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Van der Waals interactions in the self-assembly of 5-amino[6]helicene on Cu(100) and Au(111)†

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A combination of Scanning Tunnelling Microscopy and Density Functional Theory simulations highlights the role of van der Waals interactions in the self-assembly of an aminohelicene on Cu(100) and Au(111).

Chirality is a simple geometrical property that has tremendous implications for molecular recognition and biological function. As a consequence, there is an active research community working to elucidate the basic principles behind chiral phenomena.

Over the past 15 years, scanning tunnelling microscopy (STM) studies have shown that chiral expression can be explored in great detail for molecules adsorbed on metal surfaces.[1–3] Two main aspects determine chirality on 2D systems: the intrinsic chirality of the adsorbate (molecular chirality) and the chirality of the bonding geometry, *i.e.* the positions at which the molecules bind to the surface (footprint chirality).[4]

Particularly interesting model systems are helicenes, compounds with *ortho*-condensed aromatic rings presenting axial chirality. They have a fascinating chemistry due to their unique screw shaped π conjugated system. Promising applications in non-linear optics, sensors and asymmetric catalysis have recently been reviewed.[5]

While very detailed studies have been made for carbohelicenes on different solid surfaces[2,6,7] the study of functionalized helicenes with heteroatoms or polar groups and the influence of the substituents in the self-assembly is relatively new. A few examples are: [11]anthrahelicene,[8] hexathia[11]helicene,[9] heptahelicene-2-carboxylic acid,[10] 6-13-dicyano[7] helicene.[11,12] Very recently, 5-amino[6]helicene (**AH**) has been synthesized[13] and its self-assembly has been characterized at the liquid/solid interface.[14] Here we report the first investigation of these amino helicenes under ultra-high vacuum (UHV) and compare the self-assembly on Cu(100) and Au(111). **AH** represents an interesting model system for the study of the interplay of van der Waals (vdW) and H bonding groups and their influence on the chiral footprint of the enantiopure adsorbates on a solid surface. The adsorption of enantiopure *M*-**AH** on pristine Cu(100) was studied as a function of the molecular coverage. Fig. 1a–c shows STM images obtained at low, intermediate and high coverage, respectively.

Each molecule appears as a 1 nm blob indicating that tunnelling is mainly from the uppermost C6 ring of the face-on spiral, in agreement with previous measurements.[2,14] All molecular depositions were done with the surface at room *T*, while the images were acquired at 100 K.

It is interesting to observe the evolution of supramolecular assemblies: At low % of monolayer (ML) coverage the molecules adsorb preferentially at the step edges. In addition, small groups of *M*-**AH** diffuse onto the terraces. Even at these low temperatures the molecules are still highly mobile on the Cu surface: molecules diffuse away while recording the STM images, giving rise to the typical "spikes" and "cut off" features seen in Fig. 1a. Within the highly mobile phase, we could identify single molecules and supramolecular structures formed by 2, 3 or 4 molecules (circles and insets in Fig. 1a).

At intermediate coverage (60% ML), the molecules start to form rows oriented at 90° from each other (Fig. 1b). Finally, at high coverage (90% ML), two ordered structures (I and II in Fig. 1c) emerge. The two oblique unit cells are rationalized in terms of rotational domains, reflecting the C_4 rotation symmetry of the substrate. Structures obtained by reflection of domain I or II were not observed for *M*-**AH**; symmetry considerations indicate that those domains would only be expressed by *P*-**AH**.[15] The structure is formed by subunits of 4 molecules. Fig. 1d shows a high-resolution area of domain I. The unit cell vectors (**al**, **bl**) are rotated by 77° from each other with a length of (2.4 ± 0.2) nm. The vector **al** is rotated by 8° with respect to the main [110] Cu direction (black arrow Fig. 1).

