# Nanopatterning the surface with ordered supramolecular architectures of $N^9$-alkylated guanines: STM reveals†

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**STM study of the self-assembly at the solid–liquid interface of substituted guanines exposing in the $N^9$-position alkyl side chains with different lengths revealed the formation of distinct crystalline nanopatterns.**

The self-assembly of small molecular modules into non-covalently linked polymeric nanostructures is a subject of continuous interest.[1] In particular, supramolecular structures with a high degree of order can be obtained through the self-association of organic molecules on flat solid surfaces.[2] Such structures can be used as scaffolds to position electrically/optically active groups in pre-determined locations in 2D,[3] thereby paving the way towards a wide range of applications, *e.g.* in electronic and optical devices.[4] Among weak interactions, H-bonding offers high control over the process of molecular self-assembly because it combines reversibility, directionality, specificity and cooperativity. Such a unique character is the basis of sophisticated programs for self-assembly such as those based on the Watson–Crick base pairing[5] which directs the formation of the helical structure of DNA. Among nucleobases, guanine is very versatile:[6] depending on the experimental conditions it can undergo different self-assembly pathways. In the presence of certain metal ions, guanines can form G-quartet based architectures (Fig. 1b) such as octamers or columnar polymeric aggregates.[6b–c,7] In the absence of metal templates, guanines without a C(8) sterically demanding substituent[8] can self-assemble, both in solution and in the solid state, into ribbonlike architectures.[6c,9] For guanosine derivatives physisorbed at surfaces the thermodynamically stable ribbons were found to be characterized by cyclic NH(2)–O(6) and NH(1)–N(7) hydrogen bonds (Fig. 1c). In the solid state, the ribbons, by bridging gold electrodes, were found to be photoconductive.[10] More interestingly, these ribbons also exhibit rectifying properties.[11] A field-effect transistor based on these supramolecular structures was described.[12] Hitherto guanine based H-bonded supramolecular architectures were self-assembled on surfaces into highly ordered motifs and studied with scanning tunneling microscopy (STM) under ultra-high vacuum (UHV).[13] Conversely at the solid–liquid interface the effort was mainly addressed towards the study of lipophilic guanosine monolayers.[9a,14] We decided to extend our studies at the solid–liquid interface to physisorbed monolayers of $N^9$-alkylguanines because the absence of the sugar when compared to the previously studied guanosines and the presence of an aliphatic side-group can be foreseen to favor the molecular adsorption on graphite.[1d] In general, the formation of ordered motifs stabilized by hydrogen bonds on a solid surface requires the fine tuning of the interplay between the interactions among adjacent molecules and the adsorbate–substrate interactions.[15] To achieve a full understanding of the self-assembly of guanine at the solid–liquid interface, here we performed a sub-molecularly resolved STM study of physisorbed monolayers on graphite of a series of $N^9$-alkylguanines with linear alkyl side-chains from $–C_2H_5$ up to $–C_{18}H_{37}$ (Fig. 1).[16] This comparative study was carried out by applying a drop of a 1.0 ± 0.1 mM solution of the chosen guanine molecule in 1,2,4-trichlorobenzene (TCB) on freshly cleaved highly oriented pyrolytic graphite (HOPG).

For the crystalline pattern obtained from each guanine self-assembled on HOPG the unit cell parameters, *i.e.* length of vectors $a$ and $b$, $\alpha$ (angle between the vectors), unit cell area ($A$), number of molecules in the unit cell ($N_{mol}$), area occupied by a single molecule in the unit cell ($A_{mol}$, with $A_{mol} = A/N_{mol}$) and estimated projection of the molecular van der Waals volume onto surface ($A_{vdW}$) are given in Table 1. All proposed packing motifs for molecules **1–9** have been compared with theoretical models (see Supplementary Information†).

