Supporting information

Chiral expression of adsorbed *(M-P)* 5-Amino [6] helicenes: from random structures to racemic crystals by surface alloying

S1. STM experiments and chemicals

The experiments were carried out in an ultrahigh vacuum system equipped with a variable-temperature STM from Omicron Nanotechnology. The base pressure of the chamber was in the low 10^{-10} mBar range.
The Cu(100) and Au(111) surfaces were prepared by cycles of sputtering with Ar at 1.5 keV and annealing at 770 K.
The **AH** molecules were evaporated from a resistivity heated BN crucible at a rate of about 0.2 monolayer (ML) per minute. The molecules were dosed on the Cu(100) and Au(111) surfaces at RT. During the evaporations the pressure was in the low 10^{-9} mBar range.
After the preparation, the samples were transferred to the STM sample holder cooled at 100K. The STM images were obtained at 100 K using W tips. Negative sample bias voltages correspond to occupied-state images. The thermal drift was compensated automatically in real time.

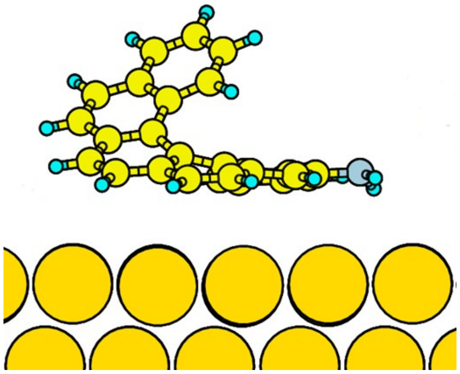
S2. Theoretical Methods

The DFT calculations were performed using the Quantum ESPRESSO package [1], which is an implementation of the plane-wave with ultrasoft-pseudopotentials approach. In order to treat adequately the vdW interactions, the correlation part of the energy was treated using the second version of van der Waals density functional (vdW-DF2) [2–5]. For the surface calculations we used the slab method with four layers, and with the upper one alloyed with Sn in the case of Sn-Cu(100) surface alloy. For all the relax calculations, we fixed the two lower layers while all other atoms are allowed to relax. We used a wave-function/charge cutoff of 30/300 Ry. For the adsorption of isolated amino-helicene (AH) on Au(111) we used a 5 × 5 supercell, and Brillouin integrations were done using a 3×3×1 k-points grid. For AH on Cu() we used a $(4\sqrt{2} \times 4\sqrt{2})R45^{o}$ supercell and a 3×3×1 k-points grid. Finally, for AH on Sn-Cu(100) we used a $(3\sqrt{2} \times 4\sqrt{2})R45^{o}$ supercell and a 4×3×1 k-points grid. The supercells used in this work are bigger than our previous published calculations [6,7], and therefore there are some small differences in the adsorption energy for AH on Au(111) and Cu(100).
The simulated STM images were calculated within the Tersoff-Hamann approximation [8], in the constant current mode.

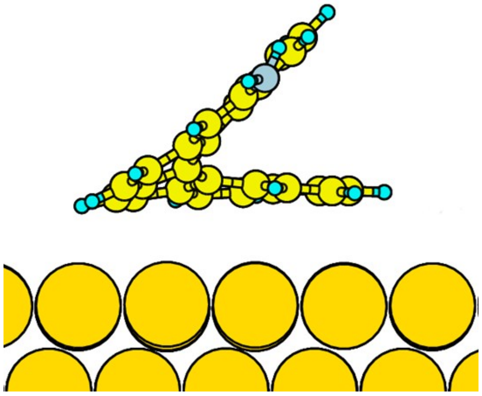
In order to estimate the adsorption energy corrugation we performed numerous calculations in the N-down configuration with different fixed xy-position of the N atom and changing the initial lateral orientation of the molecule. In this way we sampled the complex adsorption energy surface. In this case we used only the Gamma point for Brillouin integrations, except for the case of Au(111) where a 2x2x1 k-points grid was necessary to maintain a reasonable precision.

S2.1 AH/Au(111)

We considered both the molecule with the amine group close to the surface ("N-down" configuration) and the molecule with the amine group far from the surface ("N-up" configuration). The N-down configuration has the higher adsorption energy by 160 meV.