To gain insight into the adsorption geometry we performed density functional theory (DFT) calculations (S2, ESI†). We calculated the adsorption of a single molecule on Cu(100) both with the NH_2 pointing away (N-up) or towards (N-down) the Cu

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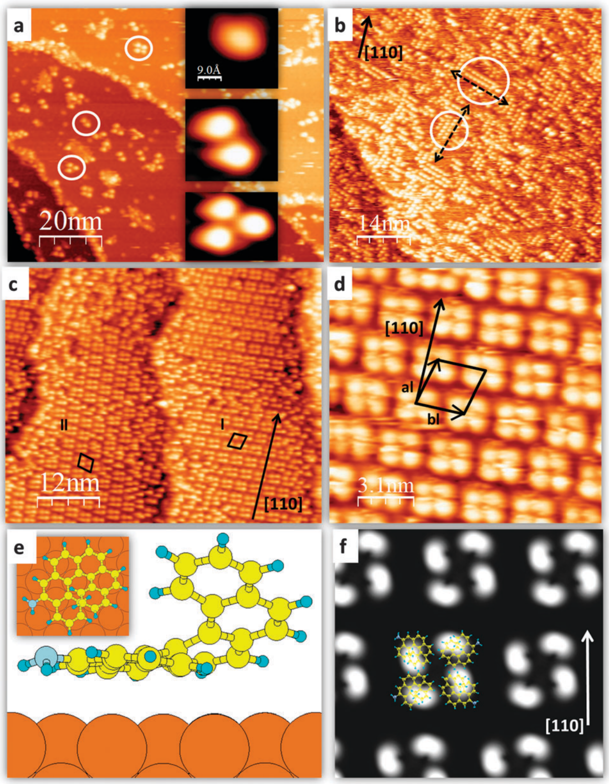

Fig. 1 STM images of *M*-**AH** on Cu(100). (a) Low coverage, insets and circles show the single molecules, duplets, triplets and quadruplets diffusing on the surface (−2 V, 50 pA). (b) 60% ML coverage, the circles and arrows indicate the formation of double rows (−2 V, 15 pA) (c, d) 90% ML coverage, in black the unit cells for the 90° rotamers (I, II) (**al** = **bl** = 2.4 nm) (−2.2 V, 10 pA), (e) DFT model of the single molecules on Cu(100), top and lateral view, (f) simulated image of calculated cell (S3, ESI†).

surface (Fig. S1, ESI†).‡ Calculations performed with the NH_2 interacting with the Cu (N-down) resulted in higher adsorption energies by ~1.85 kcal mol^{-1}. The self-assembly of molecules on Cu is greatly influenced by the presence of unsaturated rings and their preference for adsorption on hollow sites on Cu(100).[16] According to our model (Fig. 1e), the adsorption geometry with three C6 rings parallel to the surface[2,6,7] at a 3.1 Å C6–Cu distance determines the molecular footprint on the surface. The N–Cu bond at 3.4 Å contributes to the interaction to a much lesser extent. To have a stronger interaction the NH_2 would need to switch from a planar sp^2 to a sp^3 configuration implying the rigid tilting of 3 C6 rings away from the surface, weakening considerably their interaction with the surface.[17,18]

Further information regarding intermolecular binding was obtained by relaxing the crystallographic structure of an unsupported (without substrate) 2D arrangement. In order to simulate the interaction with the surface, we fixed the *z* position of the two lower C6 rings (C6–Cu distance). All other atoms were free to relax. Different starting configurations were tested (S3, ESI†). The most stable configuration has the NH_2 groups pointing outwards and gives the image shown in Fig. 1f, where the shortest intermolecular distance is 9.3 Å, in good agreement with the STM data ((9.0 ± 0.5) Å). Once formed the tetramer structures are mutually repulsive. Therefore, denser packing is not observed (S3, ESI†).

