Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Noncovalent passivation of supported phosphorene for device applications: from morphology to electronic properties

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## Electronic Supplementary Information

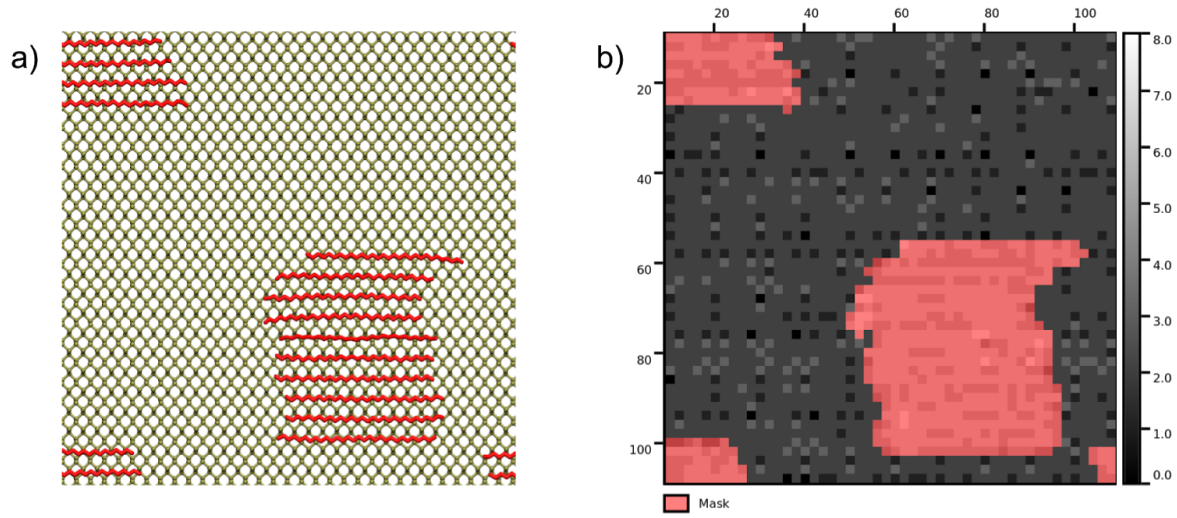


**Figure S1.** Determination of the surface area of phosphorene covered by alkane chains. The configuration obtained by MD (a) is first discretized by convolution with a van der Waals sphere with radius 2 Å and the covered surface area is computed by selecting all regions with an height that is higher than 4 Å with respect to the phosphorene surface.

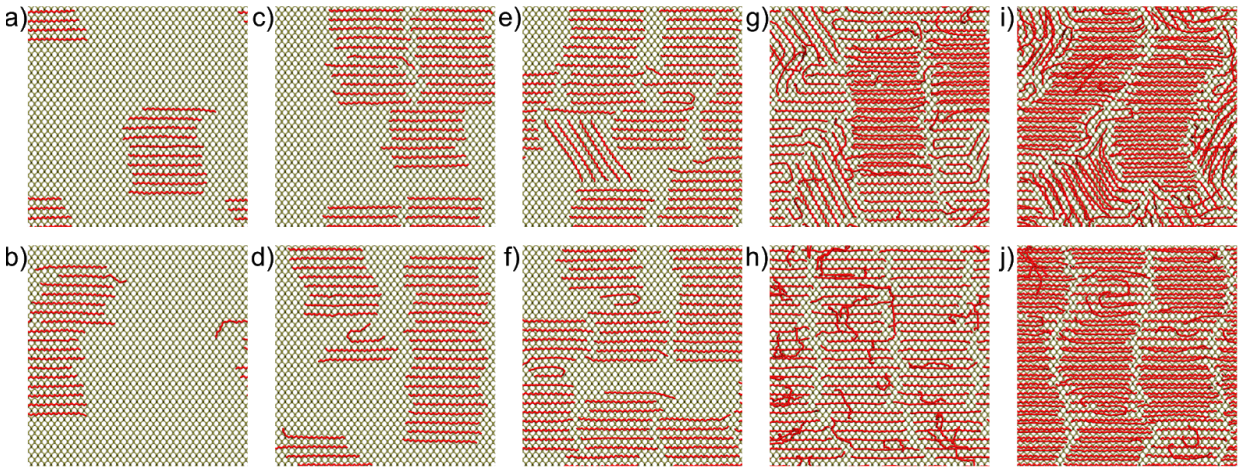


**Figure S2.** Equilibrated structures of C30 aggregates on phosphorene grown in kinetic (top) and thermodynamic (bottom) conditions, as a function of the coverage (a, b: Θ =0.25; c, d: Θ =0.50; e, f: Θ =0.75; g,h: Θ =1.50; i, j: Θ =2.00).

