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Guanosine-based Hydrogen-bonded Scaffolds: Controlling the Assembly of Oligothiophenes**

By Gian Piero Spada,* Stefano Lena, Stefano Masiero, Silvia Pieraccini, Mathieu Surin, and Paolo Samorì*

The controlled and preprogrammed self-assembly of π -conjugated rod- and disc-like oligomers into ordered and anisotropic architectures is an important goal in view of the tailoring of their physico-chemical properties and, ultimately, for their application in molecular- and nanoelectronics.^[1] Among weak interactions, π -stacking has been the first to be employed to drive the self-assembly of conjugated (macro)-molecular systems into well-defined nanoscale assemblies that feature a high degree of order at the supramolecular level.^[2] Later, other types of weak yet directional non-covalent interactions, in particular H-bonds, have been used to form both mono-^[3] and multicomponent^[4] π -conjugated architectures, and their application in the fabrication of optoelectronic device prototypes such as photovoltaic diodes and ambipolar transistors^[5] has been attempted.

Lipophilic guanosines are very versatile building blocks: depending on the experimental conditions they can undergo different self-assembly pathways, leading to the formation of either H-bonded ribbons or quartet-based columnar structures (Fig. 1).^[6] Given the possibility to functionalize the guanosines in the side-chains they appear as ideal building blocks for the fabrication of complex architectures with a controlled high rigidity,^[7] thus paving the way towards their future use for

scaffolding, that is, to locate functional units in preprogrammed positions.

Oligothiophenes are the prototypes of organic semiconductors for charge transport applications, showing high performances when used as active layers in field-effect transistors with best charge carrier mobilities over $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[8] In this context, the control of the self-assembly through molecular engineering in thiophene-based architectures, also for the case of nucleotide (or nucleobase) conjugates with oligo- or polythiophene,^[9] is an important issue in order to direct and improve the optical and electronic properties.^[10] For example, the assembly of oligothiophenes on surfaces was directed by using H-bonding urea or amide groups in the side chains, leading to one-dimensional π -stacked architectures,^[11] or by using carboxylic end-groups that led to two-dimensional H-bonding networks.^[12]

In this Communication, we report on the synthesis of an oligothiophene-functionalized guanosine **1** which, depending on the experimental conditions, can form different ordered H-bonded arrays in solution, including ribbons and quartet-based assemblies. The self-assembly on surfaces is studied by means of scanning probe microscopies (SPMs) and molecular modeling simulations. Compound **1** was prepared as shown in Scheme 1. Selective esterification of the 5' position of guanosine was achieved via condensation with a preformed mixed anhydride between acid **i** and methanesulfonyl chloride. Carboxylic acid **i** had been prepared adapting synthetic procedures described earlier in Ref.^[13] (see Supporting Information).

To obtain information on the structure of the supramolecular aggregates arising from derivative **1** in isotropic solution, a comparative NMR study was carried out in CDCl_3 , $[\text{D}_8]\text{tetrahydrofuran}$ (THF) and $[\text{D}_6]\text{dimethyl sulfoxide}$ (DMSO) solutions, the latter being a strongly competing solvent for hydrogen bonding. Signals were assigned on the basis of 2D correlated spectroscopy (COSY) experiments. The ^1H NMR spectrum in CDCl_3 at room temperature (see Supporting Information) shows a single series of peaks that are significantly broader than those observed in $[\text{D}_6]\text{DMSO}$: this line-broadening suggests the presence of highly associated species in the former solvent. In particular, the imino N1-H and amino N2-H protons, which resonate at 10.71 and 6.54 ppm, respectively, in $[\text{D}_6]\text{DMSO}$, shift downfield to 11.89 and 6.68 ppm in CDCl_3 ; this indicates progressive involvement of these groups in H-bonding. As in CDCl_3 solutions the signals were too broad to allow a detailed study, aggregation of **1** was

[*] Prof. G. P. Spada, Dr. S. Lena, Prof. S. Masiero, Dr. S. Pieraccini
Alma Mater Studiorum-Università di Bologna
Dipartimento di Chimica Organica "A. Mangini"
Via San Giacomo 11, 40126 Bologna (Italy)
E-mail: gianpiero.spada@unibo.it

