Supporting Information

Epitaxial multilayers of alkanes on two-dimensional black phosphorus as passivating and electrically insulating nanostructures

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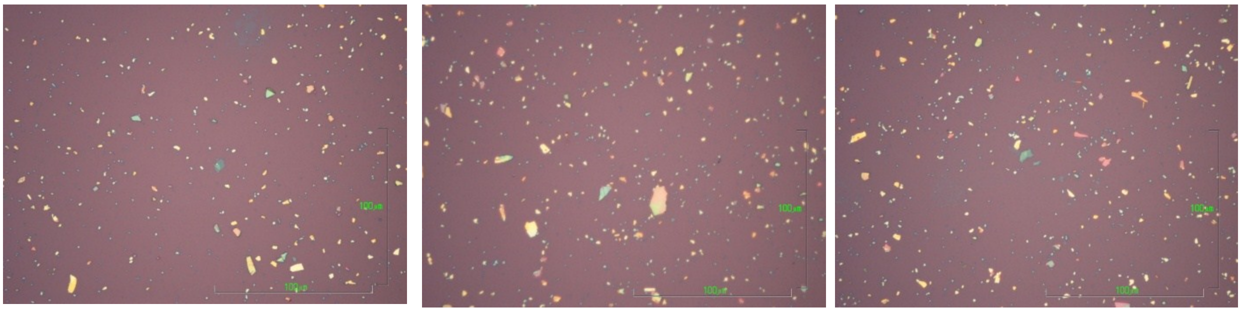

Figure S1. Optical microscopy images in different areas of a sample of mechanically exfoliated 2D bP on a Si/SiO_2 substrate.

Table S1. Parameters extrapolated from optical images in Figure 1a, b and c relative to grain coverage and size.

	Figure 1a	***Figure 1b***	***Figure 1c***
Relative coverage by grains on total image area (%)	*3.23*	*5.21*	*4.68*
Mean grain size (nm)	*1.04*	*1.28*	*0.90*

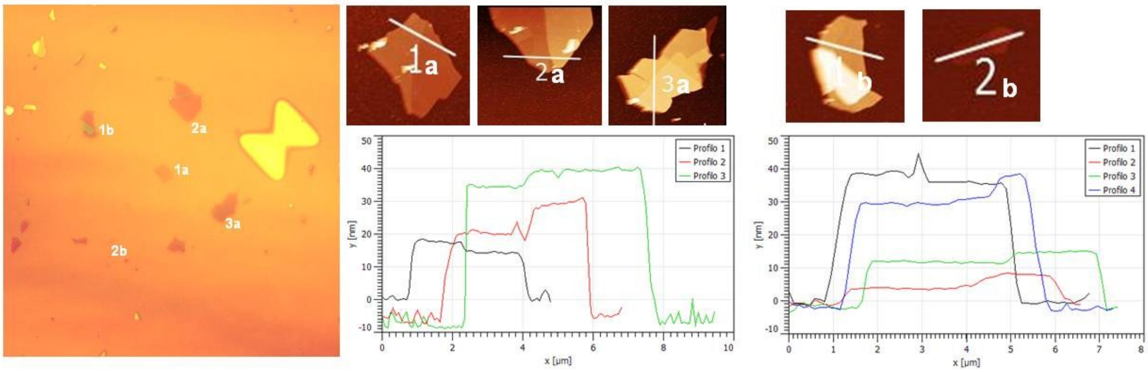

Figure S2. Left: Optical microscopy image of a sample of mechanically exfoliated 2D bP on a Si/SiO$_2$ substrate equipped with numbered reference points for mapping (i.e. butterfly mark in the image); Top: AFM height images of the flakes mapped with optical microscopy; Bottom: profiles along the lines on the flakes, as reported in images (b-f).

