Electronic Supplementary Material (ESI) for Nanoscale.

Helical Sense Selective Domains and Enantiomeric Superhelices Generated by Langmuir-Schaefer Deposition of an Axially Racemic Chiral Helical Polymer

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Electronic Supplementary Information

Contents:

Materials and Methods

CD measurements were done in a Jasco-720. The amounts of polymers used for CD measurements were 0.1 mg/mL.

UV spectra were registered in a Jasco V-630. The amounts of polymers used for CD measurements were 0.1 mg/mL.

DSC traces were obtained in a DSC Q200 Tzero Technology (TA Instruments, New Castle, UK), equipped with a refrigerated cooling system RCS90 (TA Instruments, New Castle, UK), using a Tzero low-mass aluminum pan.

GPC experiments were carried out in a Waters allianze e2695 separation module coupled with a Waters fraction collector III, using PSS standards for calibration.

The Langmuir-Schaefer monolayers were prepared in a rectangular trough made of poly(tetra-fluoroethylene) (36 cm x 11 cm x 1 cm) with a wilhelmy balance provided with a 20 mm wide filter paper as a plate for measuring the surface pressure. Stock solutions of the different polymers in $CHCl_3$ [250 µL (0.1 mg/mL)] were spread over the water surface, then the barrier is moved gradually decreasing the area at constant speed until the target pressure was reached. The monolayer was recollected on freshly cleaved HOPG (Telstar Instrumat, ZYH grade) with a deeper speed of 1mm/s.

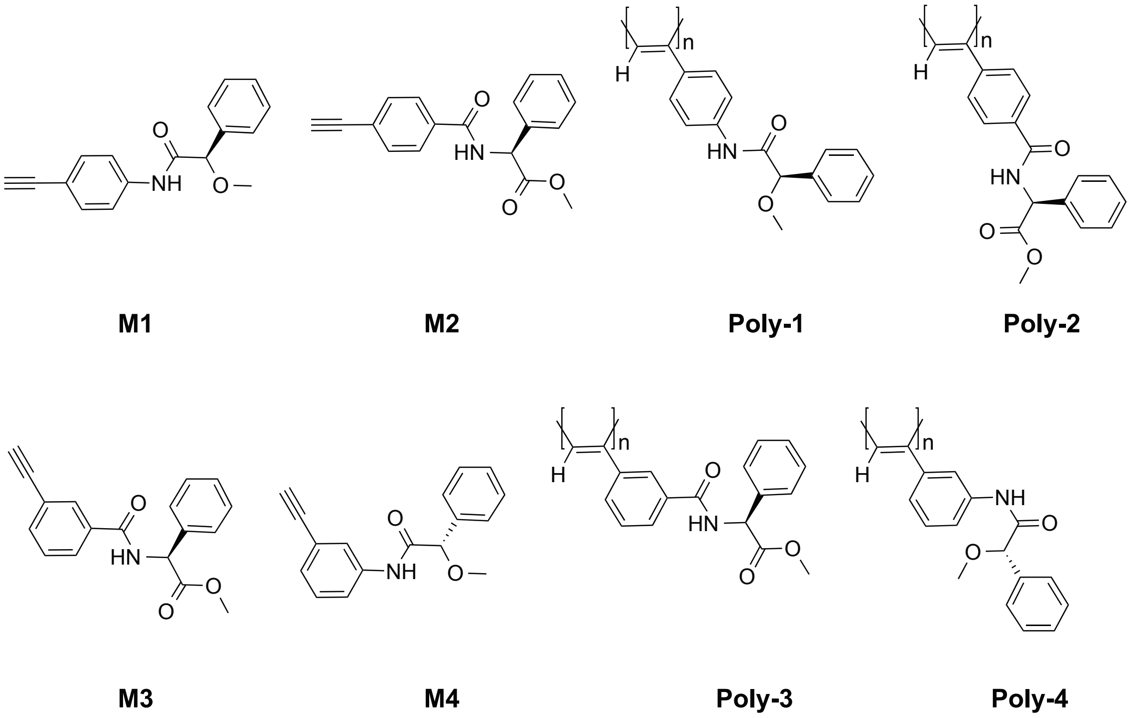
AFM measurements were performed in a MultiMode V Scanning Probe Microscope (Veeco Instruments) in air at RT with standard silicon cantilevers and super-sharp cantilevers in tapping mode using 12 µm and 1 µm scanners. Nanoscope processing software and WSxM 4.0 Beta 1.0 [4] (Nanotec Electronica, S.L.) were used for image analysis.

