Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications
www.rsc.org/chemcomm

ROYAL SOCIETY OF CHEMISTRY

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

www.rsc.org/chemcomm

PAPER

Anisotropic Growth of Thiophene-Based Layer on Si(111)-B [†‡]

**A. Rochefort,**[*a] **Y. Makoudi,**[b] **A. Maillard,**[a] **J. Jeannoutot,**[b] **J. Blier,**[a] **F. Chérioux,**[b] **and F. Palmino**[b]

The formation of large assemblies on Si(111)-B surface is discussed with the help of STM simulations and DFT calculations. Although highly regular assemblies of DTB10B along Si row direction are observed, the existence of two herringbone isomers introduces a lower periodicity within the 2D molecular network. The formation of herringbone units is explained by weak intermolecular interactions while the 1D assembling depends mainly of the interactions of the C_{10} side chains with the Si(111)-B surface.

The adsorption of oligothiophenes on semiconducting surfaces has not often been studied due to their high propensity to form covalent bonds with surface atoms.[1,2] On the other hand, the use of highly doped Si-surfaces allows, to a certain degree, to control the reactivity of Si surface atoms.[3] In contrast, the number of studies on graphite or HOPG surfaces is much more significant.[4–6] On such weakly reactive surfaces, the structure of adsorbed oligothiophene mostly depends on intermolecular interactions, more especially on the nature and structure of the functional groups attached to the thiophene unit.[7,8] The size of the molecular units used in these studies is usually quite high, and such study can rarely benefit from a theoretical support by STM simulations. Here, we used a Si(111)-B surface[‡] to weaken molecule-substrate interaction in order to achieve supramolecular network. We demonstrate that STM simulations are becoming practical for large-scale systems, and can be used to support and explain complex surfaces processes.

Figure 1 shows that the adsorption of 1,4-bis(5-(2,2'-dithienyl))-2,5-bis(decyloxy)benzene[‡] (DTB10B) on Si(111)-B can lead to a large overlayer forming 120° in-plane orientation (see orange and blue domains). In each domain, the adsorbed molecules adopt a regular herringbone pattern along the indicated lines. Such periodicity is not totally conserved in the molecular 2D network, where the herringbone units are irregularly shifted from one line to the other. From the size of this STM image, we estimate that the molecular network domains may extend over 100×100 nm^2. We want to emphasize

that for a given direction (see dashed lines), the herringbone units are without exception aligned in that unique direction.
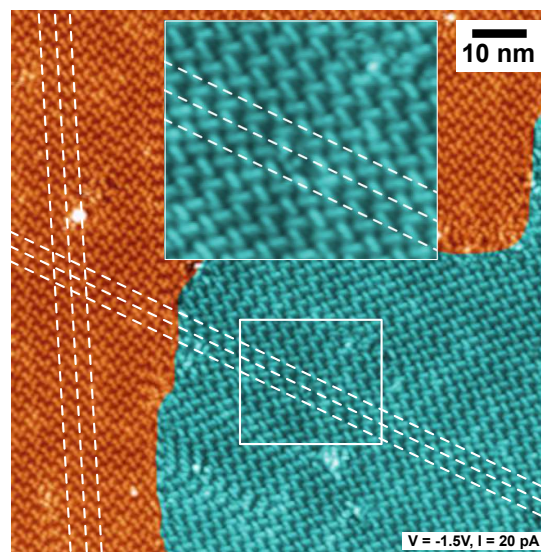
Fig. 1 STM image of the organization of DTB10B molecules on the Si(111)-B surface at high coverage.

In order to understand the influence of the Si(111)-B substrate on the overlayer growth, Figure 2A shows an STM image near the edge where Si-adatoms can be easily identified in the upper part of the image. We can clearly see that the alignment of the molecules observed in Figure 1 follows exceptionally well the Si-adatom corrugation of the Si(111)-B surface. In addition, this figure also reveals that series of well-defined Si-adatom rows are separated by an angle of 60°.