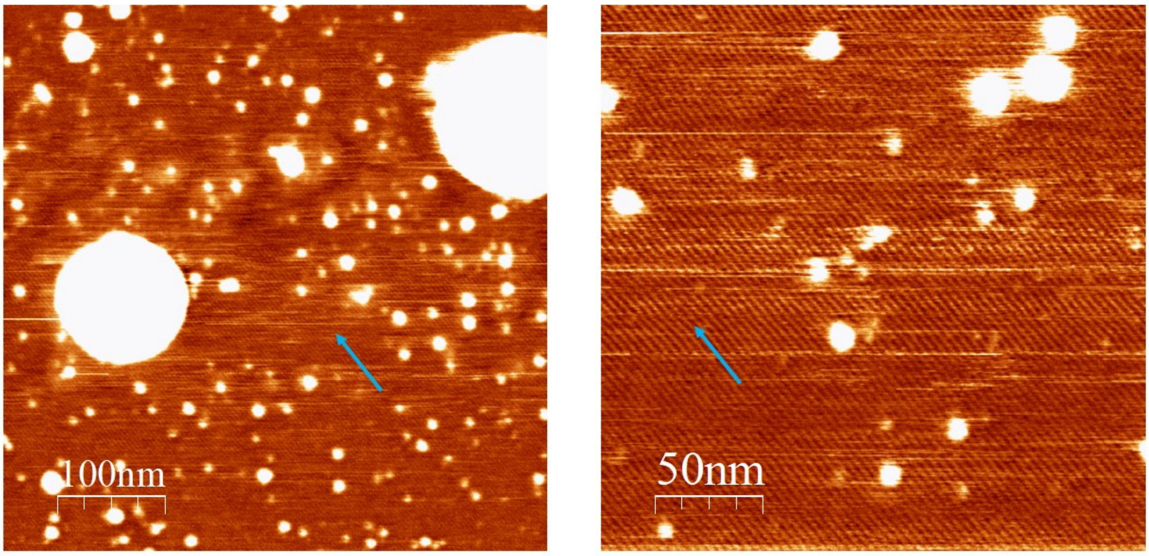

Figure S3. AFM tapping mode images of a C24 monolayer arranged on the surface of a bulk bP crystal. The sample was measured after one day of air exposure. Only one epitaxial orientation (indicated by the blue arrow) of the parallel lamellae of C24 molecules is detected on this scale. Bright features are products of bP oxidation in air.

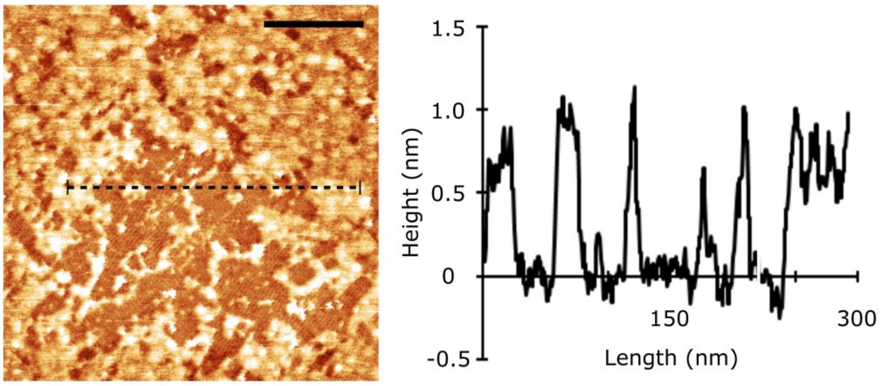

Figure S4. (Left panel): representative AFM micrograph of a 2D bP flake functionalized with a C24 monolayer from ethanolic solution (see main text figure 4). Scale bar is 100 nm. (Right panel): height profile along the dashed line plotted in the left panel, evidencing two phases having a height difference of 0.5 - 1.0 nm. The lower phase corresponds to ordered regions in the left panel.