Prof. P. Samorì, Dr. M. Surin^[†]
ISIS/CNRS UMR 7006
Université Louis Pasteur
8 allée Gaspard Monge, 67000 Strasbourg (France)
E-mail: samori@isis-ulp.org

Prof. P. Samorì
Istituto per la Sintesi Organica e la Fotoreattività
Consiglio Nazionale delle Ricerche
via Gobetti 101, 40129 Bologna (Italy)

[†] Present address: Chimie des Matériaux Nouveaux, Université de Mons-Hainaut, 20, Place du Parc, 7000 Mons, Belgium

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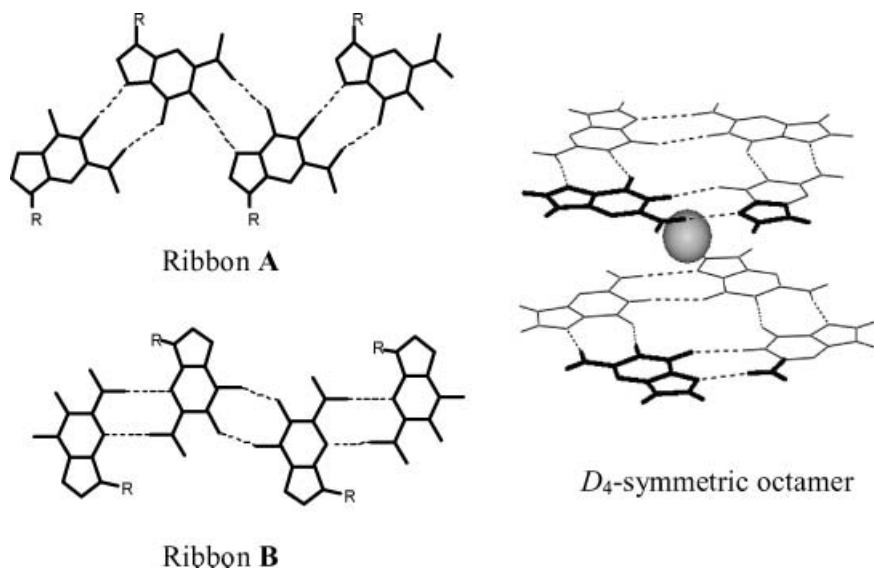


Figure 1. Three possible supramolecular architectures for guanosine derivatives: ribbon **A**, ribbon **B**, and D_4 -symmetric octamer.

investigated in $[D_8]$ THF, at different concentrations and temperatures. In this latter solvent, the imino and amino protons behave analogously to what observed in $CDCl_3$, but the signals are much narrower all over the spectrum (Fig. 2). In 15 mM $[D_8]$ THF solution at room temperature, only the N1-H proton seems to be involved in H-bonding indicating that the compound exists as a dimer, as observed before for an alkylated guanosine.^[14]

At higher concentrations and/or at lower temperatures, the amino protons are also involved in H-bonding, indicating that extended structures of the ribbon type depicted in Figure 1 start to be relevant. The existence of dimeric and oligomeric structures was confirmed by electrospray ionization (ESI) mass

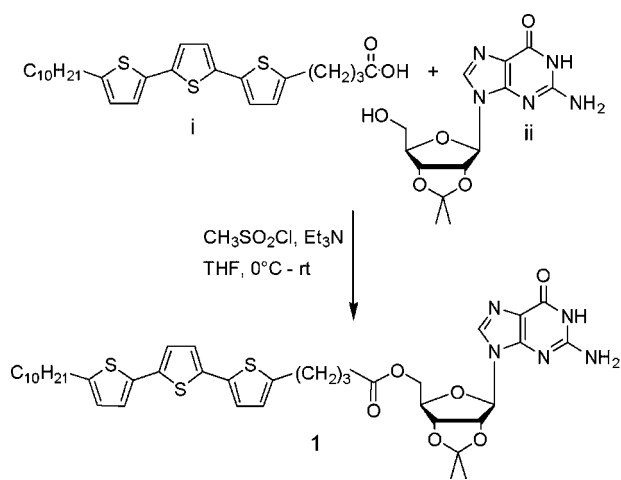
spectrometry: derivative **1** was analyzed in positive-ion mode and the spectrum (see Supporting Information) shows the presence of protonated dimers, trimers, and tetramers.