It is important to point out that even in the presence of the NH_2 polar group, the assembly seems to be dictated still by the vdW interaction between the C6 rings, in contrast to what is observed for the bis-functionalized 6,13-dicyano[7]helicene[11] for which either H bonding (at low temperatures) or metal coordination to Cu atoms (at high temperatures) determine the assembly of ordered chains at low coverages.[12]

To get an insight into the assembly process, we simulated the structures formed by duplets, triplets and rows in gas phase models. Fig. S5 (ESI†) shows some possible conformers. We notice that all the structures have similar energies per molecule and therefore it is not surprising to observe the occurrence of all of them (Fig. 1a). As we increase the coverage the structures with higher packing density are favoured. Remarkably, in all these models vdW interactions between the C6 rings drive the intermolecular assembly, as observed for unsubstituted [7]helicenes (7[*H*]).[2,6] If we now consider also the preferential absorption sites imposed by the substrate grid, we expect that at saturation coverage enantiopure 7[*H*] favours triplet (*p*3) structures on 3-fold symmetric (111) surfaces[19] and quadruplets on 4-fold symmetric Cu(100) surfaces.[20] Our observation is also in line with the recent study[14] where the assembly of **AH** on Au(111) in 1,2,4-trichlorobenzene (TBC) leads to *p*3 structures, analogous to 7[*H*].[2,6]

Interestingly, the self-assembly and the chiral 2D expression of **AH** on Au(111) depend drastically on the solvent.[14] In order to compare the influence of the surface and the solvent on the self-assembly of enantiopure **AH**, we deposited *M*-**AH** on Au(111) under UHV. Surprisingly, in contrast to the *p*3 structures formed at the Au(111)/TBC interface, under UHV (90% ML) we observe the development of 2 domains of double chains rotated by 120° (Fig. 2a, the lower inset shows the growing directions of 2 rotational domains), also surrounded by areas of highly diffusive molecules. DFT calculations of *M*-**AH** on Au(111) are shown in Fig. S6, ESI.† In agreement with previous calculations[14] the structure with the N-down configuration gives the higher adsorption energy (upper inset Fig. 2).§ We notice that the energy difference between the N-up and N-down structure on Au (~14.4 kcal mol^{-1}) is much more pronounced than on Cu (~1.85 kcal mol^{-1}). In addition, the distances N–Cu and N–Au are similar (3.4 and 3.5 Å, respectively) but the interaction of the C6 rings is stronger on Cu (3.1 Å *vs.* 3.5 Å on Au). This suggests that on Au(111) the NH_2 group governs the interaction with the surface.[18] To reproduce the supramolecular cell (Fig. 2b) we simulated the unit cell in the gas phase. The corresponding STM image reproduces the observed rows (S7 ESI,† Fig. 2c). We notice that the closest distance between the molecules forming the double rows on Au(111) (6.7 ± 0.5) Å is reduced in comparison to the rows assembled on Cu(100), Fig. 1b, (10.0 ± 0.5) Å. The same trend is observed for the quadruplets embedded in the disordered region (S8, ESI†). The packing density on Au(111) is highest for the observed rows of dimers. We attribute this to the lower interaction of the C6 rings to the Au surface that allows the molecules to get closer, maximizing vdW interactions. The fact 7[*H*] forms triangles and quadruplets, but not double chains on Au(111)