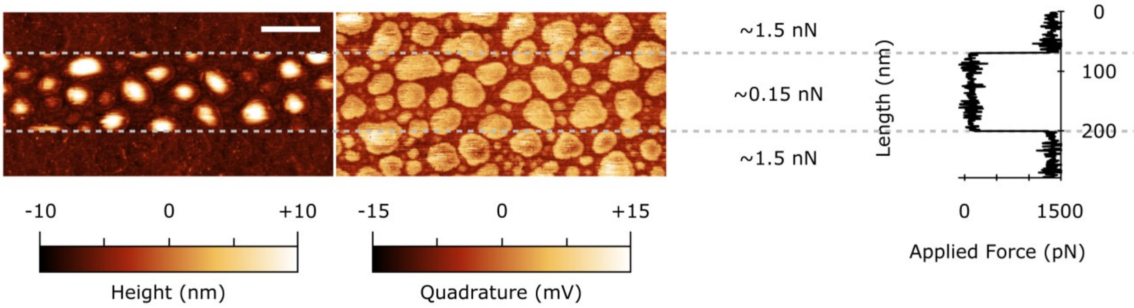

Figure S5. AFM micrographs: morphology (left) and quadrature (right) of a 2D bP flake functionalized with a C24 monolayer from ethanolic solution (see main text Figure 4), after 240 minutes of air exposure. The quadrature signal evidences diffuse oxidation damage, corresponding to raised dome-like features in the morphology plot (left panel, middle zone). Exerting a force of 1.5 nN on the raised features causes them to reversibly collapse into flat areas (left panel, top and bottom zones). Dashed lines separate zones with different applied maximum forces (plotted in the graph on the right).

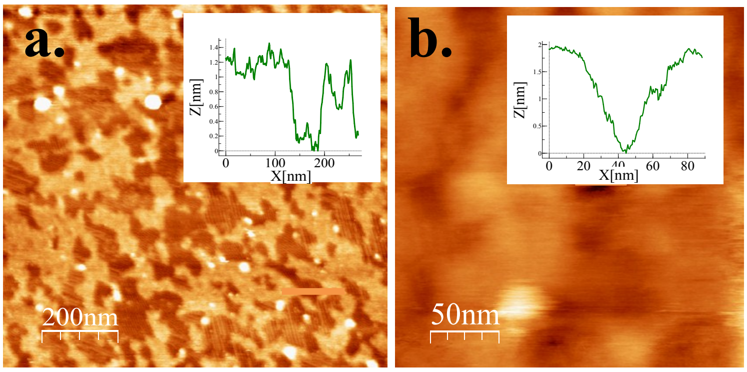

Figure S6. AFM height images of the optimized C24 multilayers on a 2D bP flake. (a) inset: height profile along the orange line in the main figure, indicating the thickness of the disordered/out of plane C24 domains with respect to the lowest plane of ordered C24 domains (1 nm);(b) inset: height profile, along the orange line in the main figure, of the scratch in one of the ordered C24 domains with respect to the underlying 2D bP surface (2 nm).

Molecular modeling procedure

bP was modelled using the interatomic potential described in the work of Sresht *et. al.* [1] Standard OPLS parameters were adopted for C24 molecules. Non-bonded interactions between C24 and bP were described by LJ parameters, obtained by geometric mixing rules. Electrostatic interactions were treated by the particle-particle particle-mesh (pppm) method and a cut-off of 1.0 nm was used for both Coulomb and van der Waals interactions. A time step of 1.0 fs was used, applying the Nose-Hoover thermostat for the simulations in the canonical ensemble (NVT) with time constant of 0.1 ps. Periodic boundary conditions (PBC) in 3 dimensions were applied.

The effect of the temperature on the morphology of C24 aggregates on bP was studied by annealing the equilibrated systems at higher temperatures by MD. Namely, the system was annealed at 320 K at a rate of 0.1 K ps^{-1}, equilibrated at 320 K for 5 ns, cooled to 300 K at a rate of 0.025 K ps^{-1} and equilibrated at 300 K for 5 ns.