Structural information on the assembled species in solution was obtained by 2D nuclear Overhauser effect spectroscopy (NOESY) experiments. In Figure 3, the NOESY spectrum of a 30 mM solution of **1** in $[D_8]$ THF at 0 °C is reported. The spectrum shows an intermolecular interaction between N2-H and H1', and a less intense cross peak between N2-H and H2' protons. It has been shown^[15] that this contact pattern is characteristic of the **B**-type ribbon-like supramolecular arrangement shown in Figure 1. Additional cross peaks are generated by intermolecular interaction of H8 and N2-H with methyl protons of the acetonide ring, confirming this type of H-bonding pattern. In addition, the spectrum also shows cross peaks

between N1-H and H8 and between N2-H and H8 signals: this contact pattern is characteristic of the **A**-type ribbon arrangement shown in Scheme 1.^[14]

Recently, we reported on the tuneable interconversion between discrete supramolecular assemblies from a lipophilic guanosine, that is, G-ribbons and G-quartet columns, fuelled by cation complexation and release.^[16] Because the G-quartet structures obtained from **1** are harnessed by the presence of a coordinated potassium cation, this offers the possibility of triggering a reversible ribbon–quartet interconversion by controlled sequential addition and removal of K^+ . A similar dynamic behavior has been observed for **1**. The addition of 1/8 eq of potassium picrate to a THF solution of **1** transforms the supramolecular ribbon **1_n** into the octameric complex $[1_8K]^+$. Upon subsequent addition to $[1_8K]^+$ of 5 eq [2.2.2] cryptand, the potassium complex reverts to the original G-ribbon. After the addition of 1.3 eq trifluoromethanesulfonic acid (HTf), K^+ is released from the cryptate and the octameric complex $[1_8K]^+$ is regenerated.^[17] Adding thereafter 1 eq of triethylamine (TEA) the free cryptand recaptures K^+ and the G-ribbon is formed again.^[18]

Circular dichroism (CD) and 1H NMR can be both exploited to monitor the ribbon–octamer **1_n** – $[1_8K]^+$ interconversion, as shown for an alkylated guanosine derivative.^[15] While the CD spectrum of **1_n** in the region of the intense π – π transitions of the guanine chromophore at ca. 260 nm is weak (Fig. 4 top, trace *a*), the stabilization of stacked G-quartet based structures induced by the K^+ ion introduces a strong negative exciton signal (Fig. 4 top, trace *b*). The adjacent quartets are rotated by a well-defined angle; this feature is indicative of an assembly of (at least) two stacked G-quartets that are chirally rotated.^[19] The sequential addition of cryptand, HTf, and TEA (Fig. 4 top, traces *c, d, e*), leads to spectra that resemble those of **1_n**, $[1_8K]^+$,



Scheme 1. Preparation of the oligothiophene-functionalized guanosine **1**. Et_3N : triethylamine. THF: tetrahydrofuran. rt: room temperature.