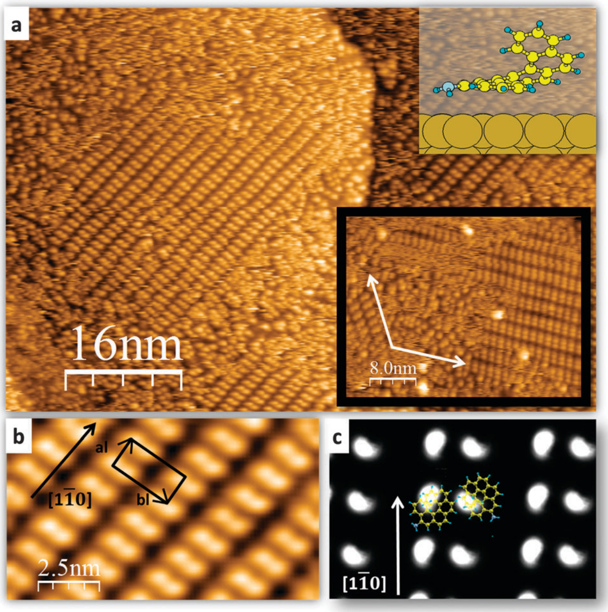

Fig. 2 STM images of *M*-**AH** on Au(111). (a) 90% ML coverage, the growth direction of the 120° rotamers is shown by the white arrows in the lower inset (−2 V, 10 pA), the upper inset shows the preferential adsorption geometry obtained by DFT (b) 90% ML coverage, a low pass filtered STM image with the unit cell (a = 1.1, b = 2.2 nm) (−2 V, 10 pA), (c) simulated STM image of the most stable structure (S7, ESI†)

reflects the role of the NH_2 groups in the assembly of *M*-**AH** on Au(111). This might also explain why if the interaction of the NH_2 with the surface is weakened by an organic solvent *p*3 structures evolve, resembling 7[*H*]. If the solvent protonates the NH_2, no order emerges.[14] The overall scenario on both surfaces suggests that the supramolecular assembly is driven by the maximization of the vdW interactions at the distances and geometries ultimately allowed by the molecule–surface interactions. Exploratory studies of (*MP*)**AH** on Cu(100), Au(111) and SnCu(100) indicate that vdW interactions also determine the assembly of the racemate.

In conclusion, we have investigated the self-assembly of *M*-**AH** on Cu(100) and Au(111). The chief difference between the two analysed surfaces is found in the origin of the molecule–surface interaction. While the C6 rings-surface interaction dominates in the case of Cu(100), the amino–surface interaction is crucial on Au(111). In both cases, it is significant that the amino group does not induce polar interactions *via* hydrogen bonding but rather that the maximization of vdW interactions drives the self-assembly.

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Notes and references

‡ By comparison with similar molecules having NH_2 and unsaturated rings, on Cu surfaces we expect the NH_2 group not to dissociate below 400 K.[3,21]

§ We remark that the total adsorption energy of the stable structures is considerably higher (by ∼16 kcal mol^{-1}) than the one informed in ref. 14. We attribute this difference to the functional we used (vdW-DF2) which considers the vdW interactions already in the calculation.

1 S. M. Barlow and R. Raval, *Curr. Opin. Colloid Interface Sci.*, 2008, **13**, 65; D. B. Amabilino, S. De Feyter, R. Lazzaroni, E. Gomar-Nadal, J. Veciana, C. Rovira, M. M. Abdel-Mottaleb, W. Mamdouh, P. Iavicoli, K. Psychogyiopoulou, M. Linares, A. Minoia, H. Xu and J. Puigmarti-Luis, *J. Phys.: Condens. Matter*, 2008, **20**, 184003; K. S. Mali, J. Adisoejoso, E. Ghijsens, I. De Cat and S. De Feyter, *Acc. Chem. Res.*, 2012, **45**, 1309.

2 R. Fasel, M. Parschau and K. H. Ernst, *Angew. Chem., Int. Ed.*, 2003, **42**, 5178.

3 M. Lingenfelder, G. Tomba, G. Costantini, L. C. Ciacchi, A. De Vita and K. Kern, *Angew. Chem., Int. Ed.*, 2007, **46**, 4492.

4 A. G. Mark, M. Forster and R. Raval, *ChemPhysChem*, 2011, **12**, 1474.

5 M. Gingras, *Chem. Soc. Rev.*, 2013, **42**, 1051.

6 R. Fasel, M. Parschau and K. H. Ernst, *Nature*, 2006, **439**, 449.

7 M. Parschau, R. Fasel and K.-H. Ernst, *Cryst. Growth Des.*, 2008, **8**, 1890; M. Parschau, U. Ellerbeck and K.-H. Ernst, *Colloids Surf., A*, 2010, **354**, 240; R. Fasel, A. Cossy, K. H. Ernst, F. Baumberger, T. Greber and J. Osterwalder, *J. Chem. Phys.*, 2001, **115**, 1020; K. H. Ernst, Y. Kuster, R. Fasel, C. F. McFadden and U. Ellerbeck, *Surf. Sci.*, 2003, **530**, 195.