The energetics and the dynamics of a small planar aggregate of C24 molecules on bP was assessed by MD simulations. To this end, 10 C24 molecules were initially aligned to form a planar cluster, with a morphology that is compatible with the in-plane structure of C24 crystals, and subsequently optimized in vacuum. The optimized layer was then inserted above the bP surface, varying the initial orientation angle $\boldsymbol{\varphi}$ (angle formed between *e1* and the long axis of each alkane molecule), and the system was equilibrated at 300 K for 5 ns. This procedure was repeated for different C24 orientations. In particular, C24 chains were inserted in the simulation box, above the bP surface, at $\boldsymbol{\varphi}$=0°, 25°, 55°, 75° and 90°. Equilibrating at 300 K the systems with the systems studied, we observed that C24 chains spontaneously arranged along the *e1* (zig-zag direction) and *e3* directions, namely at 0° and 55°, as represented in the Figures below. In particular, the systems with the initial configurations at $\boldsymbol{\varphi}$ = 0° and 55° did not change their orientation during the equilibration on the bP surface, while the alkanes with an initial orientation $\boldsymbol{\varphi}$=25°, 75° and 90° arranged at $\boldsymbol{\varphi}$=0° or 55°, during the equilibration at 300 K. The reorientation of the C24 chains is attributable to the more thermodynamic stability of the two orientations $\boldsymbol{\varphi}$ = 0° and 55°.

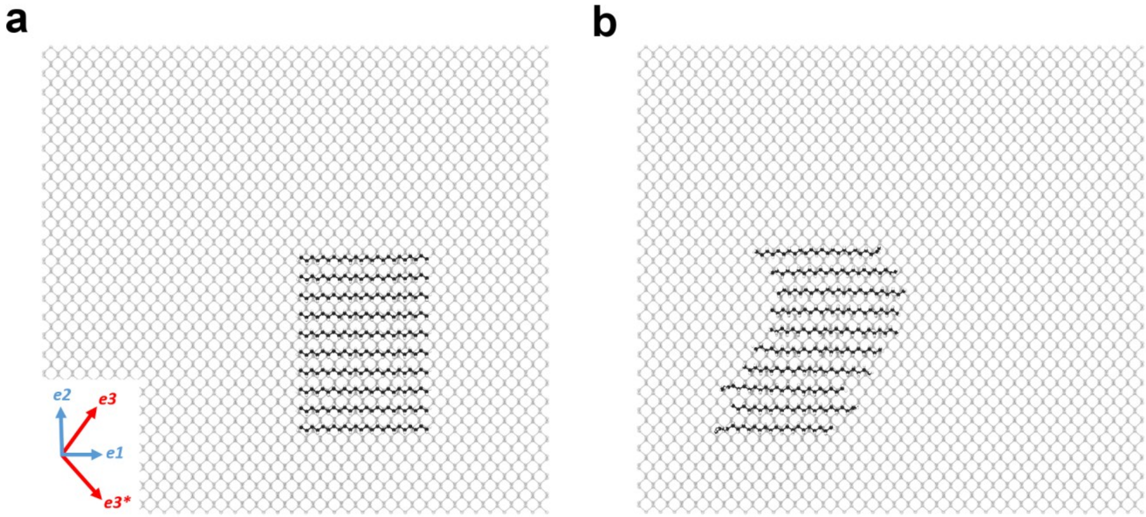

Figure S7. C24 with an initial orientation angle $\boldsymbol{\varphi}$=0°: configuration of the initial structure (a) and snapshot after the equilibration at 300 K (b).