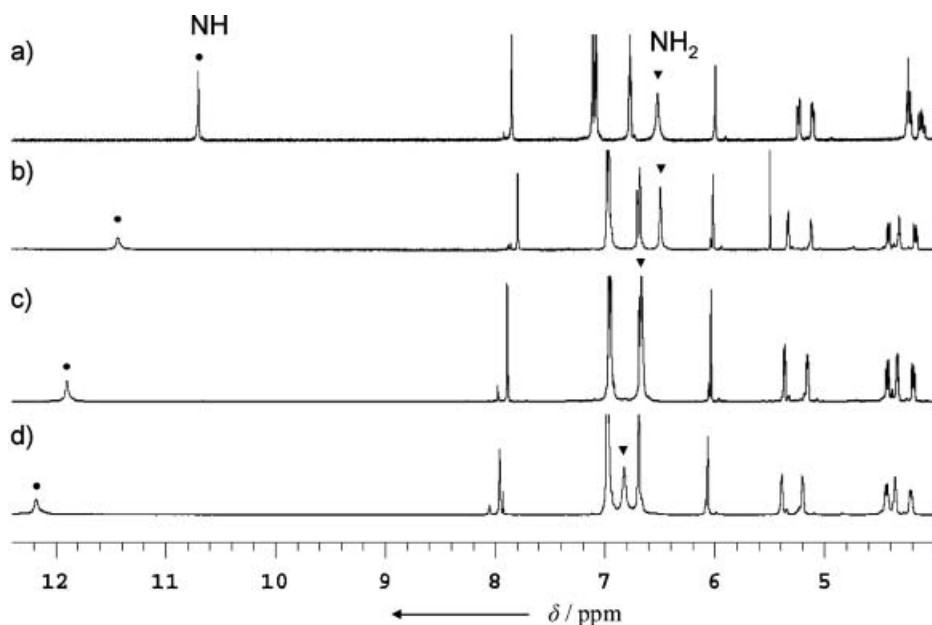


Figure 2. Portions of ^1H NMR spectra for solutions of **1**. a) 14 mM in $[\text{D}_6]\text{DMSO}$, 25 $^\circ\text{C}$; b) 15 mM in $[\text{D}_8]\text{THF}$, 25 $^\circ\text{C}$; c) 30 mM in $[\text{D}_8]\text{THF}$, 25 $^\circ\text{C}$; and d) 30 mM in $[\text{D}_8]\text{THF}$, 0 $^\circ\text{C}$. Triangles and dots mark the amino (N2-H) and imino (N1-H) protons, respectively.

and $\mathbf{1}_n$.^[20] In addition, ^1H NMR spectroscopy (in particular the spectral region between 5 and 13 ppm), gives an unambiguous signature of the ribbon–octamer conversion: the H8 and N1-H signals at 7.9 and 12.1 ppm, respectively, in $\mathbf{1}_n$ (Fig. 4 bottom, trace *a*) move at 7.4 and 12.5 ppm when the supramolecular complex $[\mathbf{1}_8\text{K}]^+$ is formed (Fig. 4 bottom, trace *b*). The N2-H signal (at 6.8 ppm in the initial solution) is split in two broad bands at 9.6 (N2-H_A) and 6.5 ppm (N2-H_B) after K-Pic addition. This downfield resonance for N2-H_A is characteristic of G-quartet formation where this proton is involved in the cyclic H-bonded scheme.^[21] Because only one set of signals were observed, all the molecules must adopt the same conformation and the G-quartets must stack with a D_4 -symmetry (i.e., in a head-to-head or tail-to-tail manner).^[22]

As also observed by CD spectroscopy, the sequential addition of cryptand, acid, and base (Fig. 4 bottom, traces *c, d, e*) allows the switching between the two signatures of the ribbon and the octamer,^[23] thus leading to two interconvertible chromophore–chromophore types of arrangements between adjacent oligothiophenes.

After having studied the self-assembly in solution, scanning probe microscopies (SPMs) were used to investigate the self-assembly of **1** in sub-monolayer films. Scanning tunneling microscopy (STM) of dry films shows large domains, extending over hundreds nanometers, each domain being made of parallel lamellae; see the bright lines Figure 5a. Within each domain (Fig. 5b), along the bright lines we observe regularly spaced spots, showing the following unit cell parameters: $a = 0.58 \pm 0.10$ nm; $b = 10.7 \pm 0.3$ nm (2×5.36 nm); angle $\alpha = -97 \pm 2^\circ$ (area = 3.069 nm²). We attribute the brightest lines to the guanine, taking into account the measured line width

(around 0.7 nm) is closer to the length of the guanine than that of the terthiophene (around 0.8 nm and 1.2 nm along their long axis, respectively). These lamellae (bright lines) are indeed made of adjacent ribbons arising from H-bonds between guanosines. Every two bright lines in Fig. 5b (see arrows), we can observe bright elongated streaks oriented almost perpendicular to the bright lines (parallel streaks at a distance of ca. 0.6 nm), which are likely to be the oligothiophene or alkyl groups. Molecular modeling simulations have been used to find whether these structures result from the formation of A-type or B-type ribbon (see Fig. 1). Owing to the imposed, restricted angle between the guanine and the ribose, the orientation of the terthiophene-decyl group with respect to the H-bonding network is very different in the two cases (see Supporting