Spartan 10 (MMFF94) was used for molecular modeling. The molecular models (Figures 4, 5 and 7) were obtained according to a previously described method (see supporting references **S1** and **S2**).

PyMOL was used as a molecular visualization system.

Synthesis

General procedures for the synthesis of monomers and polymers can be found in references **S1** and **S2**.



M1 **M2** **Poly-1** **Poly-2**

M3 **M4** **Poly-3** **Poly-4**

Figure S1: Structure of the different monomers and polymers used in this work.

AFM studies of poly-1

All the AFM measurements were performed at CACTI (Vigo University, Spain) in a Multimode Nanoscope (Veeco Instruments) in air at rt with standard silicon cantilevers and super sharp NCHV-A cantilevers in tapping mode using 12 and 1 µm scanners. All the images were processed with Nanoscope v8.10 and Gwyddion 2.30.

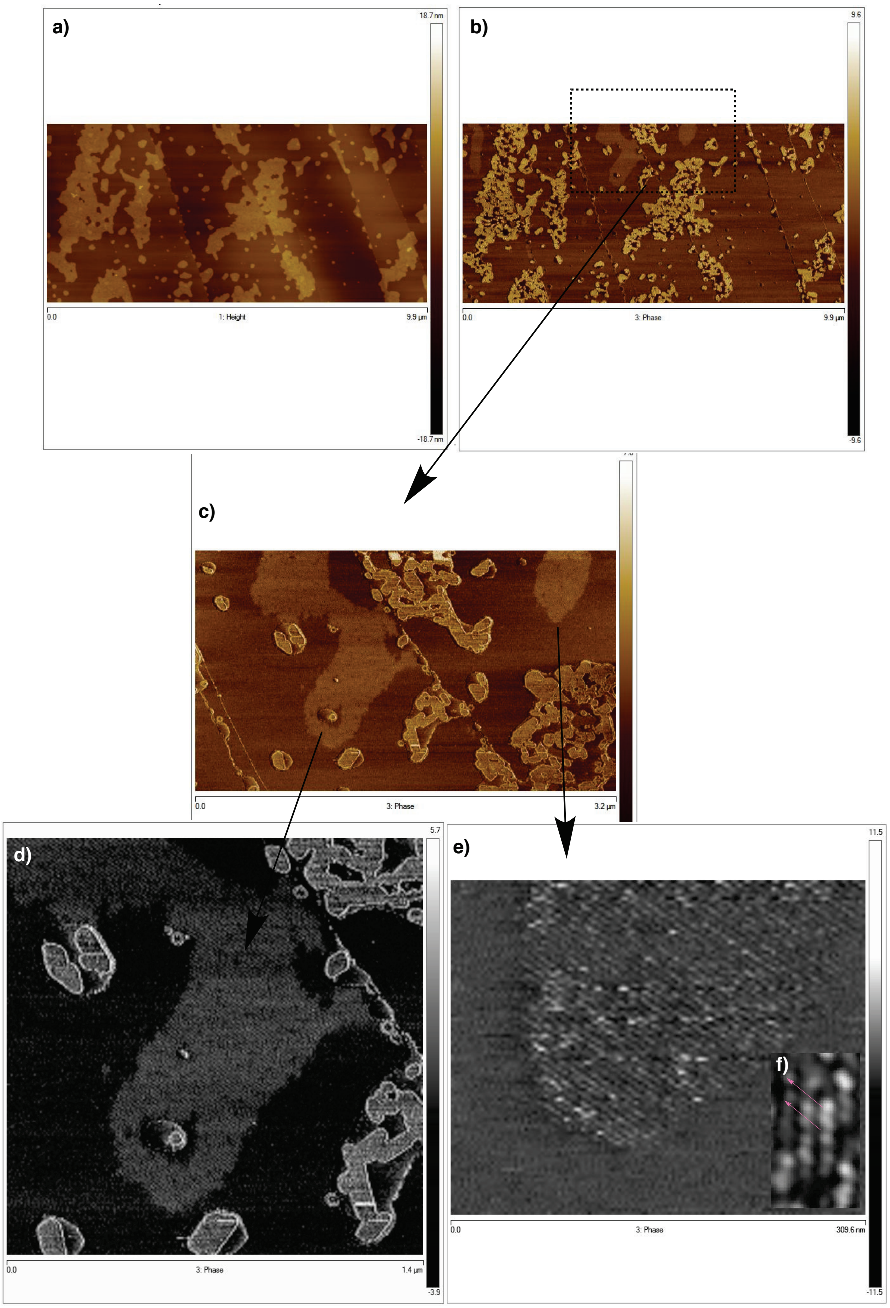


Figure S2. AFM images of poly-**1** showing left-handed helical monolayers. Phase images are shown for the sake of clarity.