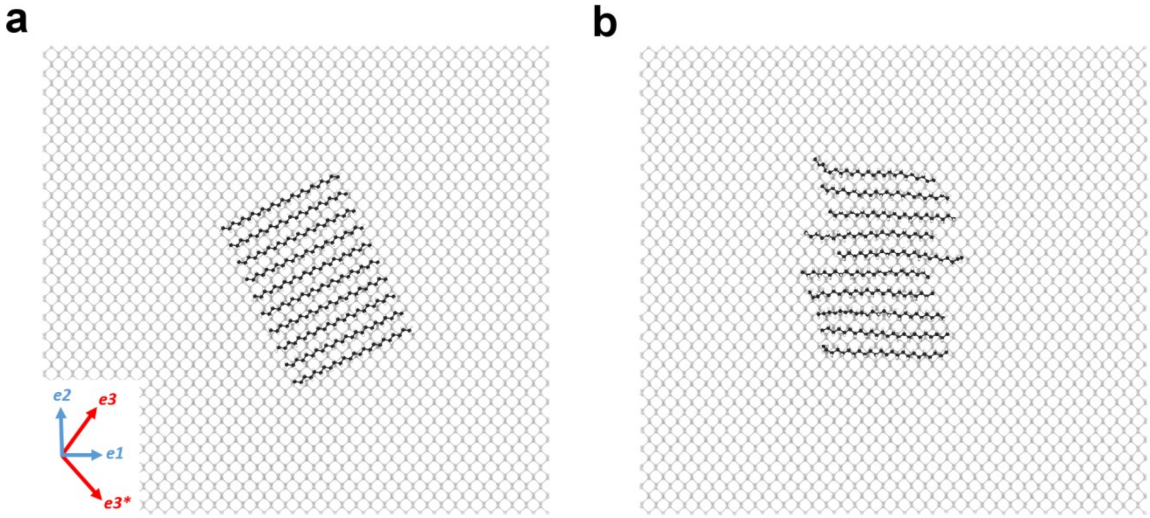

Figure S8. C24 with an initial orientation angle $\boldsymbol{\varphi}$=25°: configuration of the initial structure (a) and snapshot after the equilibration at 300 K (b).

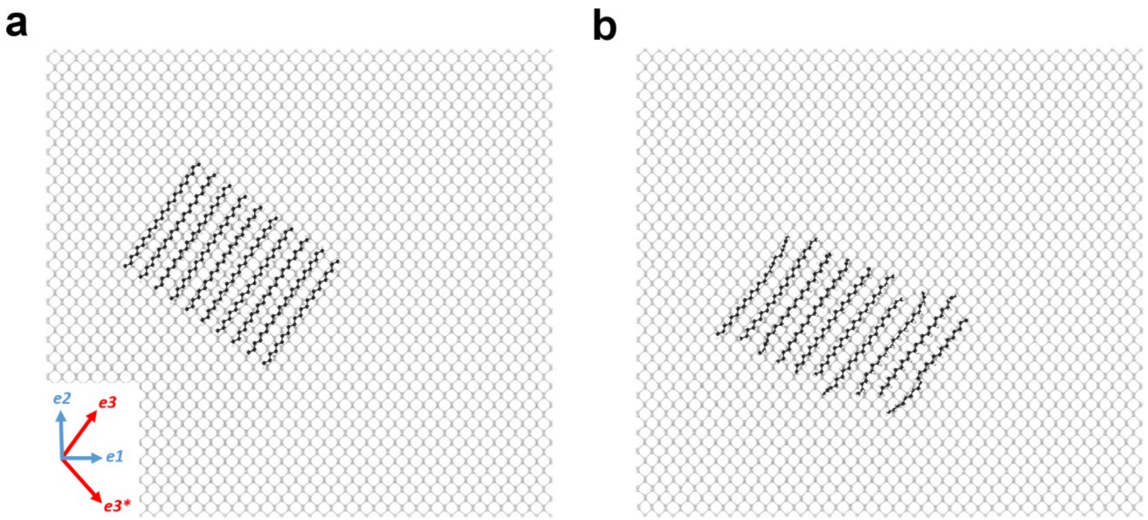

Figure S9. C24 with an initial orientation angle φ=55°: configuration of the initial structure (a) and snapshot after the equilibration at 300 K (b).