Information). In the A-type, the tilt angle between the terthiophene-decyl groups and the H-bond network axis is small (around 30 $^\circ$), leading to a large steric crowding between the lateral groups. In contrast, in the B-type ribbon, the guanosines are in a staggered configuration, with the terthiophene-decyl groups nearly perpendicular to the ribbon axis, and an additional H-bond is possible between the ribose and the guanine (leading to ten “possible” H-bonds between four molecules). Together with the fact that in the STM images we only observe the lateral groups (the streaks) almost perpendicular to the brightest lines, this suggests that only the B-type network is formed under our experimental conditions. In the modeled B-type network, the total H-bonding energy (derived from the Dreiding force field) amounts to around 14 kcal mol⁻¹ for 8 H-bonds, that is, 1.8 kcal mol⁻¹ per H-bond in average. In Figure 5c, we show a molecular model of two adjacent B-type ribbons each made from eight molecules, fitting the unit cell measured in the STM experiments (the model in Fig. 5c shows 8×1 units cells along *a* and *b*, respectively). In this packing configuration, the neighboring terthiophenes of adjacent ribbons are not directly π -stacked because of both the steric hindrance and interdigitation of decyl groups,^[24] and of their propensity to commensurate with the underlying graphite plane. Note that π -type interactions between each oligothiophene and the graphite plane can lead both to parallel or “T-shape” conformations.^[25]

The fact that we only observed the B-type H-bonding network on graphite is in contrast with previous results on alkylated guanosine derivatives,^[14] which show only A-type network on highly oriented pyrolytic graphite (HOPG). Nevertheless, it is worth pointing out that **1** possesses only

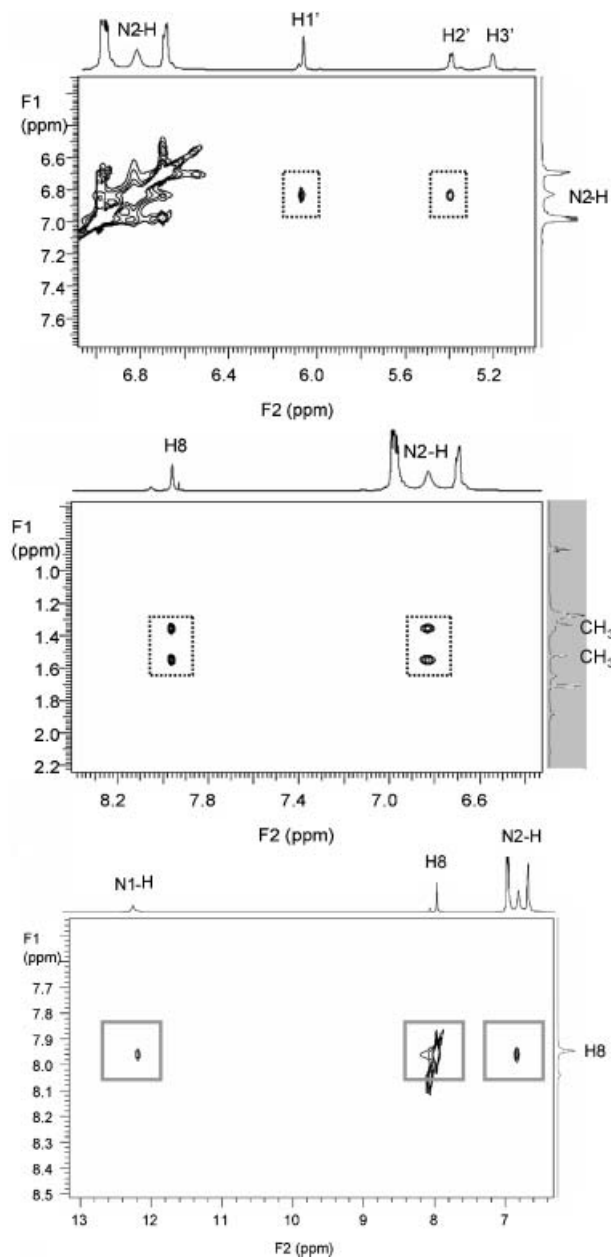


Figure 3. Portions of the NOESY spectrum (mixing time 200 ms) of 30 mM in [D8]THF at 0 °C. Relevant intermolecular cross peaks for the **A**- and **B**-type ribbon-like architectures are boxed in gray lines and black dashed lines, respectively.

one alkyl group (at the end of the terthiophene moiety), while the derivatives previously studied were doubly alkylated. Moreover, **1** possesses a sugar exposing an acetonide unit (pointing perpendicularly to the molecule's main plane), while the riboses were unsubstituted in ref.^[15]. These differences lead to several restrictions that favor the formation of the **B**-type network.

