

Supramolecular engineering of guanine-based self-assembled architectures at surfaces and interfaces

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Abstract The self-assembly of small organic molecules interacting *via* non-covalent forces is a viable approach towards the generation of highly ordered nanostructured materials. Among various molecular building blocks, supramolecular architectures with specific motifs can be obtained through self-association of natural nucleobases on flat surfaces. Such structures can be used as scaffolds to position electrically/optically active units in pre-determined locations in 2D, thereby paving the way towards materials suitable for a wide range of applications, e.g. in electronic, spintronics and optical devices. In this mini-review, we discuss the supramolecular engineering of guanine derivatives and their self-assembly processes on conductive solid substrates, as investigated by scanning tunnelling microscopy (STM).

Keywords Self-assembly, guanine, scanning tunnelling microscopy, hydrogen bonding.

Résumé L'ingénierie supramoléculaire d'architectures auto-assemblées à base de guanine sur des surfaces et interfaces

L'auto-assemblage de petites molécules organiques interagissant par des forces non covalentes est une approche pertinente pour construire des matériaux nanostructurés hautement ordonnés. Parmi les différents composants moléculaires, des architectures supramoléculaires présentant des motifs spécifiques peuvent être obtenues par l'auto-association de bases nucléiques naturelles sur des surfaces planes. Ces structures peuvent être utilisées comme échafaudages pour placer des unités électriquement ou optiquement actives dans des positions prédéterminées en 2D, ouvrant ainsi la voie à de nombreuses applications, par exemple pour l'électronique, la spintronique et les dispositifs optiques. Cette mini-revue présente l'ingénierie supramoléculaire de dérivés de guanine et leurs processus d'auto-assemblage sur des substrats solides conducteurs, tels qu'étudiés par microscopie à effet tunnel (STM).

Mots-clés Auto-assemblage, guanine, microscopie à effet tunnel, liaison hydrogène.

Achieving a full control over the position and organization of molecules into monolayers on solid surfaces with a nanoscale precision is a key step towards the fabrication of multifunctional nanodevices. The self-assembly of small organic molecules interacting *via* non-covalent forces is a practical method for developing highly ordered nanostructured materials. Among weak interactions, hydrogen-bonding offers high control over the process of molecular self-assembly [1] because it combines specificity, directionality, reversibility and cooperativity. Such a unique character is the basis of sophisticated programs for self-assembly such as those relying on the Watson-Crick base pairing [2] that govern the generation of the complex architectures like the fascinating DNA double helix.

Alongside Watson-Crick base pairing, nucleobases can interact through other kinds of hydrogen-bonded motifs to form various complex supramolecular architectures [3], such as guanine (G) quartets and quadruplexes [4]. The G-quartet (hereafter G₄), an hydrogen-bonded macrocycle typically

formed by cation-templated assembly, was first identified in 1962 as the basis for the aggregation of 5'-guanosine monophosphate (5'-GMP) [5], and fits particularly well with contemporary studies in molecular self-assembly and non-covalent synthesis [6]. Furthermore, it can be also used to study component selection and amplification in constitutional dynamic hydrogels based on G-quartet formation and reversible covalent connections [7]. Among nucleobases, G (figure 1a) is very versatile [8]: depending on the experimental conditions it can undergo different self-assembly pathways.

In the presence of certain metal ions, guan(os)ines can form G₄-based architectures (figure 1b) such as octamers or columnar polymeric aggregates. In the absence of metal templating centers, guan(os)ines can self-assemble into ribbon-like architectures both in solution and in the solid state (figure 1c) [9].