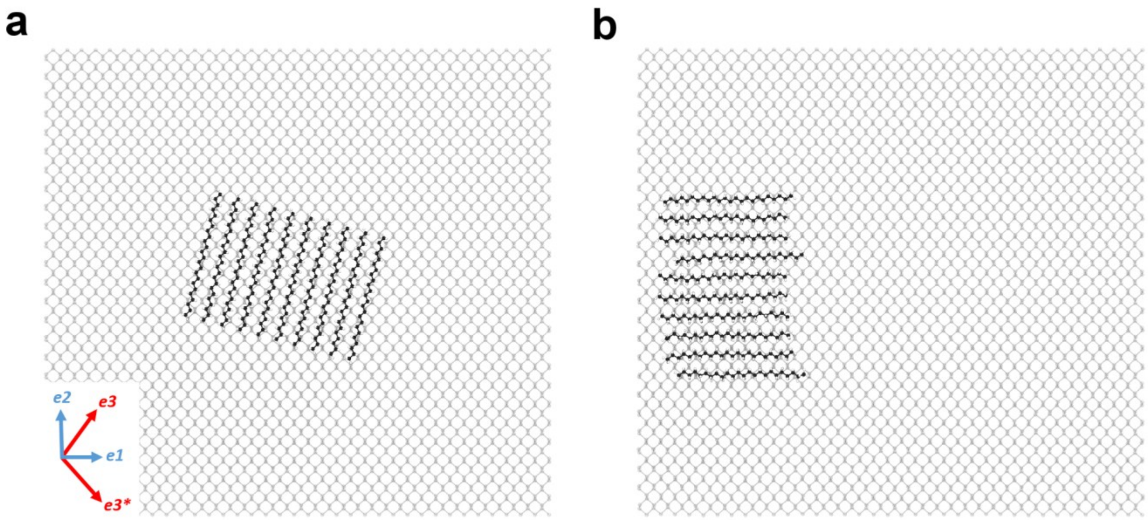

Figure S10. C24 with an initial orientation angle φ=75°: configuration of the initial structure (a) and snapshot after the equilibration at 300 K (b).

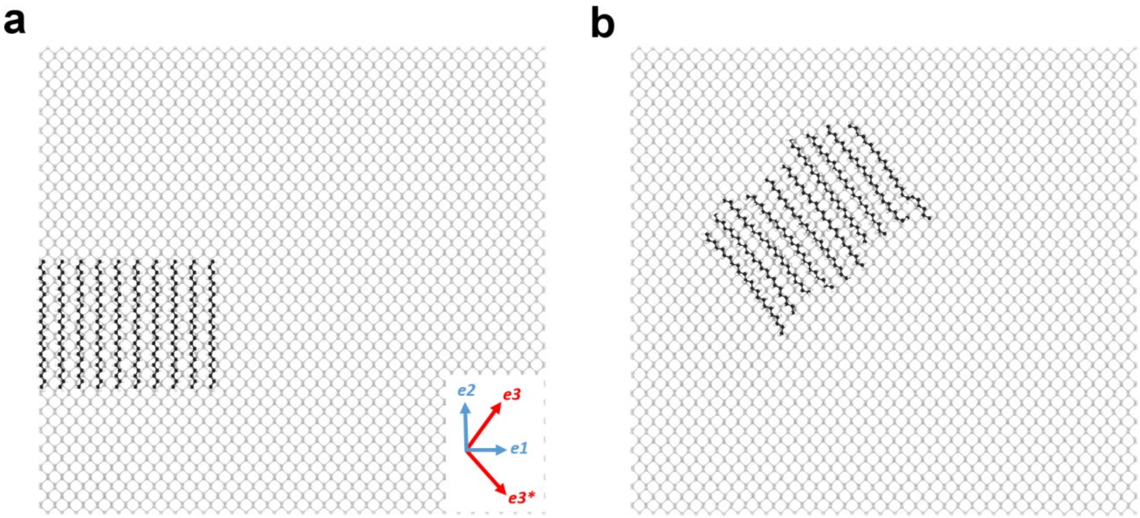

Figure S11. C24 with an initial orientation angle ***φ***=90°: configuration of the initial structure (a) and snapshot after the equilibration at 300 K (b).