Fig. 2a shows an STM image of the monolayer obtained from molecule **1**: it reveals a crystalline ribbon-like architecture. In this 2D crystal the ethyl side chains are most likely

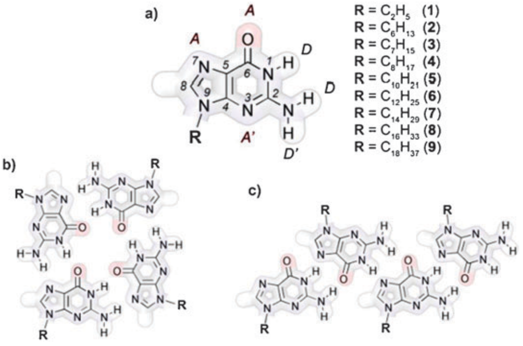

**Fig. 1** (a) Chemical formulae of the different investigated guanines; H-bonded motifs of self-assembled guanines; (b) quartet based (involved pairing: NH(2)–N(7) and NH(1)–O(6)) and (c) ribbon based (involved pairing: NH(2)–O(6) and NH(1)–N(7)) architectures.

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**Table 1** Unit cell parameters of all guanine derivatives at the solid–liquid interface

| | | Unit cell parameters[a] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Guanine derivative | Side chain | *a*/nm | *b*/nm | α | *A*/nm$^2$ | $N_{mol}$ | $A_{mol}$/nm$^2$ | $A_{vdW}$/nm$^2$ |
| **1** | $C_2H_5$ | 1.00 ± 0.2 | 1.51 ± 0.2 | (92 ± 3)° | 1.51 ± 0.21 | 2 | 0.75 ± 0.1 | 0.55 ± 0.02 |
| **2** | $C_6H_{13}$ | 0.98 ± 0.2 | 1.63 ± 0.2 | (84 ± 3)° | 1.58 ± 0.20 | 1 | 1.58 ± 0.2 | 0.75 ± 0.02 |
| **3** | $C_7H_{15}$ | 0.97 ± 0.2 | 1.85 ± 0.2 | (81 ± 3)° | 1.77 ± 0.19 | 2 | 0.88 ± 0.1 | 0.80 ± 0.02 |
| **4** | $C_8H_{17}$ | 1.27 ± 0.2 | 2.01 ± 0.2 | (58 ± 3)° | 2.15 ± 0.22 | 2 | 1.07 ± 0.1 | 0.85 ± 0.02 |
| **5** | $C_{10}H_{21}$ | 1.19 ± 0.2 | 1.46 ± 0.2 | (96 ± 3)° | 1.72 ± 0.21 | 1 | 1.72 ± 0.2 | 0.90 ± 0.02 |
| **6** | $C_{12}H_{25}$ | 1.00 ± 0.2 | 4.19 ± 0.2 | (68 ± 3)° | 3.76 ± 0.21 | 4 | 0.94 ± 0.1 | 1.00 ± 0.02 |
| **7** | $C_{14}H_{29}$ | 1.00 ± 0.2 | 4.73 ± 0.2 | (68 ± 3)° | 4.25 ± 0.21 | 4 | 1.06 ± 0.1 | 1.10 ± 0.02 |
| **8** | $C_{16}H_{33}$ | 1.00 ± 0.2 | 5.27 ± 0.2 | (68 ± 3)° | 4.73 ± 0.21 | 4 | 1.18 ± 0.1 | 1.20 ± 0.02 |
| **9** | $C_{18}H_{37}$ | 1.00 ± 0.2 | 5.81 ± 0.2 | (68 ± 3)° | 5.22 ± 0.21 | 4 | 1.31 ± 0.1 | 1.30 ± 0.02 |

[a] *a* and *b* are the vector lengths and α the angle between those vectors; *A* is the unit cell area, $N_{mol}$ the number of molecules in the unit cell and $A_{mol}$ (= $A/N_{mol}$) is the area occupied by single molecules within the unit cell; $A_{vdW}$ is the estimated van der Waals area.

physisorbed flat on the surface, although due to their high conformational dynamics they could not be resolved. The area occupied by a single molecule **1** corresponds to 0.75 ± 0.1 nm$^2$, being in good agreement with the van der Waals area of **1**.