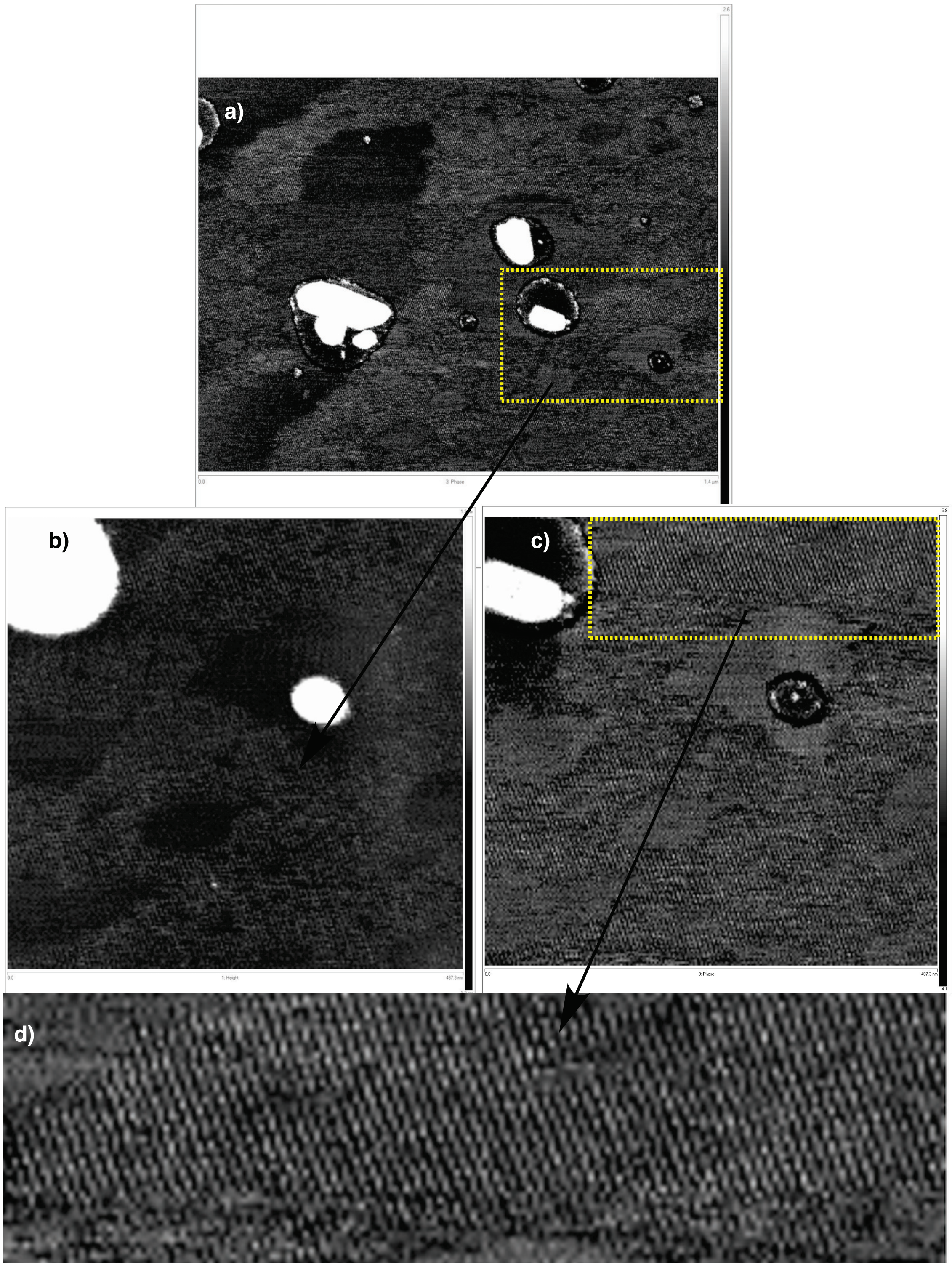


Figure S3. AFM images of poly-**1** showing right-handed helical monolayers. Phase images are shown for the sake of clarity.

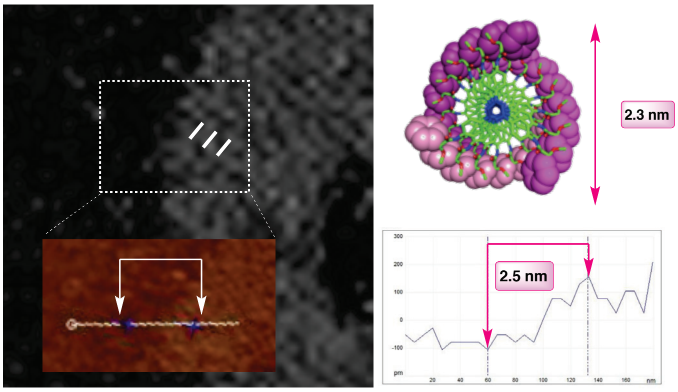


Figure S4. AFM image and height profile of a monolayer, indicating that the polymer structure is not affected (oblate or flattered) during the deposition on HOPG with the LS technique.

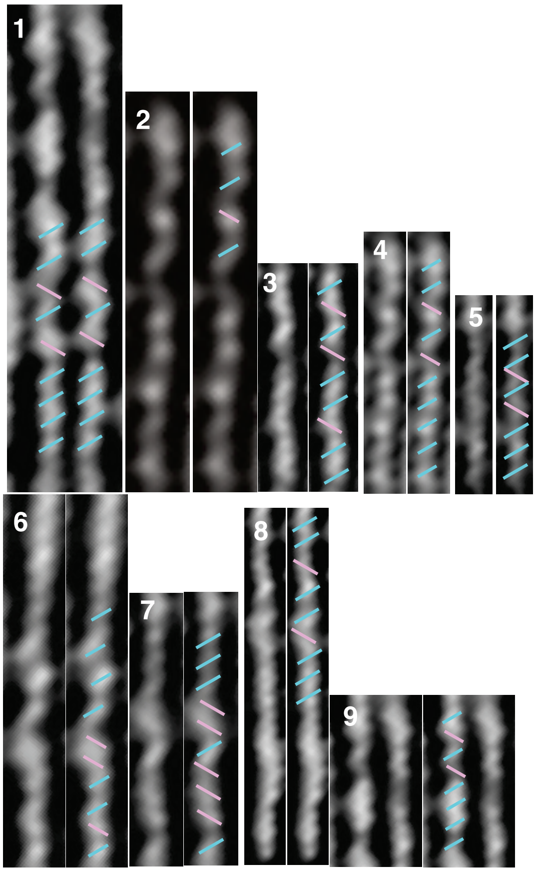


Figure S5. AFM images (1-9) show different polymer chains with the double reversal motifs (highlighted for the sake of clarity) that allow maintaining the predominant chirality among the monolayer.