The effect of temperature on morphology was also investigated by annealing the planar C24 clusters on bP in the two most favorable configurations (along *e1* and *e3* directions). In particular, the equilibrated structures of C24 at ***φ***≈0° and ***φ***≈55° were annealed and equilibrated at 320 K at a rate of 0.1 K ps^{-1}, equilibrated at 320 K for 5 ns, cooled to 300 K at a rate of 0.025 K ps^{-1} and equilibrated at 300 K for 5 ns., as described before. The C24 layer, initially oriented along *e1* direction, was essentially not affected by thermal annealing. Conversely, the C24 layer initially oriented along *e3* direction, underwent a dramatic relaxation, leading to a final equilibrated structure corresponding to ***φ***≈0°, suggesting this configuration as the most thermodynamically stable.

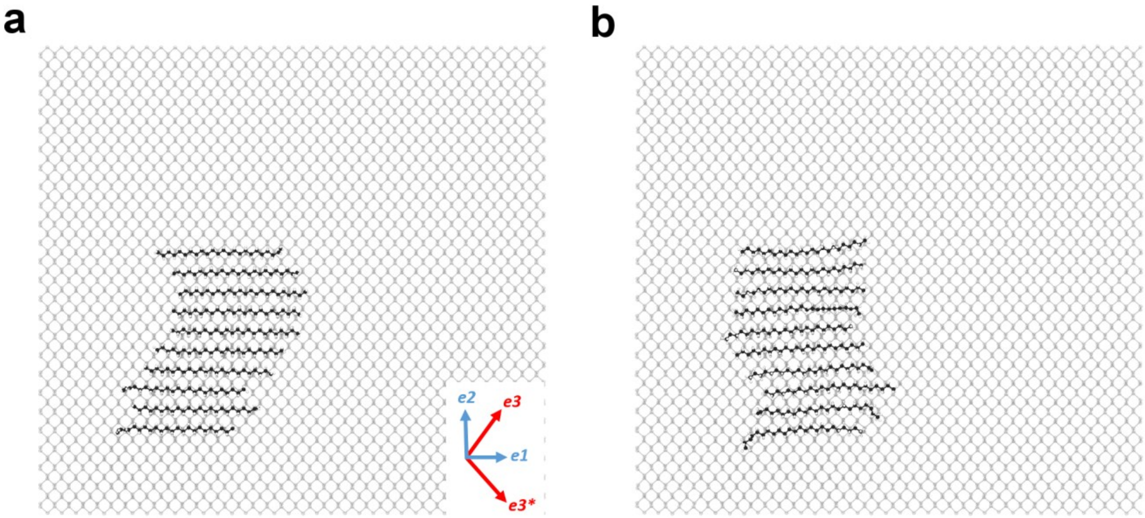

Figure S12. C24 with an orientation angle ***φ***=0° before (a) and after (b) the annealing at 320 K.