Interestingly, with atomic force microscopy we also observe a ribbonlike morphology for deposits of **1** onto mica substrates.

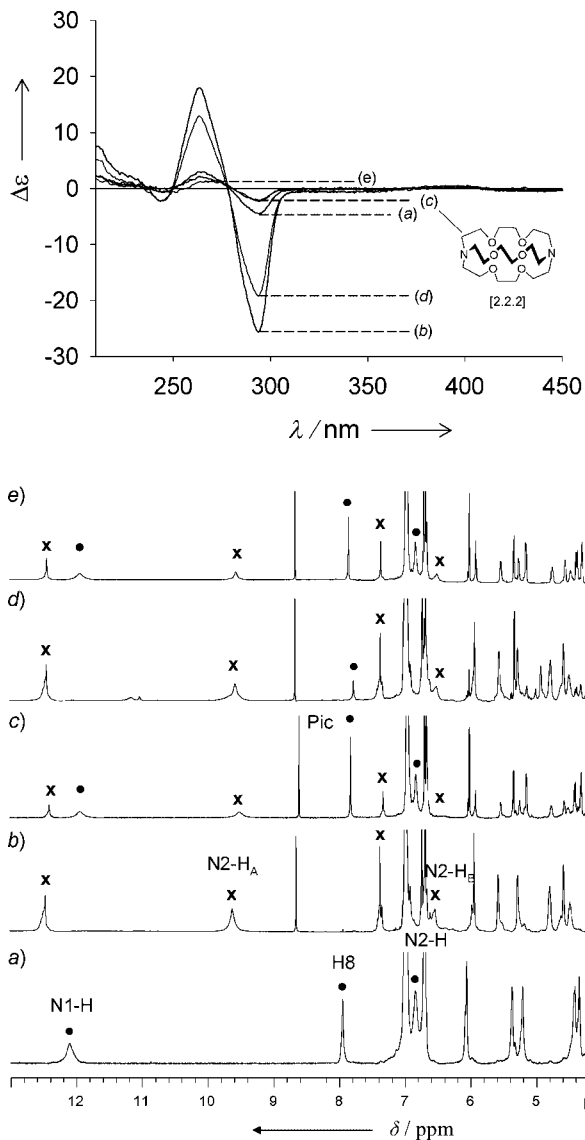


Figure 4. CD (top, 3 mm) and ¹H NMR (bottom, 30 mm) spectra of **1** in [D8]THF at 0 °C. a) Initial solution; b) after addition of 1/8 eq of K-Pic; c) after further addition of 5 eq cryptand [2.2.2]; d) after further addition of 1.3 eq HTF; and e) after further addition of 1 eq TEA. Dots and crosses mark the signals for the ribbon and octamer species, respectively.

The length of the ribbon varies from a few tens of nanometers to a few micrometers depending on the solvent: the use of solvents evaporating slowly allows for the formation of longer ribbons (see Supporting Information). However, the width and thickness of the ribbons are constant, that is, 11.2 ± 3 nm or a multiple of this value (corrected value taking into account the tip broadening)^[2a] and 0.6 ± 0.2 nm, respectively. The thickness indeed suggests that the ribbons are one-molecule thick structures. Note that the natural presence of alkali ions (e.g., K⁺) randomly distributed over the mica surface could lead to the formation of G-quartets. However, the observed ribbons are more likely to be due to H-bonded stacking into **B**-type