A more careful analysis of the STM features can be performed on Figure 2. According to the molecular lengths shown in the inset of Figure 2A, the core of DTB10B containing the oligothiophene fragment corresponds to the brightest STM features composed of four protuberances well separated by a lower contrast region in the middle. The aliphatic C_{10} side chains are revealed in STM through less intense but linear features on both sides of the DTB10B core. More importantly, these side chains are well-aligned along Si-adatom rows direction (see white dashed lines) and are invariably located be-
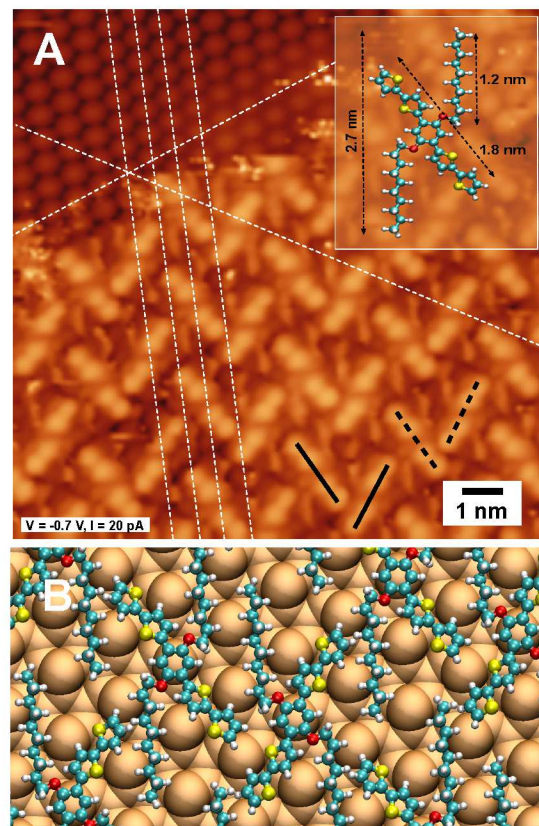
Fig. 2 A) STM image of DTB10B/Si(111)-B near overlayer edge. Si adatom rows are identified by white dashed lines. The two types of herringbone dimers are indicated by the black lines. The inset gives the structural parameters of isolated DTB10B molecule. B) Adsorption model of a well-ordered DTB10B/Si(111)-B network.

tween Si-adatom rows. This result strongly suggests that the C_{10} chains play a major role in the orientation of the DTB10B units. From the STM contrasts in this well-organized region, an adsorption model shown in Figure 2B can be proposed.

Following the STM simulations approach developed by Boulanger-Lewandowski and Rochefort[9] on large atomic models, we used a finite model containing about 6600 atoms as a starting point of our STM simulations.‡ The advantage of this approach is the possibility to consider independent structural modifications within the assembled layer without imposing a spatial periodicity in the calculations. For simplicity, we used a periodic DTB10B network, an Hamiltonian based on extended Huckel method, and the STM image was obtained at the Tersoff-Hamann level of theory. Instead of focusing on the more stable adsorbed phase at 0 K resulting from a nearly impractical DFT calculation in the present case, we rather introduced appropriate structural modifications on the adsorption model to reproduce experimental STM features. Since the orientation of the C_{10} chains on the substrate is clear, we have

