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Stacks of Nucleic Acids as Molecular Wires: Direct Measurement of the Intermolecular Band Dispersion in Multilayer Guanine Assemblies

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Abstract: The intermolecular band dispersion related to the highest occupied molecular orbital in highly ordered, hydrated multilayer films of the DNA base guanine has been measured using photon-energy-dependent ultraviolet photoelectron spectroscopy. A bandwidth of 331 ± 8 meV at room temperature and a small effective mass of about 1.11 times that of a free charge suggest a high intrinsic hole mobility along quasi-one-dimensional stacks formed perpendicular to layered, hydrogen-bound networks.

Inspired by life itself, numerous applications in biotechnology[1] and organic electronics[2] rely on template-mediated molecular self-assembly.[3] Prominently, the transcription of genetic information employs deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) replication that is based on hydrogen-bonding (H-bond) interactions between base pairs of nucleic acids bound to backbones composed of phosphates and sugars.[4]

In bottom-up approaches, employing highly directional H-bonds is considered to be one of the most promising ways to build up nanodevices in a controlled way on well-defined substrates.[3] Different from homocyclic molecules like the oligoacenes, structural motifs may be largely decoupled from the electronic functions provided by π orbitals. Quite obviously, this potential has generated significant interest in the electrical properties of one-dimensional assemblies of nucleic acids.[5−9] The DNA molecule itself may be considered a system with well-defined energetic disorder because individual bases in the sequence exhibit distinguishable ionization potentials and affinities.[6,7] On the other hand, assemblies made of a single nucleic acid component, and in particular of the base with the lowest ionization potential, guanine (inset of Figure 1), have attracted attention since the $\pi-\pi$ orbital overlap along the stacking direction may lead to band-like charge transport and high mobilities.[6−9]

First-principle measurements of microscopic electronic parameters related to the hole mobility are possible using photon-energy dependent ultraviolet photoelectron spectroscopy (UPS) on multilayer thin films exhibiting a uniaxial molecular orientation and homeotropic alignment.[10] In the normal emission geometry, the in-plane wave vector component ($k_{\|}$) of the photoelectron vanishes. By changing the photon energy, $h\nu$, different values of the out-of plane component $k_{\perp} \propto (h\nu - E_B - \phi + V_0)^{1/2}$ are accessed such that the intermolecular band dispersion $E_B(k_{\perp})$ in the direction normal to the substrate may be obtained. E_B is the binding energy with respect to the Fermi level E_F of the spectrometer, ϕ the work function, and V_0 the inner potential.[10]

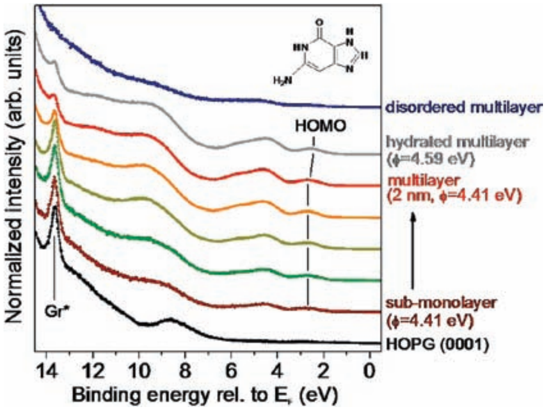

Figure 1. Wide-range He I UPS spectra of pristine guanine films on HOPG(0001), for increasing coverage. The spectra of a hydrated, ordered multilayer and of a disordered multilayer film obtained by fast deposition are shown for comparison. A peak related to a graphite-derived resonance and the position of the molecular HOMO are marked as "Gr*" and "HOMO", respectively.