The need for exploring ordered architectures at the molecular scale has made scanning tunneling microscopy (STM) [10] a widely employed yet extremely powerful tool to

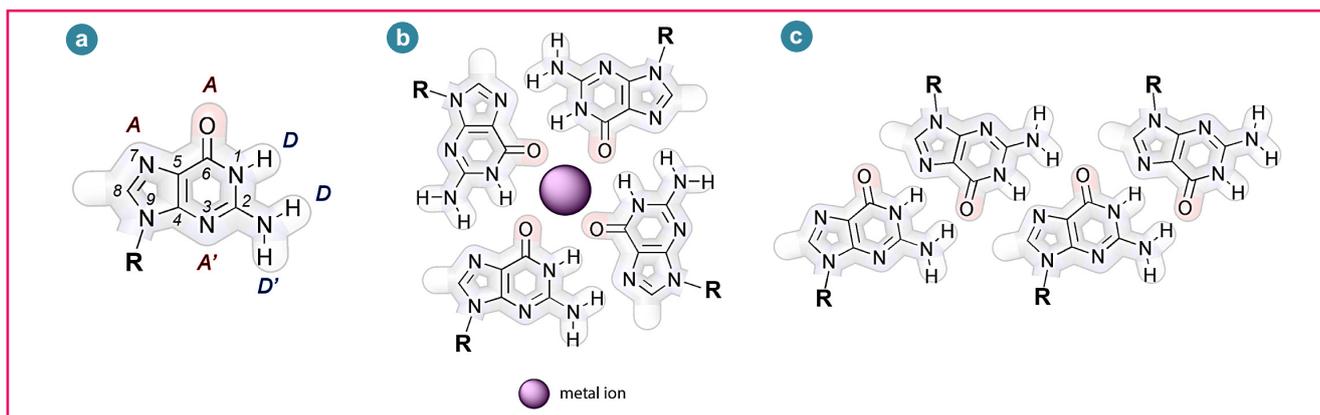


Figure 1 - a) Chemical structure of guanine (**G**). Examples of H-bonded motifs of guanines: b) **G₄** (involving pairing: N(2)-H···N(7) and N(1)-H···O(6)), and c) ribbon-like (involving pairing: N(2)-H···O(6) and N(1)-H···N(7)).

investigate supramolecular materials at interfaces with sub-molecular resolution, providing direct insight into the supramolecular world [11]. The working principle of STM is the tunneling of electrons from a sharp metal tip to a substrate. When adsorbed on graphite, the STM current images show a brighter contrast for conjugated moieties and darker for aliphatic groups. Such a contrast is ruled by the resonant tunneling between the Fermi level of the substrate (in this case graphite) and the frontier orbital of the molecules. The energy difference between them is inversely proportional to the tunneling probability [12]. The spatial subnanometer resolution that can be achieved by STM imaging allows one to gain detailed insight into molecular interactions. STM is therefore the tool of choice to assist the design of molecular modules, that can undergo controlled self-assembly at surfaces under precise conditions (temperature, pressure and concentration) to form the chosen supramolecular structures, and to investigate complex functional architectures such as dynamers. Currently, the adsorption of molecules on conductive substrates can be studied by STM under different environmental conditions including ultra-high vacuum (UHV), atmospheric pressure to image dry films or with the tip immersed into a liquid to investigate the solid/liquid interface. The solid/liquid interface provides a particularly interesting environment to carry out the self-assembly experiments and their investigation by STM. Compared to sample preparation and imaging under UHV conditions, the solid/liquid interface has in fact several advantages: (i) the experimental approach is straightforward and does not require complicated and expensive infrastructures; (ii) the dynamic exchange of molecules adsorbed on the surface and the ones in the liquid phase promotes self-healing of defects in the self-assembled layers [13]; (iii) the solid/liquid interface provides an excellent environment for *in situ* chemical modifications of adsorbed molecules. When working under such condition, it is possible to monitor the reversible changes in the monolayers structure upon addition of external chemical stimuli, e.g. varying pH [14] or by coordination of organic molecules to metallic centers [11f, 15], whereas in most examples of molecular re-organizations investigated under UHV conditions the changes are irreversible.