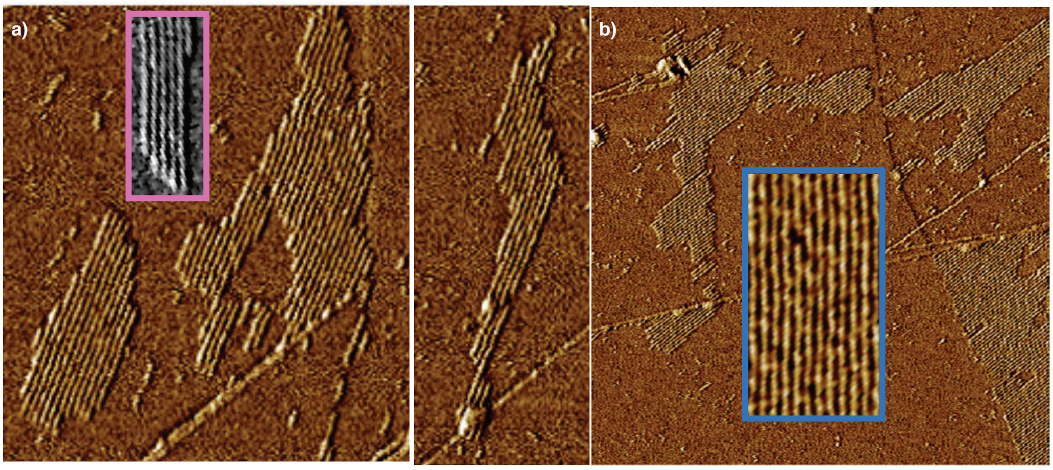


Figure S6. AFM images showing left and right-handed polymer chains (a and b respectively) with different sizes, proving that there is no relationship between the molecular weight of the polymer and the helical sense.

Moreover, GPC fractionation of poly-**1** was performed. CD experiments of a fraction of poly-**1** with low molecular weight (Mn= 1826) also showed a null CD in the main chain polyene region (385 nm).

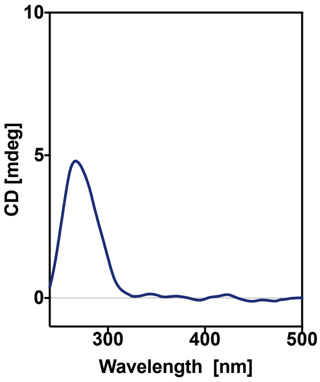


Figure S7 . CD spectrum of low molecular weight poly-**1** ($CHCl_3$, 0.1 mg/mL)