concentrated our effort on the geometry of the oligothiophene core. We found an excellent agreement between experimental (Figure 2) and simulated STM (see Figure 3) images when the four thiophene units are rigidly rotated by around 35° with respect to the more central benzene ring that appears totally flat, such as the C_{10} chains, on the Si(111)-B surface.
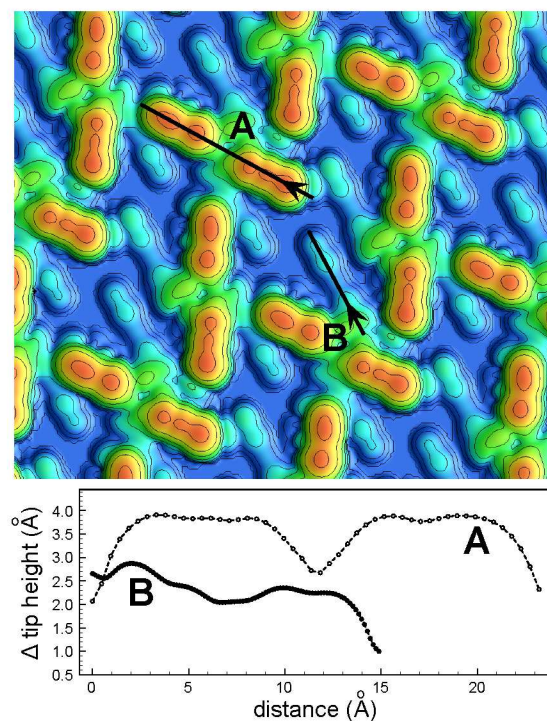

Fig. 3 Simulated STM image (upper panel) obtained at TH level (V = -1.5 eV, I = 0.1 nA), and variation of the calculated tip height (lower) along the A and B pathways reported in the upper panel.

The description of experimental STM image given above is totally consistent with our STM simulations shown at Figure 3. The upper part of Figure 3 shows a calculated STM image of a well-organized DTB10B overlayer where the C_{10} chains are located between Si-adatom rows and aligned along these rows direction. As observed experimentally, the molecular core appears as four bright protusions and the side chains located on both sides of the core are less intense. As reported in the lower panel, we analyzed the profile of the STM image along the A and B straight lines. We distinguish the presence of the protusion associated to the DTB10B core and to the depletion of conducting states in the more central region. Along the B pattern, the highest height near 2 Å is due to the presence of oxygen atoms on which the C_{10} side chains are attached. Otherwise, the lengths of the calculated profiles are in excellent agreement with the size of the molecule reported in the inset of Figure 2. The geometry of the adsorbed phase proposed from STM simulations is also consistent with the re-

sults of DFT/B3LYP/6-31G calculations performed on the isolated DTB10B molecule.[‡] Ground state geometry of DTB10B shows that C_{10} chains are not flat with respect to the oligothiophene core but are twisted by around 50°. Since STM reveals that the C_{10} chains are lying down the Si(111)-B surface in the adsorbed phase, including the more central benzene core, the thiophene units need to rotate in order to minimize steric repulsion with the C_{10} chains that become flatter. This forced planarization should provoke the tilting of all thiophene units in a unique direction. This geometry agrees with the profiles calculated at Figure 3, where the bright protusions are well-aligned rather than forming a zig-zag shape as it is the case when the thiophene units are independantly rotated from one to the others (see S4, ESI[‡]).

We turn now to the formation of the DTB10B network. A systematic alignment of DTB10B dimers and C_{10} side chains along the direction of Si-adatom rows is observe, but we are not recovering a similar periodicity in the 2D overlayer which shows several *defects*. For example, the two herringbone arrangements identified by full and dashed black lines in Figure 2A contribute to break this 2D network periodicity. It is also very interesting to note that molecules that form herringbones are flipped by 180° from one to the other. Statistically, the adsorption of DTB10B should equally lead to two different adsorbed species (N,M), one being the mirror image of the other. Although the observed herringbone dimers have different arrangement, they are strickly formed from a N-M pair. First, the large proportion of herringbone dimers in the network strongly suggest that DTB10B molecules form herringbone dimers that diffuse, and assemble along the 1D direction of Si-adatoms under the influence of the interaction of the C_{10} chains with the surface. Second, the presence of two different herringbone dimers can be explained by weak interactions such as CH-π attraction[10] between DTB10B units. As the thiophene units are rotated, isomers of DTB10B dimer are proposed at Figure 4, where the black lines give the thiophene core position (see also Fig.2A). In principle, the proportion of both herringbone isomers should be nearly equal, and once a dimer is assembled within the 1D direction, the periodicity in the 2D direction will only depend on the type of isomer that will adsorb in the next 1D assembly. Although a more quantitative description of the elementary adsorption steps would need additional experimental and theoretical efforts, a simple analysis of gas phase species and STM simulations can provide vital structural information of adsorbed phases.