The supramolecular motif can be well described by the formation of a one-dimensional H-bonded ribbon involving the following pairing: NH(2)–O(6) and NH(1)–N(7) (model in Fig. 1c), in good accordance with previous observations on $N^9$-octadecylguanine **9**[1d] and guanosine[9a] derivatives.

Self-assembled structures of molecule **2** exhibit a 2D crystal with the hexyl side-chains physisorbed flat on the surface (Fig. 2b). Differently from the monolayer of **1**, self-assembly of **2** is not dictated by the formation of H-bonding between adjacent molecules, but rather unspecific van der Waals interactions between molecules and the substrate rule the generation of an ordered monolayer. A similar motif was observed in a monolayer of **5** (Fig. 2c). The packing is very loose as proved by the large discrepancy between $A_{mol}$ and $A_{vdW}$. Despite such large voids which could host a second ad-molecule, we observed only one molecule per unit cell as probably ruled by the registry with the substrate.

Fig. 3a portrays the STM image recorded for a monolayer of molecule **3**. It reveals large ordered lamellae featuring a dimer packing motif involving the following pairing: NH(2)–N(7) and NH(1)–O(6). The comparison of the area occupied by a single molecule, *i.e.* 0.88 ± 0.1 nm$^2$, with the van der Waals molecule's size of 0.80 ± 0.02 nm$^2$ suggests that the heptyl side chains are physisorbed at the surface, though due to their high conformational dynamics they could not be resolved.

Fig. 3b shows a monolayer of **4** at the HOPG–solution interface. As in the case of **3**, the packing can be described by the formation of a dimer involving the pairing NH(2)–(7) and NH(1)–O(6). The octyl side chains are supposedly physisorbed on the graphite surface. However, differently from the case of the pattern formed through self-assembly of **3**, within the dimers only one alkyl chain is physisorbed on the HOPG surface.

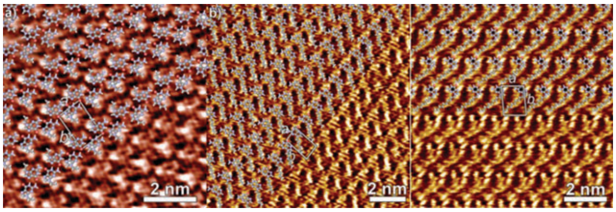

**Fig. 2** STM images of monolayers of **1**, **2** and **5**. Ribbon-like structure of **1** (a) and crystalline structures of **2** (b) and **5** (c). Tunneling parameters: average tunneling current ($I_t$) = 15 pA, bias voltage ($V_t$) = 350 mV.

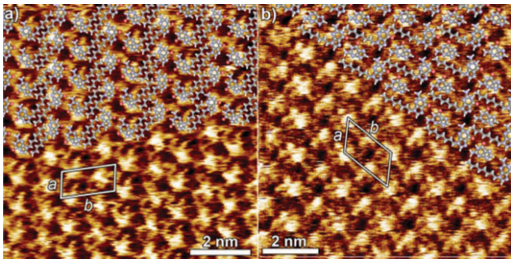

**Fig. 3** STM images of monolayers of (a) **3** and (b) **4** forming dimers. Tunneling parameters: $I_t$ = 17 pA, $V_t$ = 360 mV.