Thermal studies of poly-1

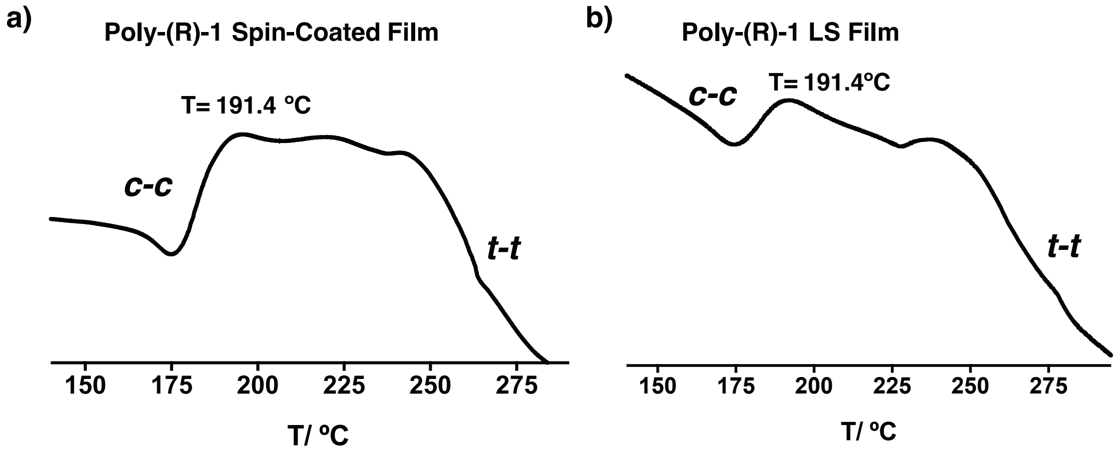


Figure S8. DSC traces of a spin-coated film and LS film of poly-**1** (a and b respectively). In both cases, the exothermic transition from *cis-cisoidal* to *trans-transoidal* starts at the same temperature, proving that the LS methodology does not modify the structure of the polymer.