E_{ads} = 1.51 eV

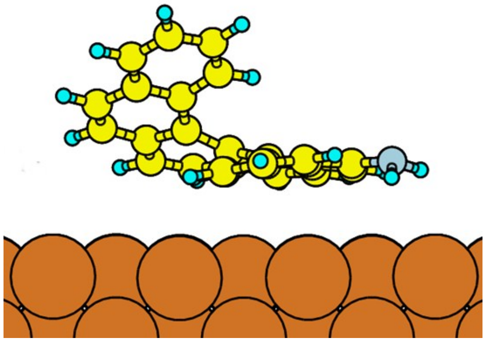


E_{ads} = 1.35 eV

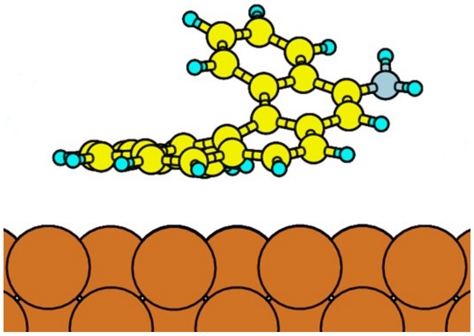
Adsorption energy corrugation: from 35 configurations 0.5 Kcal/mol

S2.2 AH/Cu(100)

As before, we considered both the N-down and N-up configurations. The N-down configuration has the higher adsorption energy by 90 meV.



$E_{ads} = 1.47$ eV

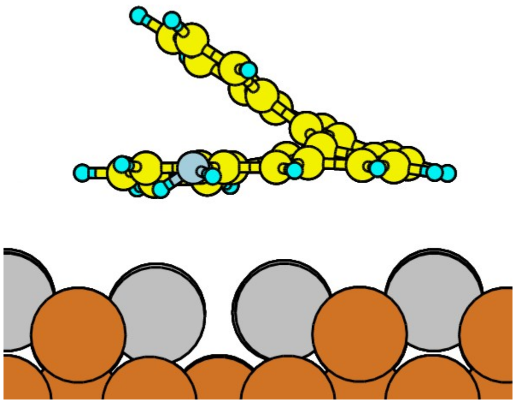


$E_{ads} = 1.38$ eV

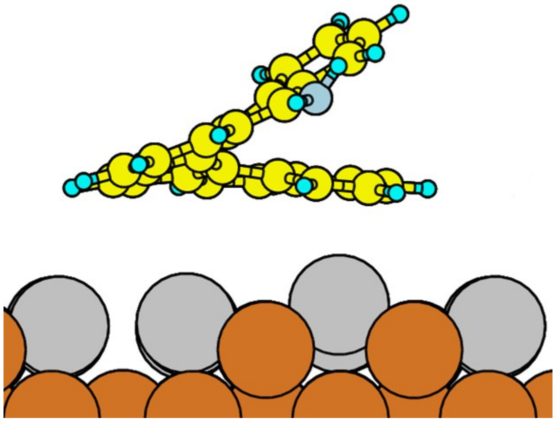
I **Adsorption energy corrugation**. From 35 calculations, we obtained a maximum difference from the optimal configuration of 110 meV (2,53 Kcal/mol) , with a mean value of E_{ads} lower by 60 meV (1.4 Kcal/mol)

S2.3 AH/Sn-Cu(100)

As before, we considered both the N-down and N-up configurations. The N-down configuration has the higher adsorption energy by 80 meV.



$E_{ads} = 1.16$ eV



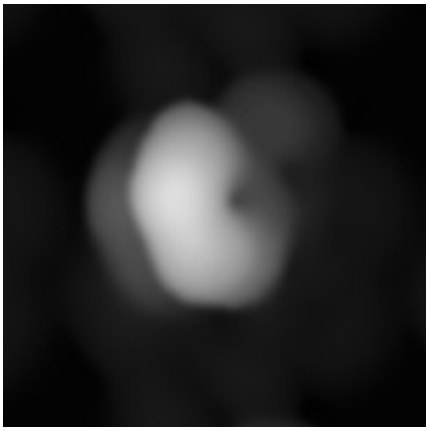
$E_{ads} = 1.08$ eV

We also estimated the **adsorption energy corrugation** as for the Cu(100) surface. In this case we performed 45 calculations, and we obtained a maximum difference from the optimal configuration of 55 meV (1,26 Kcal/mol), with a mean value of E_{ads} lower by 30 meV (~0.7 Kcal/mol)We can see that the surface alloying reduce the adsorption energy corrugation by half.