In this mini-review, we will discuss the supramolecular engineering of **G** derivatives and their self-assembly processes on a conductive solid substrate, *i.e.* highly oriented pyrolytic graphite (HOPG), as investigated by STM. In the first section, we will focus on the exploration of systems engi-

neered to form assemblies through the formation of hydrogen-bonds and van der Waals (vdW) interactions. We then present recent examples in 2D crystal engineering using alkylated **G** derivatives. Further on, we give a perspective into the strategies employing alkyl chains interdigitation as the main building strategy for nanopatterning surfaces with guanine molecules. In the second section, we will describe systems based on metallo-ligand interactions as well as protonation as a way to trigger dynamic processes in **G**-based dynamers. In the final section, we will discuss the use of **G** derivatives as scaffolds for the controlled positioning of electrically/optically active groups in 2D.

Self-assemblies generated via H-bonds and van der Waals interactions

The self-assembly of hydrogen-bonded networks of a lipophilic **G** derivative can be utilized to design highly-ordered supramolecular structures, not only in 3D crystal, but also in 2D when adsorbed on solid surfaces and in solution. For instance, micrometer-long nanoribbons with a molecular cross section can be grown on a mica surface from deposits of lipophilic **G** derivatives bearing two alkyl groups (*figure 2a*). This arises from the self-assembly into highly directional A-type ribbons (N(2)-H···O(6) and N(1)-H···N(7)), ultimately forming 2D polycrystalline structures of parallel ribbons at the solution-graphite interface (*figure 2a-c*) [9]. This latter structure reflects the supramolecular motif that has been detected both in the single crystal [16] and as a metastable state in solution by NMR spectroscopy [9]. Moreover this architecture is of interest for its ability to rectify currents, making it a potential building block for the construction of nanoscale bio-electronic devices and circuits [17].

In an effort to modify and enhance the electronic properties of guanosine derivatives, we broadened our scope to investigate 8-substituted lipophilic oxoguanosine derivatives [18]. The cooperative effect of hydrogen-bonding and solvophobic interactions induces the 8-oxoguanosines (*figure 2d*) to self-assemble into helical architectures both in the liquid crystalline phase, in solution and at the solid-liquid interface (*figure 2e-f*). These arrangements, which are markedly different from the structures obtained by the spontaneous self-assembly of **G** derivatives unsubstituted at the C(8) position, are of interest for their optical properties.

To achieve an in-depth understanding of the self-assembly of guanine at the solid-liquid interface, we performed a

sub-molecularly resolved STM study of physisorbed monolayers on graphite of a series of N^9 -alkylated guanines with linear alkyl side-chains from $-C_2H_5$ up to $-C_{18}H_{37}$ (figure 3)

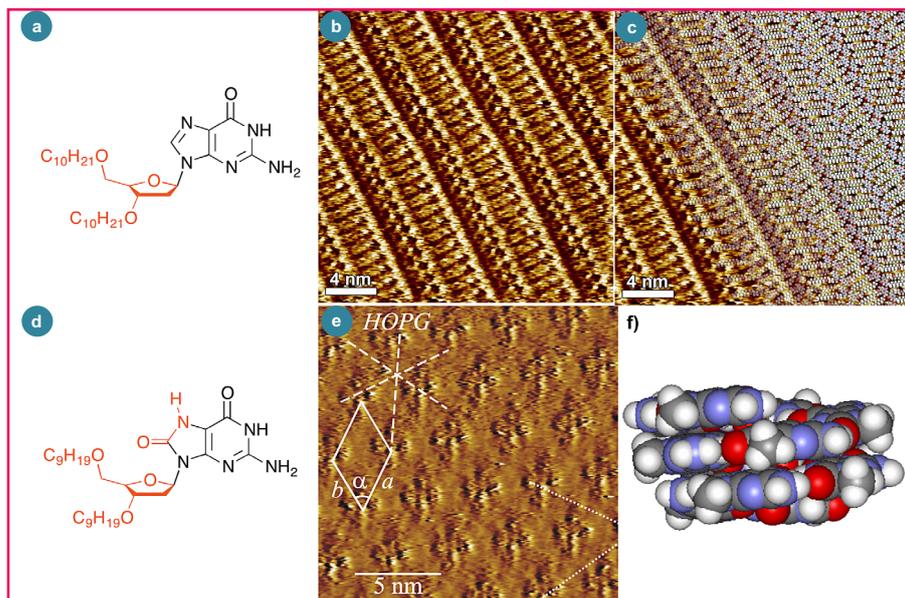


Figure 2 - a) Chemical structure of studied guanosine derivative, b) STM current images, and c) proposed packing motif of molecular model of an A-type ribbon-like architecture on a graphite surface. d) Chemical representation of investigated oxoguanosine derivative, e) STM current image, and f) schematic illustration of acylated oxoguanosine forming helical structures. Images (e-f) adapted with permission from [18], © 2003 American Chemical Society.