AFM studies of poly-2

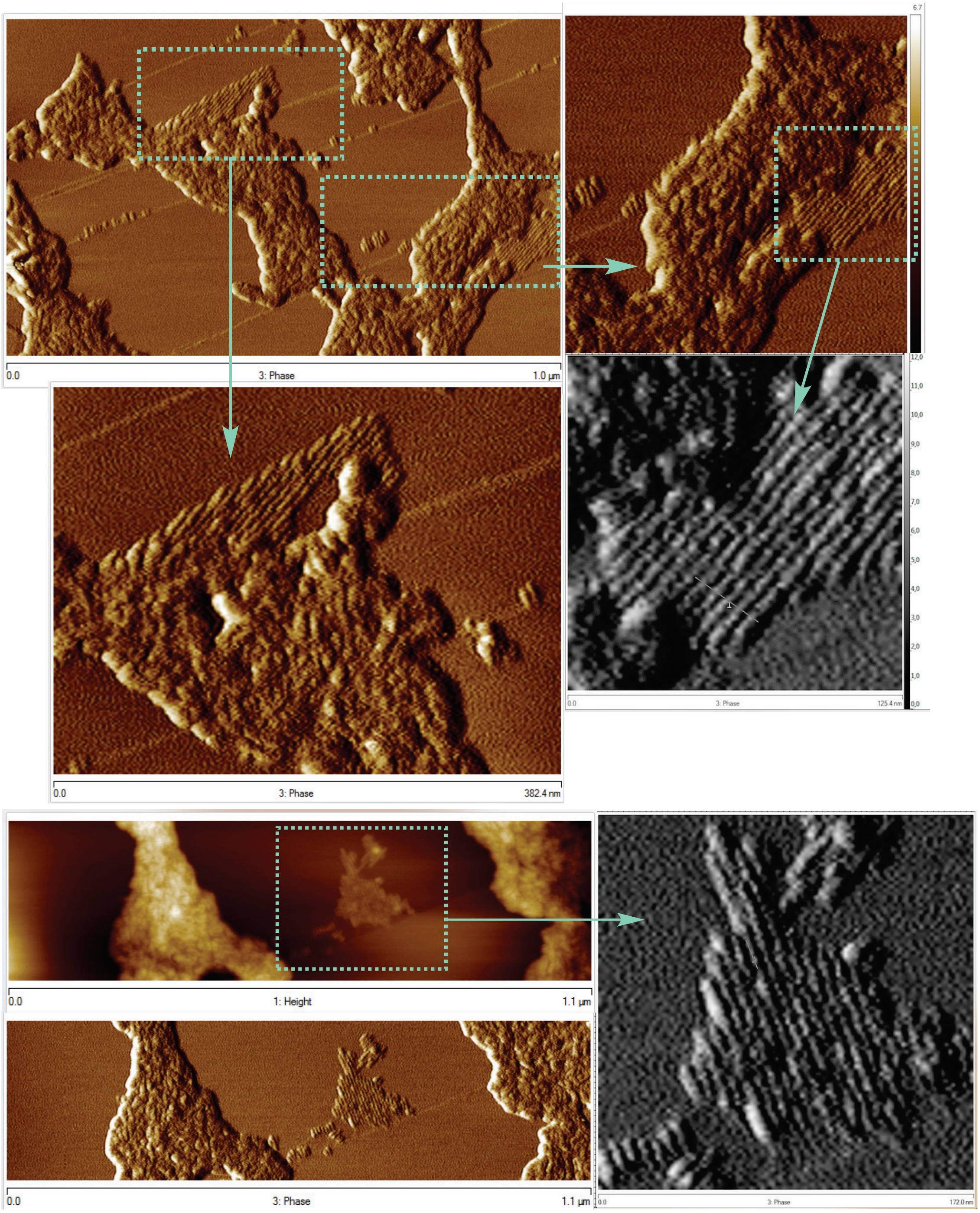


Figure S9. AFM images of poly-**2** showing monolayers of well packed polymer chains.

AFM studies of poly-3

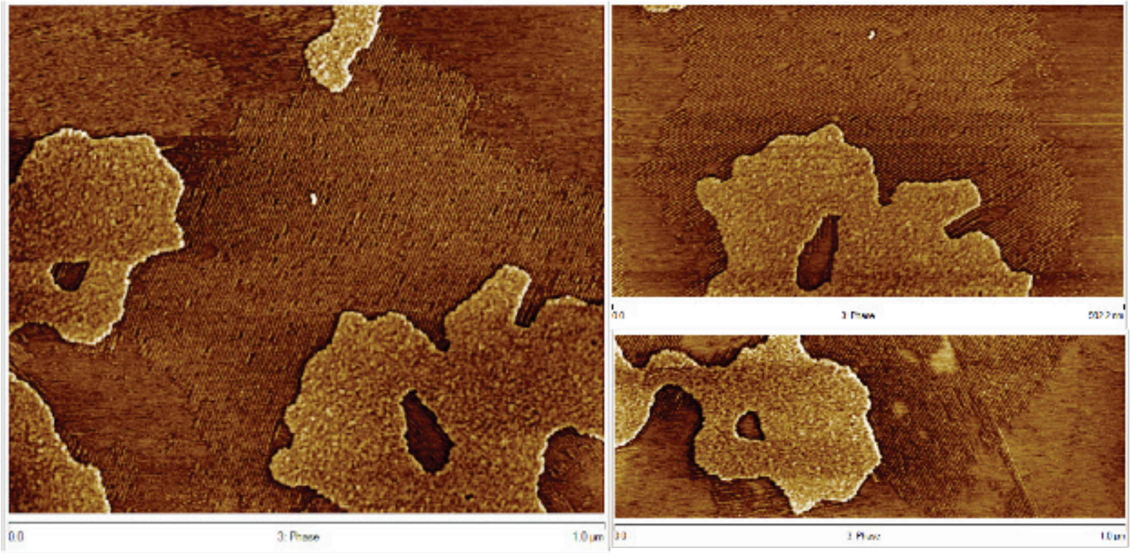


Figure S10. AFM images of poly-**3** showing monolayers of well packed polymer chains.