S2. 4 STM of AH/Cu(100)

We simulated STM images for isolated AH molecules adsorbed on Cu(100) in both N-up and N-down configurations. We used a bias voltage of -2V. We can see that the main difference is that the N-down configuration appears as a larger spot than the N-up configuration. Moreover, both simulations are shown in the same grey scale and we can see the spot for N-up is slightly darker.

N-down



N-up

S2.5 Racemic model

The model for the racemic ordered phase on Sn-Cu(100) consists of rows formed by the N-up dimers of molecules with the same chirality, linked by N-down molecules of the opposite chirality. The ordered phase alternate rows of MM dimers linked by P molecules, with rows of PP dimers linked by M molecules. A detailed description of all the calculations that support this model on Au(111) was described in [7]. To obtain the optimal structure we performed an unsupported (without substrate) relaxation where we fixed the unit cell as the experimental one on Sn/Cu(100). Moreover, to simulate the interaction with the surface we kept the z-position of the three lower C-rings of the N-down molecules fixed at the corresponding height of the lowest energy configuration when adsorbed on the surface.

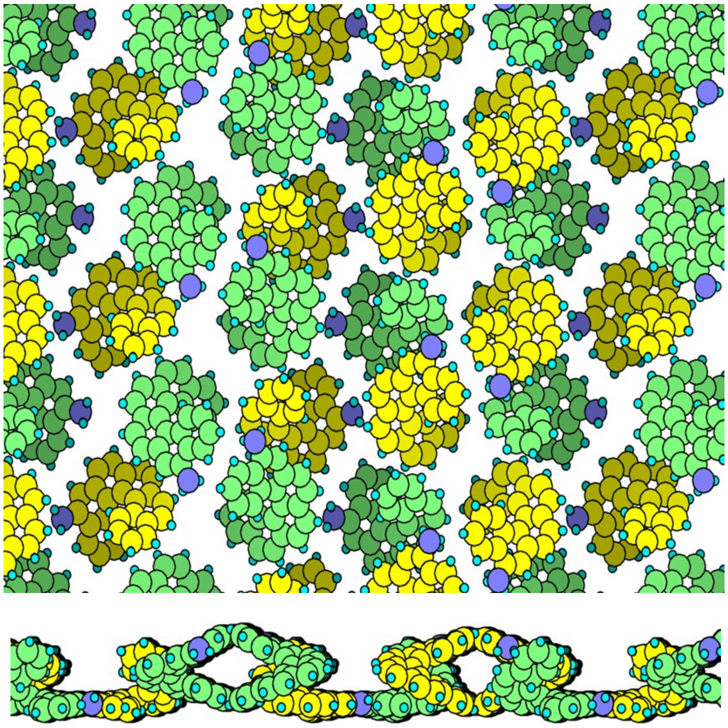
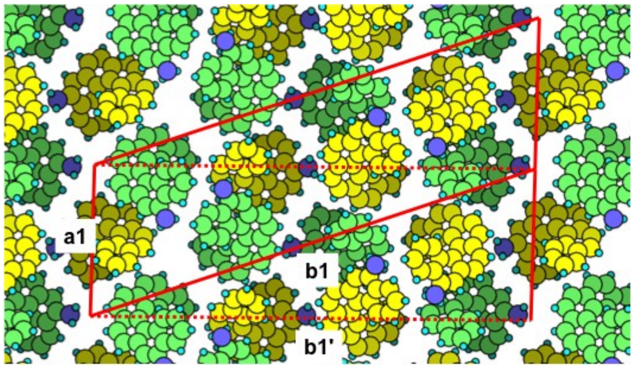


Figure S2: Model for the racemic ordered phase. The color of the molecule denote its chirality: P (green) or M (yellow). There are two molecular configurations: (i) N-up molecules forming MM or PP duplets, which are partially detached from the surface; (ii) N-down molecules which the duplets with the opposite chirality

Experimental cell on Sn/Cu(100)