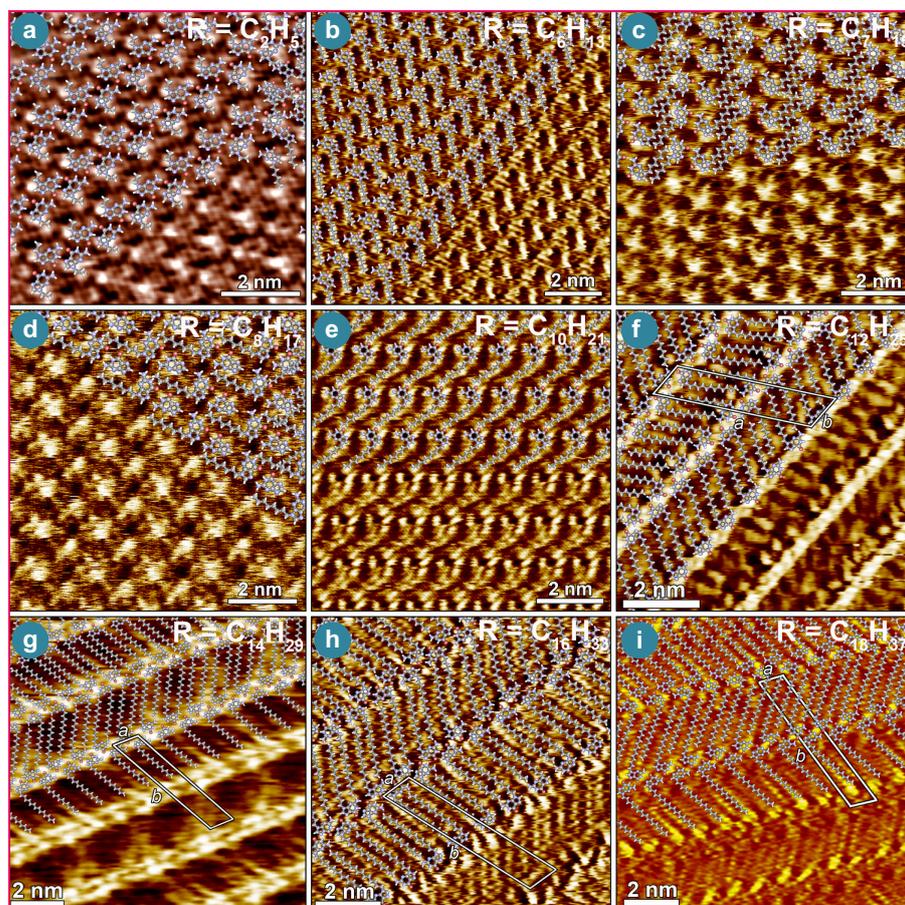


Figure 3 - STM current images of monolayers of alkylated guanines showing (a, f, g, h and i) ribbon-like, (b, e) crystalline and (c, d) dimeric structures formed on the HOPG surface. Images (a-i) adapted with permission from [19], © 2010 Royal Society of Chemistry.

[19]. This comparative study was carried out by applying a drop of a solution of the chosen alkyl substituted guanine in 1,2,4-trichlorobenzene (TCB) on freshly cleaved HOPG surface.

The presence of a long aliphatic side chain and the absence of the sugar with respect to previously studied guanines were expected to promote the molecular physisorption on HOPG. All **G** derivatives were found to form monomorphic 2D crystals, which are stable on the several tens of minutes timescale and with size of domains exceeding several hundreds of nm^2 . Subtle changes in the length of the alkyl side-chains dramatically influenced the 2D patterns on graphite. The derivatives with alkyl tails consisting of at least 12 carbon atoms ($\geq C_{12}$) (figure 3f-i) were found to self-assemble into linear H-bonded ribbons through the $N(2)-H \cdots O(6)$ and $N(1)-H \cdots N(7)$ pairing, with each unit cell being containing four molecules.