**Table S1.** Relationship between nominal coverage ($\Theta$) and effective coverage ($\eta$) for C30 alkane chains grown of phosphorene in kinetic and thermodynamic conditions.

| Nominal coverage ($\Theta$) | Effective coverage ($\eta$) | |
|---|---|---|
| | Kinetic conditions | Thermodynamic conditions |
| 0.25 | 0.26 | 0.26 |
| 0.50 | 0.53 | 0.52 |
| 0.75 | 0.80 | 0.77 |
| 1.00 | 0.99 | 0.99 |
| 1.50 | 0.99 + 0.51* | 1.00 + 0.40* |
| 2.00 | 1.00 + 0.94* | 1.00 + 0.91* |

*Coverage of the first monolayer + coverage of the second monolayer.

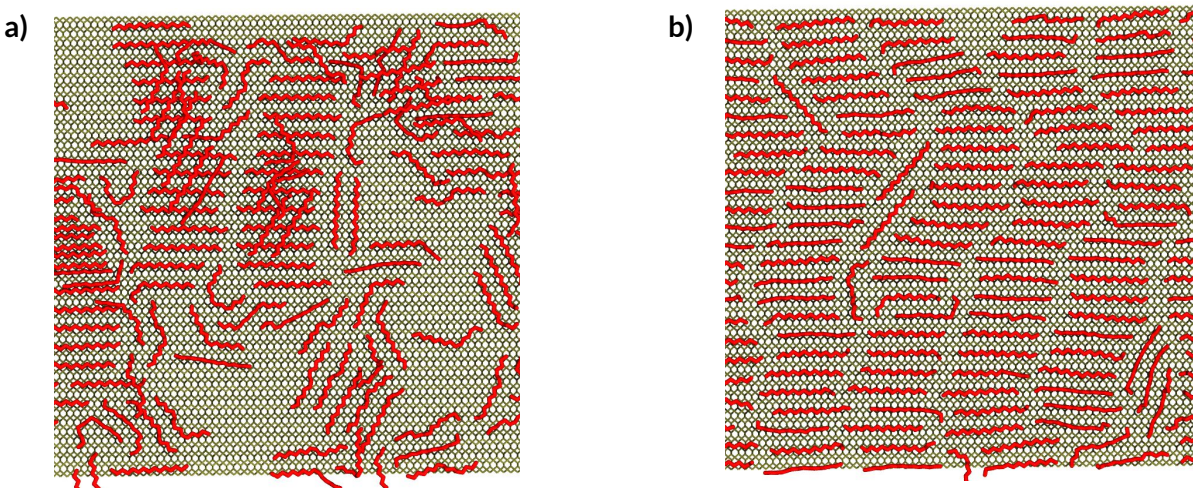


**Figure S3.** Configuration of C30 grown on a phosphorene layer model of about 10x10 nm at the nominal coverage $\Theta$=1.0 in strongly (interval of 10ps between insertion of new molecules) kinetically-controlled conditions a) before and b) after annealing at 400K for 20 ns and further equilibration at 300K for 10 ns.