"Rectangular”: a1 = 15 A, b1' = 45 A, a1^a2=89º

“Oblique”:   a1 = 15A, b1 = 46.4 A, a1^a2=73º



For comparison purposes, the Experimental cell on Au(111) is

“Oblique”: a1 = 14A, b1 = 45 A, a1^a2=74º

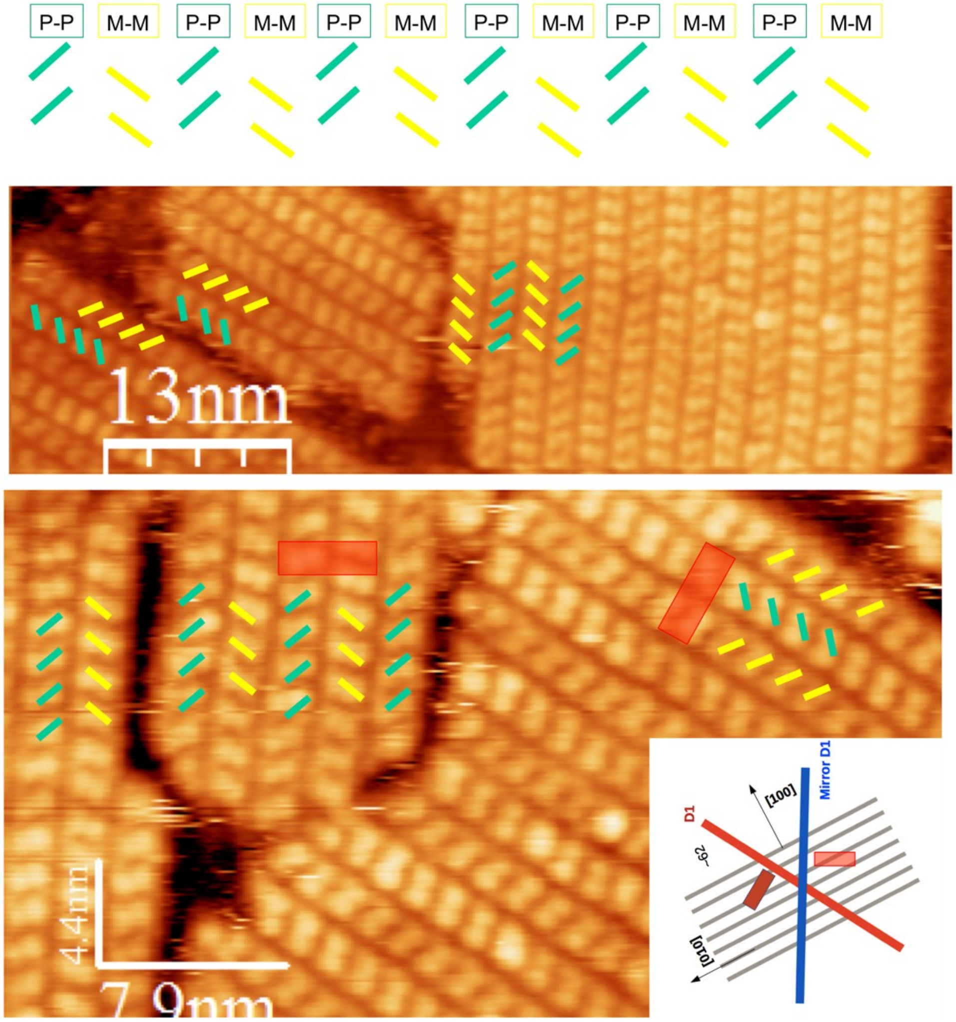


Figure S2.1 2   Islands of AH on Sn/Cu(100). Both equivalent MM-PP or PP-MM starting domains can growth in 2 directions rotated by +/-62 degrees from the [100] surface direction.

S3 Estimation of racemic model adsorption energy

We have then estimated the energy of the model as follows. (i) We start from the relaxed configuration of the racemic model obtained from an unsupported calculation. For this relaxation we kept fixed the unit cell as the experimental one (the unit cell measured on the surface alloy is very similar to that obtained on Au(111)). Moreover, to simulate the interaction with the surface, we fixed the z-positions of the three lower C-rings of the N-down molecules to those of the lowest-energy adsorbed configuration. (ii) We then estimate the adsorption energy of the racemic model on the surface with two contributions:

$E_{\text{model}} = E_{\text{mol-mol}} + E_{\text{mol-surf}}$

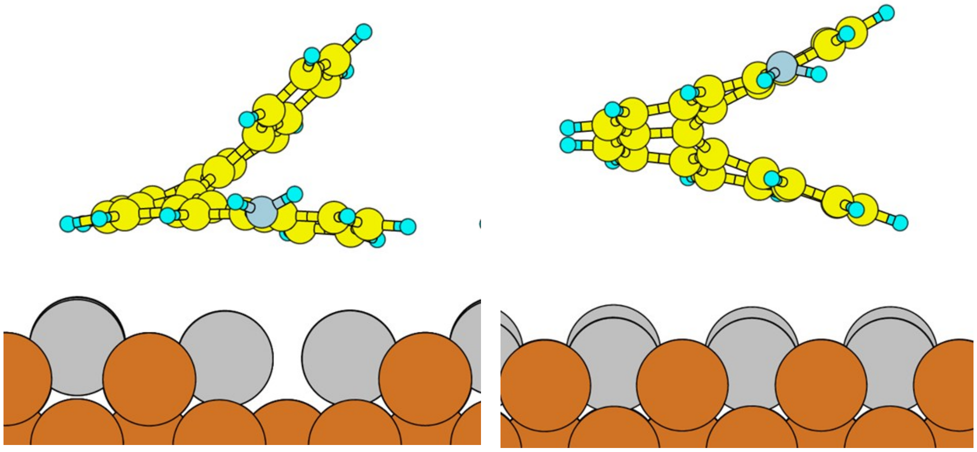
The first term corresponds to the inter-molecular interaction calculated as:

$E_{\text{mol-mol}} = E_{\text{model-unsup}} - 4\,E_{\text{N-down-unsup}} - 4\,E_{\text{N-up-unsup}}$

with $E_{\text{N-down-unsup}}$ and $E_{\text{N-up-unsup}}$ the energies for isolated molecules with exactly the same configuration as in the racemic model. The second term is calculated as:

$E_{\text{mol-surf}} = 4\,E_{\text{N-down-ads}} + 4\,E_{\text{N-up-ads}}$,

where $E_{\text{N-down-ads}}$ and $E_{\text{N-up-ads}}$ are the adsorption energies for isolated molecules deposited on the surface, but with the same configuration as in the racemic model. The reference for the distance of the molecules to the surface is the three fixed lower C-rings of the N-down molecules. The following figure shows this two configurations for the case of the Sn-Cu(100) surface:



This is a first approximation to the racemic model energy which does not take into account several aspects of the real model deposited on the substrate: (i) the change of the inter-molecular interaction due to the presence of the surface; (ii) the different adsorption energies due to the different registry of the molecules, specially for the N-down molecules, which determine the orientation of the lines with respect to the substrate; (iii) further relaxation to maximize the interaction with the surface at expense of the inter-molecular interaction.

In the following table we present the contribution of the two terms for each surface that we have considered. The term $E_{\text{mol-surf}}$ is shown in the table as change in adsorption energy with respect to the lowest energy configuration.

	$\Delta E_{\text{mol-surf}}$ (eV)	$E_{\text{mol-mol}}$ (eV)	E_{model} (eV)
Cu(100)	3.66	-4.10	-0.44
Au(111)	3.62	-4.13	-0.51
Sn-Cu(100)	2.93	-4.05	-1.19

S4 Racemic Model Commensurability on Sn/Cu (100) and Cu (100). The effect of the adsorption-potential corrugation.