An identical H-bonding pattern was observed for N^9 -ethylguanine (figure 3a), but the packing shows only two molecules per unit cell. 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 rows of (non-H-bonded) molecules (figure 3b and 3e) or H-bonded dimers (figure 3c and 3d) were rather observed.

Assembly/reassembly processes on surfaces

As a building block for the fabrication of dynamers [11k], we studied lipophilic guanines [9, 18, 20], and guanine derivatives [19, 21]. Recently, we have provided direct evidence on the subnanometer scale metal-templated reversible assembly/reassembly process of an octadecyl-substituted **G** into highly ordered quartets (G_4) and ribbons [21] (figure 4). The self-assembly of octadecyl guanines alone on HOPG has been studied, and, upon subsequent addition in stoichiometric ratio of [2.2.2]cryptand, potassium picrate ($K^+(\text{pic}^-)$), and trifluoromethanesulfonic acid (HTf), the reversible interconversion between two different highly-ordered supramolecular motifs was triggered. In the absence of metal ions, the obtained monolayer shows a crystalline structure consisting of ribbon-like architectures (figure 4b). This self-assembly behaviour is in good agreement with previous observations on guanine derivatives [9, 18, 20]. Upon *in situ* addition of 10 mM potassium picrate solution in TCB to the initial ribbon-like motif in figure 4b, the G_4 supramolecular motif was obtained (figure 4c). Upon subsequent *in situ* addition of a 10 mM solution of [2.2.2]cryptand in TCB to the G_4 supramolecular architectures on HOPG, the guanine reassembled into the original ribbon (figure 4d). By adding

