Co-adsorption of Guanine and Cytosine on Graphite: Ordered Structure Based on GC Pairing

Sailong Xu,∗ Mingdong Dong,† Eva Rauls, Roberto Otero, Trolle R. Linderoth,* Flemming Besenbacher*

Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, University of Aarhus, Ny Munkegade, DK-8000 Aarhus C, Denmark

* Corresponding authors. Telephone: +45-8942 5536; Fax: (+45) 8942 3690; E-mail: trolle@inano.dk, fbe@inano.dk.
† These authors contributed equally to this work.

Experimental section

Solutions were prepared by dissolving the DNA bases guanine (Sigma Aldrich, 98% purity) and cytosine (Sigma Aldrich, 97% purity), respectively, into 1-octanol (Sigma Aldrich, 99.5% purity). A solution of the mixture was prepared from equal amounts of these saturated stock solutions, leading to an unsaturated solution with ~1:10 G:C molar ratio (the solubilities of guanine and cytosine in octanol were determined by measuring the volume of solvent needed to dissolve a fixed amount of solutes). To form the observed structures, a drop of solution was applied onto a freshly cleaved HOPG (Grade ZYA, Reliability & Quality BV, the Netherlands) surface, followed by annealing at 50°C for 1 h. Octanol was chosen as solvent because it has an appropriate solubility of the DNA bases investigated, combined with a slow evaporation rate providing a relatively long-term availability of a liquid/solid interface. As compared to a more strongly polar water buffer, the use of octanol is expected to reduce the solvent–solute hydrogen bonding interactions and hence facilitate the formation of hydrogen bonds between the dissolved DNA-base molecules.
The STM experiments were performed under ambient conditions at the liquid/solid interface with a commercial Digital Instruments Nanoscope IV MultiMode SPM system (Veeco Instruments, Santa Barbara, CA). STM tips were mechanically cut from a 0.25 mm Pt/Ir wire (80/20) and tested on freshly cleaved HOPG surfaces. Several different tips and HOPG samples were used to ensure reproducibility. All STM images were recorded in the constant current mode under various tunneling conditions (typical tunneling currents 0.5 - 1.0 nA and tunneling voltages 0.5 - 0.8 V) and with the sample positively biased. The STM scanner was calibrated from images of clean HOPG using the Scanning Probe Image Processor (SPIP™) software (Image Metrology ApS).

The error bars in table 1 reflect one standard deviation on the calibration constants, including possible effects of thermal drift. Alignment difficulties prevented identification of the lattice directions of the underlying HOPG substrate in the images of molecular overlayers. STM images are shown either as unprocessed images (except for background subtraction and a slight low-pass filtering) or processed by the correlation averaging method of the SPIP™ software. In correlation averaging a template area is defined, and an average is performed over the N (here N = 100) equivalently sized regions in the image that provide a best match (correlation) to this template.

Theoretical simulations were performed within the framework of the Self-Consistent Charge Density-Functional based Tight-Binding (SCC-DFTB) method. Since no information on the alignment or registry of the molecules with respect to the graphite lattice was available from the STM data, the substrate was not included explicitly in the simulations which had as their scope to elucidate intermolecular interactions responsible for the formed structures. The substrate is thus considered to mainly have the effect of confining the molecules in two dimensions, which can be included by constraining the geometry of the adstructure to a planar configuration during relaxation. However, in the case under investigation, a planar configuration turned out to be the most favorable arrangement also for free relaxation without constraints applied. Concerning the energetics of the structures of Figures 4d and 4e, we expect that inclusion of the substrate would lead to a constant energy shift due to the purely van der Waals character of the molecule substrate interaction and the
same stoichiometry in the two models. For the infinite chains, periodic boundary conditions (PBC) were used while the smaller molecular structures were set up as clusters, i. e. without PBC. In the calculations, all involved atoms were fully relaxed without constraints.

References:

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