Subsequently, we have focused our attention on the self-assembly of guanines exposing longer alkyl side chains. Interestingly, regardless of the length of the side chain ($C_{12}H_{25}$ for **6**, $C_{14}H_{29}$ for **7**, $C_{16}H_{33}$ for **8** and $C_{18}H_{37}$ for **9**) the observed monolayers exhibit a similar motif consisting of H-bonded ribbons, involving the pairing NH(2)–O(6) and NH(1)–N(7) (Fig. 4). In the 2D crystals the long side chains are clearly visible: they are physisorbed flat on the surface and are interdigitated between adjacent supramolecular ribbons, thereby stabilizing the entire monolayer. Further, the comparison of the unit cell parameters of monolayers of **6–9** self-assembled at the HOPG–solution interface (Table 1) reveals that the only difference between those structures is the value of the *b* vector, thus affecting also the area occupied by a single guanine molecule ($A_{mol}$). Interestingly, the difference between $A_{mol6}$ and $A_{mol7}$ matches the difference between $A_{mol7}$ and $A_{mol8}$, *i.e.* 0.11 nm$^2$, being in good agreement with the area occupied by an ethylene group, *i.e.* 0.12 ± 0.01 nm$^2$. The difference between $A_{mol8}$ and $A_{mol9}$ amounts to 0.13 ± 0.01 nm$^2$. For monolayers of **6–9** the packing is extremely tight as revealed by the very similar values of $A_{mol}$ and $A_{vdW}$ for each system.

The thermodynamic characteristics of guanine association, obtained from the gas phase experiments,[17] revealed that the energy of supramolecular polymerization in motifs like those visualized by STM amounts to 32–36 kcal mol$^{-1}$ per molecule. In comparison the adsorption energy of alkyl chains on the HOPG surface, determined by temperature-programmed desorption experiments,[18] increases linearly with the chain

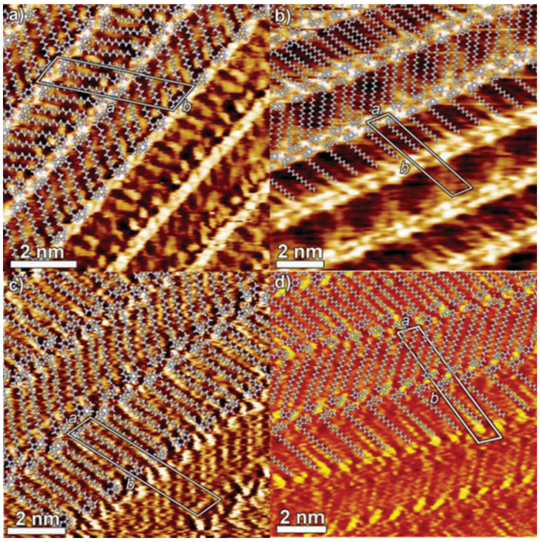

**Fig. 4** STM images of hydrogen bonded ribbons obtained from (a) **6**, (b) **7**, (c) **8**, and (d) **9**. Tunneling parameters: $I_t$ = 17 pA, $V_t$ = 360 mV.

length and is in the same energy range (see Table S1 in Supplementary Information†).

In summary, we have performed a comparative STM study on the self-assembly at the HOPG–solution interface of substituted guanines exposing in the $N^9$-position alkyl side chains with different length. Molecules **1–9** were found to form monomorphic 2D crystals, which are stable on the several tens of min time scale and exceed various hundreds of $nm^2$. Subtle changes in the length of the alkyl side-chains dramatically influenced the 2D patterns on graphite. Derivatives with alkyl tails longer than $C_{12}$ (**6–9**) self-assembled into linear H-bonded ribbons through the NH(2)–O(6) and NH(1)–N(7) pairing with 4 molecules in the unit cell. The same H-bonding pattern was observed for *N*⁹-ethylguanine **1**, but the packing shows only 2 molecules in the unit cell (the adjacent H-bonded non-centrosymmetric ribbons run indeed in a parallel way while for **6–9** they are antiparallel). For derivatives with tails of intermediate length (from $C_6$ to $C_{10}$) no H-bonded supramolecular polymers were formed at the surface: ordered monolayers of single (non-H-bonded) molecules (**2** and **5**) or H-bonded dimers (**3** and **4**) were observed. In light of the dynamic self-assembly characteristics of guanines, our results may be of interest for the generation of responsive nanopatterned surfaces featuring pre-programmed structural motifs at the supramolecular level.

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