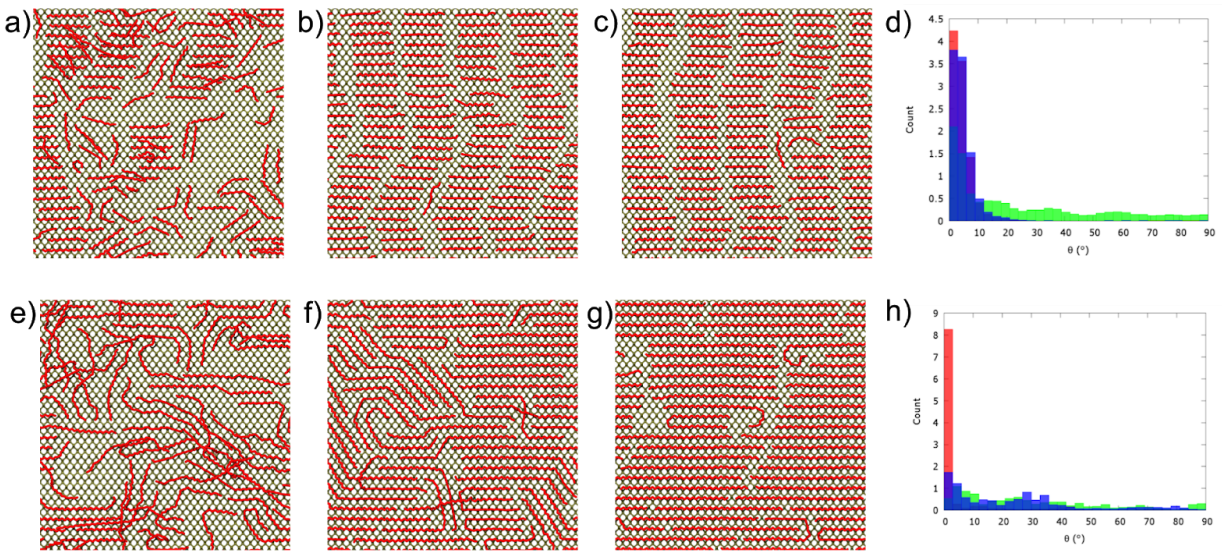


**Figure S4.** Configuration of C15 (top) and C45 (bottom) alkane chain aggregates on phosphorene as cast (a,e), and equilibrated in kinetic (b,f) and thermodynamic (c,g) conditions. Distribution of the angular parameter (d,h) for aggregates as cast (green bars), in kinetic (blue bars) and thermodynamic (red bars) conditions.

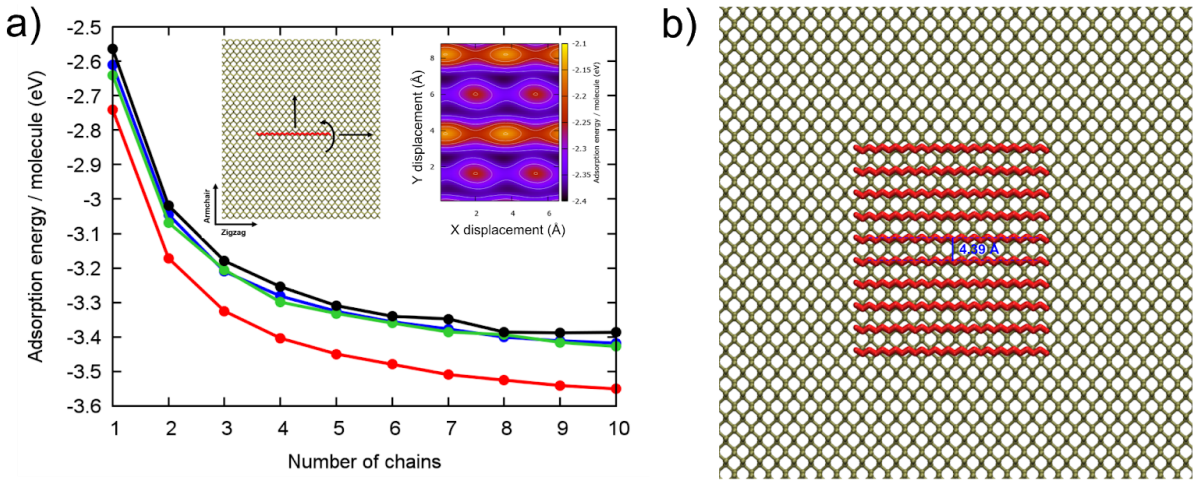


**Figure S5.** a) Adsorption energy for C30 alkane chain clusters on phosphorene as a function of the cluster size, for clusters oriented at $\phi$ = 0°(red curve), $\phi$ = 20°(blue curve), $\phi$ = 50°(green curve), $\phi$ = 90°(black curve). Energy values are computed by first scanning the potential energy surface of the cluster, rigidly translated on the phosphorene surface, followed by full geometry optimisation of the energy minimum. Inset: representative description of the procedure used to identify the local energy minimum for a single C30 alkane on phosphorene, at a distance of 3.55 Å from the mean plane of top phosphorus atoms, and energy map of a single C30 alkane chain on

phosphorene at $\phi$ = 0°. b) Relaxed configuration of a cluster of ten C30 alkane chains on phosphorene.