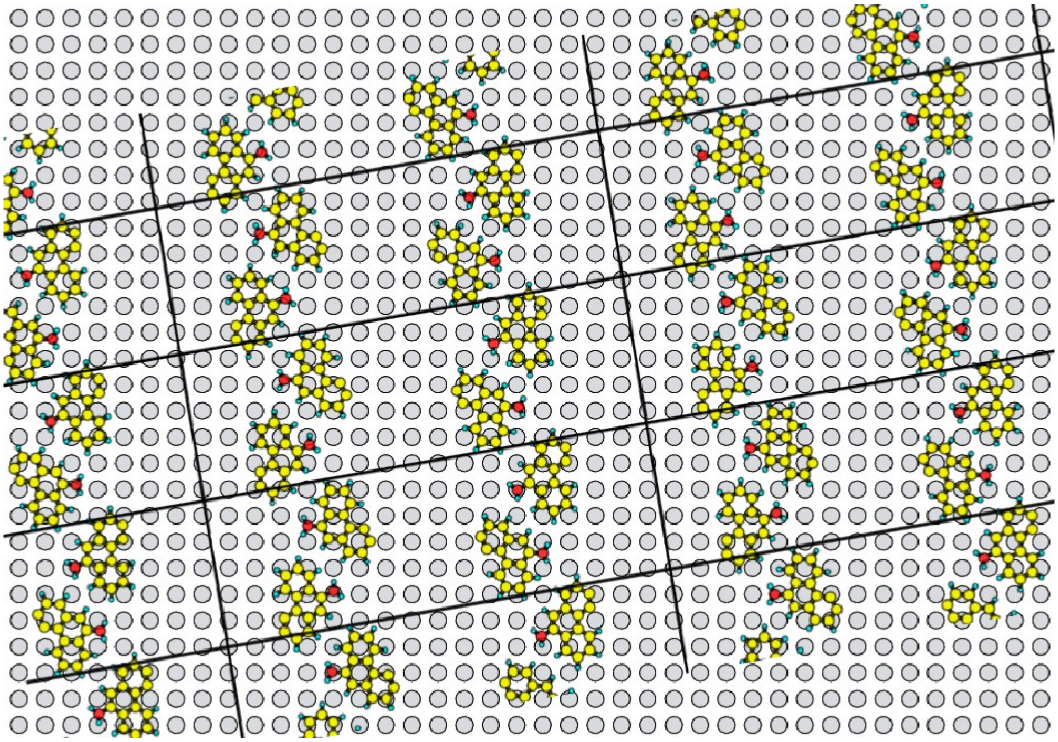
The well-defined angle of island growth (+/- 62 with respect to the [010] direction of the alloy) is the result of many interactions. Unfortunately, the gas phase structure of the racemate on the alloy is not commensurate and therefore it is not possible to assign well-defined adsorption sites on this surface for the whole assembly.

To illustrate the effect of the adsorption sites on the formation energy of the racemic model, we analyzed the case of the Cu(100) surface since it shows the highest adsorption-potential corrugation. To this aim we accommodated the model on this surface trying to maximize the number of AH molecules adsorbed with the amino group in atop sites.

To obtain an structure that is close to conmensurability on the Cu(100) surface we need to rotate the racemic model ~10° with respect to the [110] surface axis. The following figure present this configuration, for better visualization we show the substrate and only the three low-lying C-rings of the N-down AH molecules.
With this configuration we can have two of the four N-down molecules with the amine group close to its preferred atop position, and the other two close to bridged positions. Taking into account the difference in adsorption energies, we can estimate that the loss in the racemic model formation energy is ~0.2 Kcal/mol per molecule. The approximate net energy gain of this racemic structure (E_model) on Cu(100) will be reduced then from 1.3 to ~1.1 Kcal/mol per molecule, significantly lower than on Au(111) (1.5 Kcal/mol).

The other consequence of the remarkable difference in the adsorption-potential corrugation between the Cu(100) and Au(111) surfaces, is a reduced molecular mobility in the former case. Therefore, if the racemic structure were stable as suggested by the above estimation, more time would be needed to form it on Cu(100). This effect could be important in the experiments reported in this article where the cooling rate was relatively high (~ 5K/min).

In summary, the two analyzed effects originated on the higher adsorption-potential corrugation of Cu(100) with respect to Au(111) are consistent with the observed results.



References

[1] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, and et.al. J. Phys.: Condens. Matter, 21:395502, 2009.

[2] M. Dion, H. Rydberg, E. Schroder, D. C. Langreth, and B. I. Lundqvist. Phys. Rev. Lett., 92:246401, 2004.

[3] T. Thonhauser, V. R. Cooper, A. Puzder S. Li, P. Hyldgaard, and D. C. Langreth. Phys. Rev. B, 76:125112, 2007.

[4] G. Roman-Perez and J. M. Soler. Phys. Rev. Lett., 103:096102, 2009.

[5] K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist, , and D. C. Langreth. Phys. Rev. B, 82:081101, 2010.

[6] H. Ascolani, M. W. van der Meijden, L. J. Cristina, J. E. Gayone, R. M. Kellogg, J. D. Fuhr and M. Lingenfelder, Chem. Commun., 2014, 50, 13907.

[7] M. W. van der Meijden, E. Gelens, N. Murillo Quirós, J. D. Fuhr, J. E. Gayone, H. Ascolani, K. Wurst, M. Lingenfelder, and R. M. Kellogg, Chem. Eur. J. 2016, 22, 1484 – 1492.

[8] J. Tersoff and D. R. Hamann. Phys. Rev. B, 31:805, 1985.