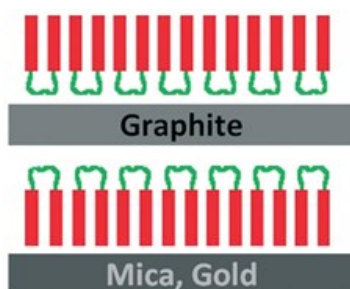


Fig. S21. Possible scheme of the orientation of the amine and carboxyl functional groups (peptide antennas) of DPT molecule in the adsorption layer on the surfaces of graphite, gold and mica.