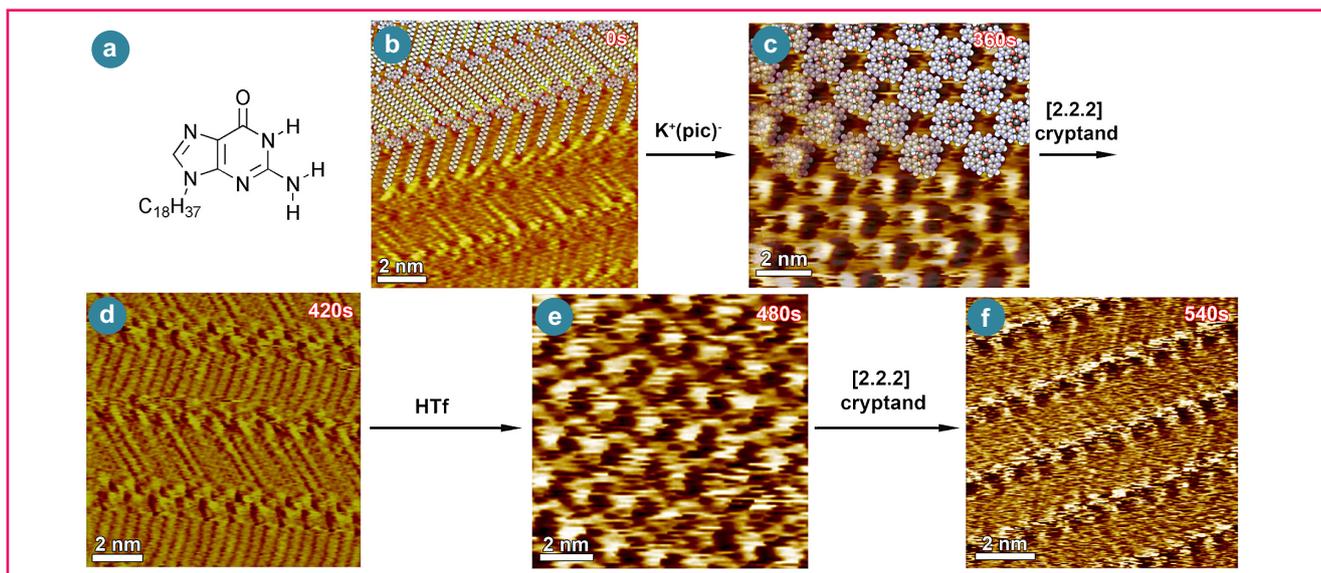


Figure 4 - a) Chemical structure of octadecyl guanine; (b-f) consecutive STM images showing the structural evolution of a monolayer of octadecyl guanine over a 9 minutes time scale (time range displays in the upper right part of the images correspond to the time that was needed to reach the equilibrium after addition of reacting agents). Images b), d) and f) show ribbon-like structure, whereas c) and e) exhibit G_4 -based architectures. Images (b-f) adapted with permission from [21], © 2008 John Wiley and Sons.

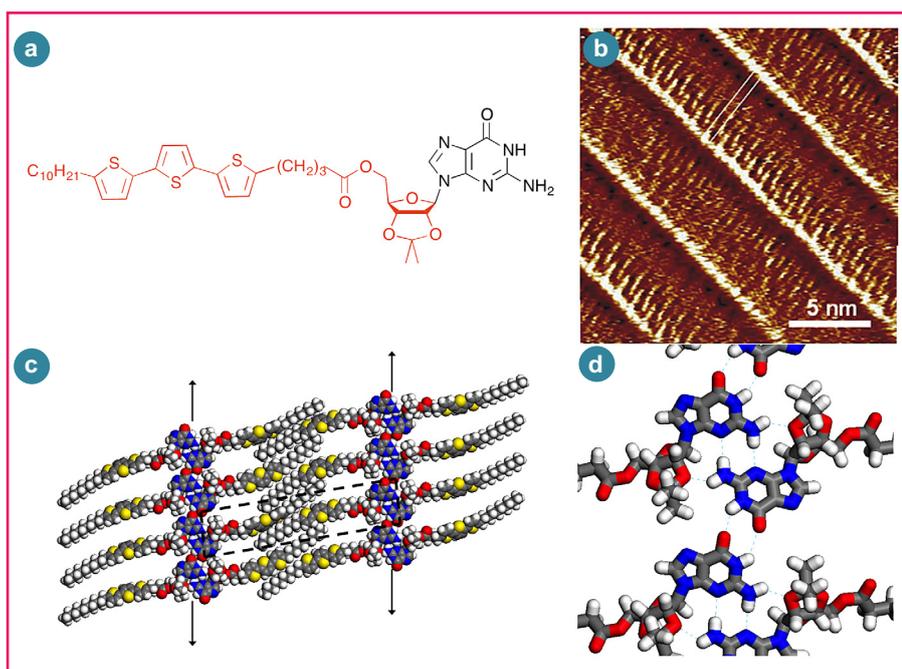


Figure 5 - a) Chemical structures of the studied guanidine-terthiophene derivative. b) STM current image of a monolayer on HOPG surface, showing highly-directional parallel structures. c) Proposed packing motif into ribbons based on molecular modelling simulations. d) Detailed view of ribbon packing characterized by $N(1)-H\cdots O(6)$ and $N(2)-H\cdots N(3)$ pairing. Adapted with permission from [22], © 2008 John Wiley and Sons.

Guanine-based supramolecular architectures as scaffolds for organic electronics

Given the possibility to functionalize lipophilic guanosines in the side-chains, they appear as ideal building blocks for the fabrication of complex architectures with a controlled high rigidity, thus paving the way towards their future use for scaffolding, *i.e.* to locate functional units in pre-programmed positions [22]. Harmonizing the functionalities of individual moieties in a supramolecular network represents a tunable method for generating distinct polymeric architectures with programmed conformations and tailored properties. In this context, we have designed a guanosine derivative bearing a terthiophene moiety linked to the sugar unit (figure 5a). Indeed, oligo- and polythiophenes are part of the most studied structures in organic electronics, because of their interesting optical and electronic properties, with application as active material in field-effect transistors [23] and photovoltaic diodes [24] noticeably. We have shown that this guanosine-terthiophene derivative can form (in solution) different types of H-bonded supra-