8 J. S. Prauzner-Bechcicki, S. Godlewski, J. Budzioch, G. Goryl, L. Walczak, P. Sehnal, I. G. Stara, I. Stary, F. Ample, C. Joachim and M. Szymonski, *ChemPhysChem*, 2010, **11**, 3522; S. Godlewski, J. S. Prauzner-Bechcicki, J. Budzioch, L. Walczak, I. G. Stara, I. Stary, P. Sehnal and M. Szymonski, *Surf. Sci.*, 2012, **606**, 1600.

9 M. Taniguchi, H. Nakagawa, A. Yamagishi and K. Yamada, *J. Mol. Catal. A: Chem.*, 2003, **199**, 65.

10 P. Rahe, M. Nimmrich, A. Greuling, J. Schuette, I. G. Stara, J. Rybacek, G. Huerta-Angeles, I. Stary, M. Rohlfing and A. Kuehnle, *J. Phys. Chem. C*, 2010, **114**, 1547; C. M. Hauke, P. Rahe, M. Nimmrich, J. Schuette, M. Kittelmann, I. G. Stara, I. Stary, J. Rybacek and A. Kuehnle, *J. Phys. Chem. C*, 2012, **116**, 4637.

11 M. Stohr, S. Boz, M. Schaer, N. Manh-Thuong, C. A. Pignedoli, D. Passerone, W. B. Schweizer, C. Thilgen, T. A. Jung and F. Diederich, *Angew. Chem., Int. Ed.*, 2011, **50**, 9982.

12 A. Shchyrba, N. Manh-Thuong, C. Waeckerlin, S. Martens, S. Nowakowska, T. Ivas, J. Roose, T. Nijs, S. Boz, M. Schaer, M. Stohr, C. A. Pignedoli, C. Thilgen, F. Diederich, D. Passerone and T. A. Jung, *J. Am. Chem. Soc.*, 2013, **135**, 15270.

13 A. Perzyna, C. Dal Zotto, J.-O. Durand, M. Granier, M. Smietana, O. Melnyk, I. G. Stara, I. Stary, B. Klepetarova and D. Saman, *Eur. J. Org. Chem.*, 2007, 4032.

14 T. Balandina, M. W. van der Meijden, O. Ivasenko, D. Cornil, J. Cornil, R. Lazzaroni, R. M. Kellogg and S. De Feyter, *Chem. Commun.*, 2013, **49**, 2207.

15 S. M. Barlow and R. Raval, *Surf. Sci. Rep.*, 2003, **50**, 201.

16 N. Lorente, M. F. G. Hedouin, R. E. Palmer and M. Persson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **68**, 155401; A. P. Seitsonen, M. Lingenfelder, H. Spillmann, A. Dmitriev, S. Stepanow, N. Lin, K. Kern and J. V. Barth, *J. Am. Chem. Soc.*, 2006, **128**, 5634.

17 M. Preuss, W. G. Schmidt and F. Bechstedt, *Phys. Rev. Lett.*, 2005, **94**, 236102.

18 L. Duy, M. Aminpour, A. Kiejna and T. S. Rahman, *J. Phys.: Condens. Matter*, 2012, **24**, 222001.

19 J. Seibel, M. Parschau and K.-H. Ernst, *J. Phys. Chem. C*, DOI: 10.1021/jp504673g.

20 J. Seibel, L. Zoppi and K.-H. Ernst, *Chem. Commun.*, 2014, **50**, 8751.

21 Q. Chen, D. J. Frankel and N. V. Richardson, *Langmuir*, 2002, **18**, 3219; G. Tomba, M. Lingenfelder, G. Costantini, K. Kern, F. Klappenberger, J. V. Barth, L. C. Ciacchi and A. De Vita, *J. Phys. Chem. A*, 2007, **111**, 12740; V. Feyer, O. Plekan, K. C. Prince, F. Sutara, T. Skala, V. Chab, V. Matolin, G. Stenuit and P. Umari, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **79**, 155432.