In conclusion, experiments reveals that adsorption of DTB10B is dominated by the anisotropic interaction of the C_{10} chains with Si(111)-B. Supported by STM simulations, we showed that weak intermolecular interactions such as CH-π bonding direct the orientation of DTB10B in the formation of a herringbone dimer. Hence, the adsorption of DTB10B is highly periodic in one direction but not in the 2D direction.
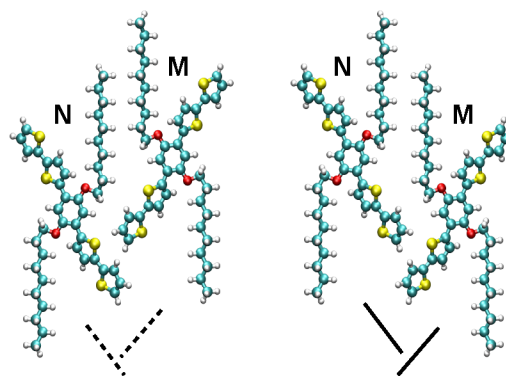
Fig. 4 Structural arrangement of DTB10B molecules forming two isomers of a herringbone dimer.

References

1 Y. Cao, K.S. Yong, Z.H.Wang, J.F. Deng, Y.H. Lai, G.Q. Xu, *J. Chem. Phys.*, 2001, **115**, 3287.

2 N. Isobe, T. Shibayama, Y. Mori, K. Shobatake, K. Sawabe, *Chem. Phys. Lett.*, 2007, **443**, 347.

3 (a) B. Baris, V. Luzet, E. Duverger, P. Sonnet, F. Palmino and F. Chérioux, *Angew. Chem. Int. Ed.*, 2011, **50**, 4094; (b) B. Baris, J. Jeannoutot, V. Luzet, F. Palmino, A. Rochefort, F. Chérioux, *ACS Nano* 2012, **6**, 6905; (c) S. R. Wagner, R. R. Lunt, P. Zhang, *Phys. Rev. Lett.*, 2013, **110**, 086107.

4 M. Linares, L. Scifo, R. Demadrille, P. Brocorens, D. Beljonne, R. Lazzaroni, B. Grevin, *J. Phys. Chem. C*, 2008, **112**, 6850.

5 M. Bonini, L. Zalewski, E. Orgiu, T. Breiner, F. Dötz, M. Kastler, P. Samori, *J. Phys. Chem. C*, 2011, **115**, 9753.

6 R. Gutzler, C. Fu, A. Dadvand, Y. Hua, J.M. MacLeod, F. Rosei, D.F. Perepichka, *Nanoscale*, 2012, **4**, 5965.

7 I. F. Perepichka, D. F. Perepichka, *Handbook of Thiophene-Based Materials: Applications in Organic Electronics and Photonics*, John Wiley & Sons, 2009.

8 E. Mena-Osteritz, M. Urdanpilleta, E. El-Hosseiny, B. Koslowski, P. Ziemann, P. Bäuerle, *Beilstein J. Nanotechnol.* 2011, **2**, 802.

9 N. Boulanger-Lewandowski, A. Rochefort, *Phys. Rev. B*, 2011, **83** 115430.

10 E. R. T. Tiekink, J. Zukerman-Schpector, *The Importance of Pi-Interactions in Crystal Engineering: Frontiers in Crystal Engineering*, John Wiley & Sons, 2012.