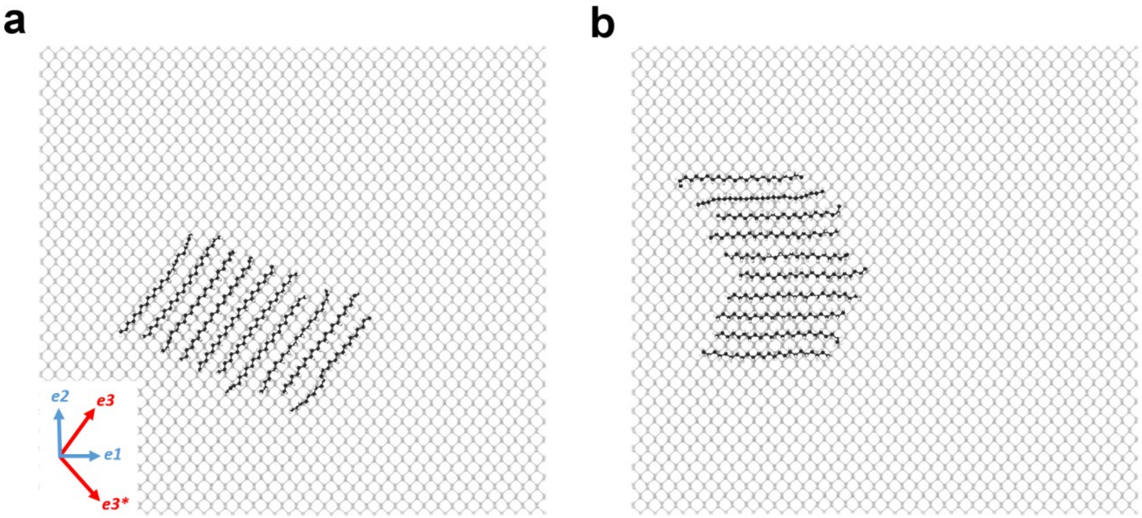

Figure S13. C24 with an orientation angle φ=55° before (a) and after (b) the annealing at 320 K.

Electronic calculations:

In order to further validate the results obtained with classical MD a series of simulations were carried out at DFT level of theory on smaller systems. DFT calculations were performed at the gradient-corrected level by applying the PBE exchange-correlation functional within the GPW approach as implemented in the CP2K program package. Grimme DFT-D3 dispersion correction was used throughout. Geometry optimisation were carried out employing the BFGS algorithm and tight convergence criteria. Electronic states were expanded by a double-ζ plus polarisation basis set, DZVP, with norm-conserving pseudo-potentials for the description of core levels and a plane-wave representation of the charge density with a cut-off of 500 Ry.

In all the calculations, periodic boundary conditions (PBC) in 3 dimensions were used for the simulation of the 2D systems, by inserting a vacuum region of about 1.5 nm along the direction perpendicular to the surface. The same series of calculations were reproduced for C24 chains on top of a stack of 3-layers bP (ABA stacking) for investigating the influence of BP structure obtaining essentially the same qualitative results.

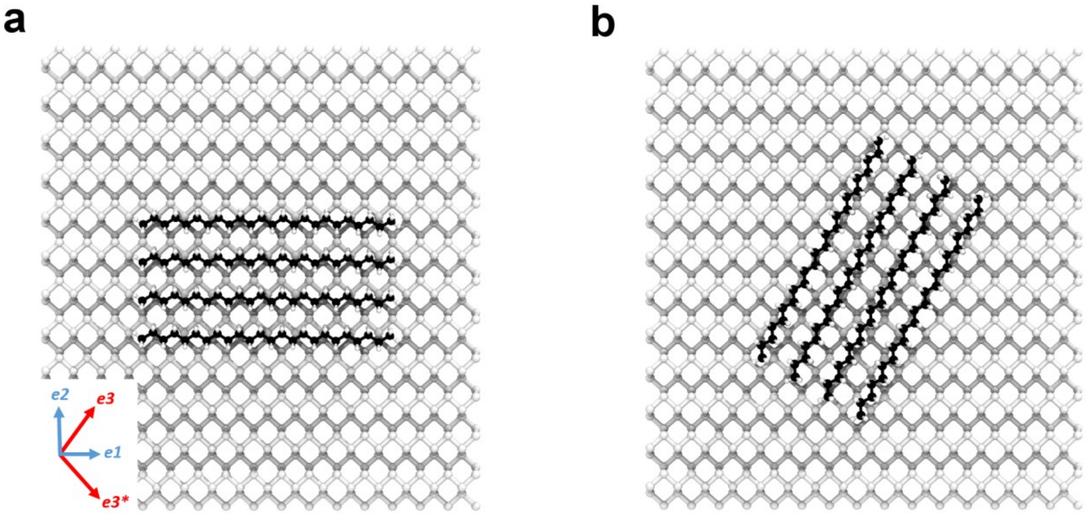

Figure S14. DFT-D3 optimized structures of C24 chains with orientations $\varphi = 0°$ (a) and $\varphi = 55°$ (b).

References:

[1] V. Sresht, A. A. H. Pádua and D. Blankschtein, *ACS Nano,* 2015, **9**, 8255.