AFM studies of poly-4

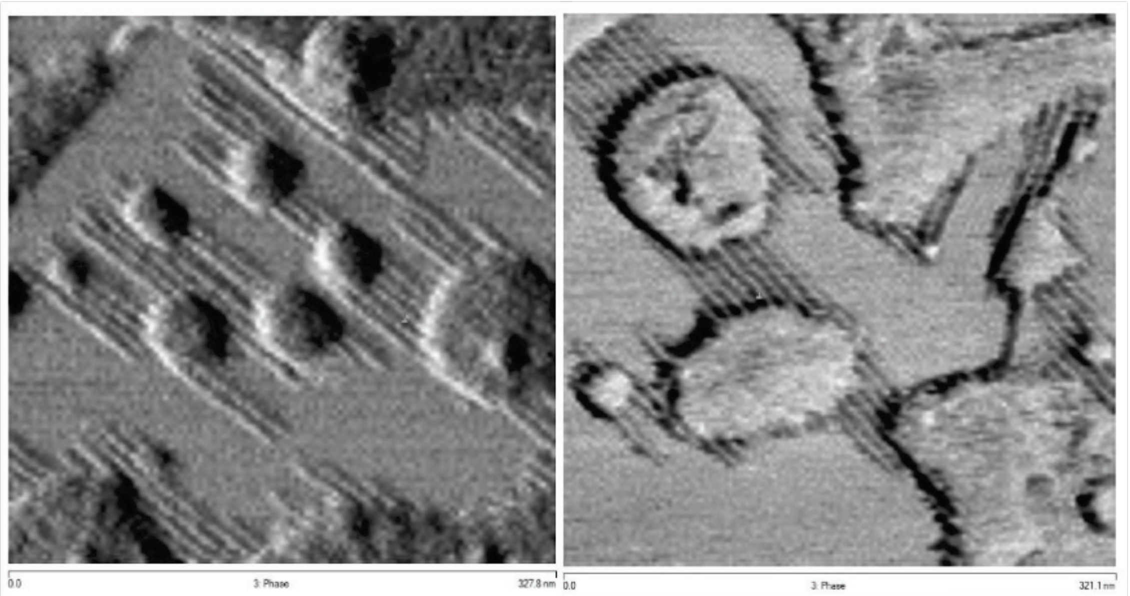


Figure S11. AFM images of poly-**4** showing monolayers of well packed polymer chains.

Langmuir-Schaefer instrument

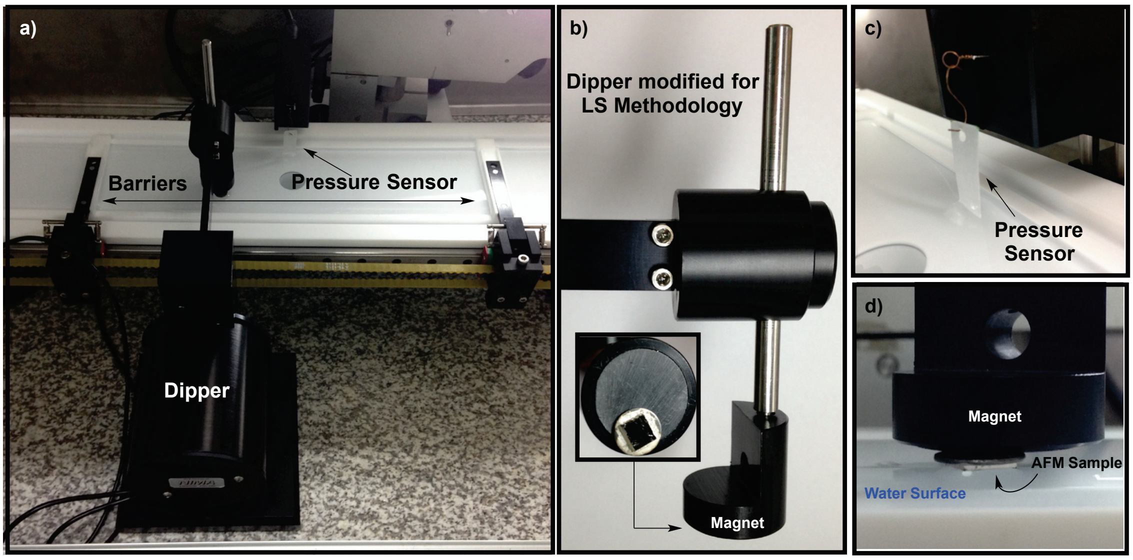


Figure S12. a) Picture of the Langmuir instrument used in this work. b) Picture of the dipper modified for the LS methodology and (inset picture) typical disposition of the AFM substrate on the magnet of the dipper. c) Pressure sensor of the system. d) Picture showing the interaction between the HOPG and the water surface during the exfoliation of the monolayer.

Supporting references

S1 I. Louzao, J. M. Seco, E. Quiñoá, R. Riguera, *Angew. Chem., Int. Ed.* **2010**, *49*, 1430-1433.

S2 F. Freire, J. M. Seco, E. Quiñoá, R. Riguera, *Angew. Chem., Int. Ed.* **2011**, *50*, 11692–11696.