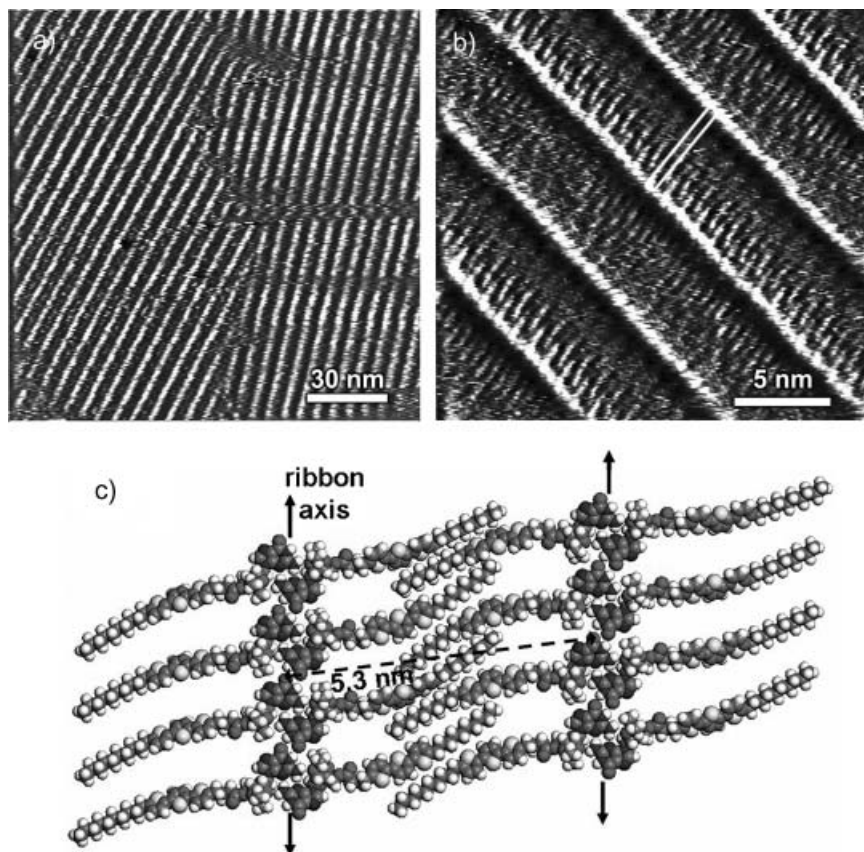


Figure 5. a,b) STM images of **1** on highly oriented pyrolytic graphite (HOPG). Tip bias $V_{\text{tip}} = -865$ mV; average tunneling current $I_t \sim 22\text{--}24$ pA. c) Molecular model of two adjacent **B**-type ribbons (each made from 8 molecules), fitting the unit cell parameters of the STM images.

ribbons as on graphite, since their width (11.2 ± 3 nm) fits in size with two parallel H-bonding networks as modeled in Fig. 5c (12.3 nm wide).

The formation of straight, parallel ribbons with lengths spanning from hundreds of nanometers to micrometers appears therefore as an intrinsic self-assembly process of **1** during the formation of thin films. Our scaffolding approach differs from those proposed taking advantage of extraordinarily stiff single polymers such as poly(isocyanodipeptide)s to form multichromophoric arrays of perylene bisimides,^[26] or on the use of single-strand DNA templates to direct the stacking of oligophenylene vinylenes,^[27] because of the much greater directionality of our supramolecular skeleton along with its high versatility determined by the use of guanosine building blocks.

In summary, here we have shown that **1** can form H-bonded ribbonlike or quartet-based supramolecular architectures in solution, depending on the conditions. SPM characterization at surfaces and molecular modeling show that **1** self-assembles into ordered crystalline architectures on surfaces. This self-assembly is governed by the formation of H-bonds between guanosines that dictates the spatial localization of oligothiophenes, ultimately forming 1D conjugated arrays that may be

employed as prototypes of supramolecular nanowires. Significantly the tuneable interconversion between the two highly ordered motifs fuelled by cation complexation and release allows the in situ reversible switch of two forms of oligothiophene–oligothiophene arrangements. The fully reversible and bistable optical and electrical properties achievable with this system may be of interest for applications in optoelectronics.

Experimental

Experimental details can be found in the Supporting Information.

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- [19] The low-intensity negative couplet present also before K-Pic addition is due to Na⁺ (or K⁺) contamination resulting from the synthetic procedure. In fact, addition of the cryptand [2.2.2] leads to a very weak monosignate CD signal as expected for an uncomplexed guanosine derivative.
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