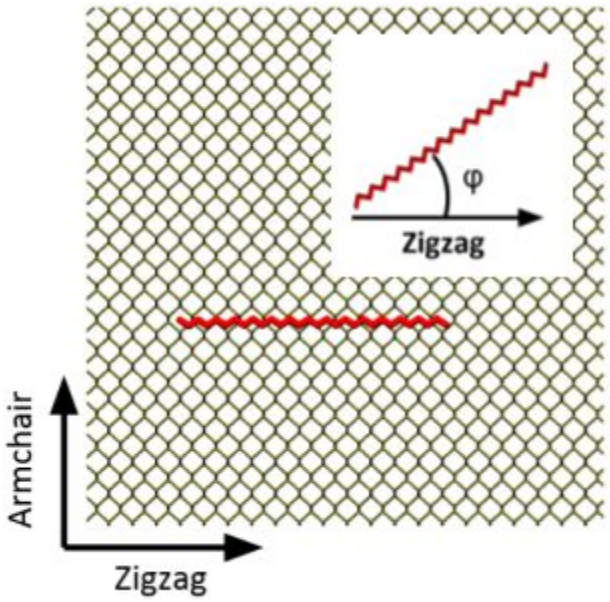


**Figure S6.** Configuration used for the evaluation of the interaction energies for single alkane chains on a phosphorene monolayer at the DFT level. Calculations were performed for C12 and C24 alkanes, as indicated in the Computational Details sections, including the Grimme correction (DFT-D3) for dispersion forces (J. Chem. Phys. 132, 154104 (2010)).

**Table S2.** DFT interaction energies evaluated for the configurations in Fig. S6.

| Chain length | $\phi$ (deg.) | Energy (eV) |
|---|---|---|
| C12 | 0 | -1.13 |
| | 55 | -1.10 |
| C24 | 0 | -2.27 |
| | 25 | -2.17 |
| | 55 | -2.20 |
| | 75 | -2.17 |

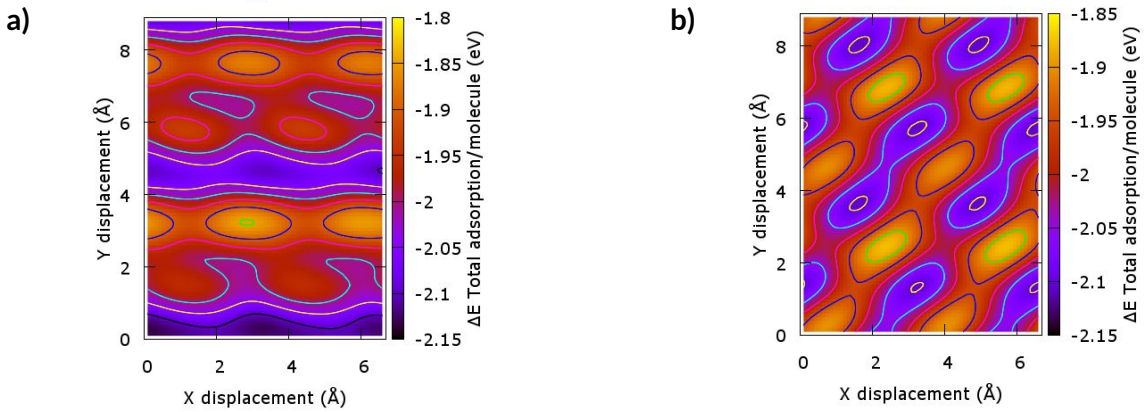


**Figure S7.** Scan of the force-field energy potential evaluated for a single C24 alkane chain rigidly translated at a constant distance of 3.50 Å with respect to the phosphorene surface and at an angle $\phi$ of a) 0° and b) 55°.