molecular architectures depending on the solution conditions: the reversible inter-conversion fuelled by potassium ion complexation/release allows the switching between ribbons and G_4 self-assemblies, thus allowing us to modify the inter-oligothiophene interactions by chemical stimuli. STM and atomic force microscopy (AFM) characterization showed that these molecules self-assemble into highly-ordered architectures on surfaces (graphite or mica) (figure 5). By combining

a 10 mM solution of trifluoromethanesulfonic acid (HTf) in TCB, the potassium ions were released from the cryptate and the G_4 assembly was regenerated (figure 4e). Upon further addition of a [2.2.2]cryptand solution, the ribbon structure was regenerated (figure 4f). This demonstrates the potential of G -based structures to behave as a 2D dyanmer, whose response to external chemical stimuli can be monitored by STM on the subnanometer scale.

STM imaging with molecular modelling simulations, it was shown that the highly-directional structures arise from self-assembly in extended, parallel ribbons characterized by a pairing (N(1)-H \cdots O(6) and N(2)-H \cdots N(3), see figure 5c-d). When adsorbed on HOPG, these ribbons have been found to extend over the micrometers scale, as observed by AFM imaging of dry films.

This is in contrast with previous results on alkylated guan(os)ine derivatives (figures 2a-c, 3, and 4), which showed on graphite another ribbons type, *i.e.* that characterized by the (N(2)-H \cdots O(6) and N(1)-H \cdots N(7)) pairing. This difference can be explained by the fact that the guanosine-terthiophene derivative possess only one alkyl group (while guanosine derivatives previously studied were doubly alkylated) and one acetonide group on the sugar unit (pointing perpendicularly to the molecule main plane), both leading to several restrictions that favour the formation of a different H-bonding network. Molecular modelling suggests the formation of H-bonds between guanosine N(2)-H and the ribose of the adjacent molecule (figure 5d), while the spacing between ribbons is dictated by the partial interdigitation of terthiophene-alkyl groups (figure 5c). Indeed, this self-assembly governed by the formation of H-bonds between guanosines dictates the spatial localization of oligothiophenes, which constitutes an elegant strategy to fabricating prototypes of supramolecular nanowires for organic electronics.

A similar approach has been undertaken more recently by E.W. Meijer and co-workers [25] who have demonstrated that oligo(*p*-phenylene-vinylene) (OPV) oligomers capped with a guanosine or a guanine moiety, in the absence of templating metal cations, can self-assemble into a mixture of H-bonded oligomers, among which the **G**-quartet structure may be predominant if the steric hindrance around the guanine base becomes important. In contrast, in the presence of sodium or potassium salts, well-defined assemblies of eight functional molecules (8-mers) were formed selectively and quantitatively.

Conclusion

In summary, we have provided extensive details on how guan(os)ine molecules, decorated with simple alkyl side chains or functional groups, are able to self-assemble forming 2D supramolecular crystalline materials. This paves the way towards supramolecular scaffolding, *i.e.* the use of molecular modules designed to undergo recognition events and incorporating functional units, to form pre-programmed architectures with a sub-ångström resolution, and ultimately functional materials with properties controlled with a high degree of precision. We have also provided direct evidence on the subnanometer scale of a dynamer operating at surfaces. The versatile guanine molecule was reversibly interconverted at the solid-liquid interface between two highly ordered supramolecular motifs, *i.e.* hydrogen-bonded ribbons and **G₄**-based architectures, upon subsequent addition of [2.2.2]cryptand, potassium picrate, and trifluoromethanesulfonic acid. The visualization of such supramolecular interconversion at the solid-liquid interface opens new avenues towards understanding the mechanism of formation and function of complex nucleobase architectures such as DNA or RNA. Furthermore, the *in situ* reversible assembly and reassembly between two highly ordered supramolecular structures at the surfaces represents the first step towards the generation of nanopatterned responsive architectures.

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