Here, we report on the preparation of highly ordered guanine films on the surface of highly oriented pyrolytic graphite, HOPG(0001), its hydration, and the measurement of the intermolecular band dispersion along quasi-one-dimensional stacks present within the guanine multilayer crystal. Note that the self-complementary interaction between guanine molecules leads to the formation of monolayer networks on HOPG(0001) even when prepared from aqueous solutions.[11] The proposed structure has an epitaxial relation with the substrate[11] and is different from that of individual layers within the guanine monohydrate crystal.[12]

As shown in Figure 1, at 80 °C, highly ordered, pristine guanine films grow layer by layer, as recognized in He I UPS spectra from the slow disappearance of a graphite-related spectral feature,[13] denoted "Gr*", and the formation of well-defined peaks related to the molecular orbitals. Since spectra remain largely unchanged as a function of the thickness, it is concluded that the aromatic molecular cores in subsequent layers are parallel to the substrate surface, as they are for the monolayer.[11] Disordered guanine films obtained with a high evaporation rate, on the other hand, exhibit broad features with low spectral intensities. Films are structurally stable upon hydration, even if some of the H-bonds may be replaced by bonds to water molecules.[14] Spectral features related to molecular orbitals shift rigidly by the small amount of about 150 meV toward a lower binding energy whereas the work function increases by about the same amount. This leaves the ionization potential and hence the molecular orientation[13] unchanged. Atomic force microscopy (AFM) images confirm that about 2-nm-thick, hydrated multilayer films are smooth and cover the substrate completely.

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Photon-energy dependent spectra of a first hydrated and then air-exposed multilayer film are plotted within the low-binding energy region in Figure 2. Note that at normal emission, due to cross-sectional effects, the graphite π band dominates at intermediate photon energies of 40 to 60 eV. Its binding energy of about 8 eV, however, is far away from the binding energy region related to the highest molecular orbital (HOMO) of guanine. Accordingly, at energies between about 2 and 3 eV, a clearly recognizable, strongly dispersing spectral feature develops into a distinctive peak at intermediate $h\nu$ and is assigned to electronic states related to the HOMO. The dispersion can be traced over two periods and is evidence for the formation of at least one intermolecular band or, more likely, of the parallel dispersion of several bands predicted for the guanine monohydrate crystal.[6] Note in this context that the width of this peak is on the order of 1.0 eV which is too broad to account for a single band. As discussed theoretically,[7] a large bandwidth can only be obtained for optimal geometries where guanine molecules face each other in a flipped configuration, with a vanishing in-plane rotation with respect to each other. Since hydrogen bonding does not give rise to delocalized electronic states,[7] the electronic system is considered to be highly anisotropic. This justifies an evaluation of the peak positions as a function of $k_\perp$ using a single-band, one-dimensional tight-binding model $E_B(k_\perp) = E_B^0 - 2t\cos(k_\perp a)$. As shown in Figure 3, the best fit is obtained for a value of $V_0 = -11.5$ eV (see Supporting Information), of the position of the center of the band of $E_B^0 = 2.67$ eV, a bandwidth of 331 ± 8 meV corresponding to a $\pi-\pi$ overlap (or transfer) integral of $t = 83 \pm 2$ meV, and a unit cell consisting of two molecules along the stacking direction. Note that the double of the interlayer distance corresponding to the length of the unit cell of $a = 6.4 \pm 0.1$ Å obtained in this way is slightly smaller than that of the monohydrate crystal of 6.60 Å which has a monoclinic structure.[12]

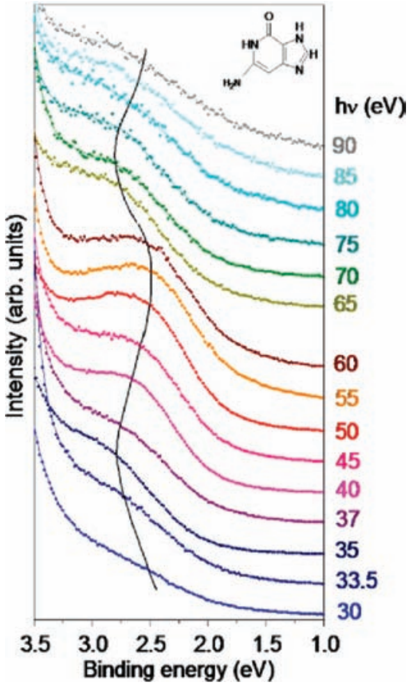

Figure 2. Photon-energy dependent UPS spectra of the hydrated multilayer recorded in the binding energy region of electronic states related to the guanine HOMO.

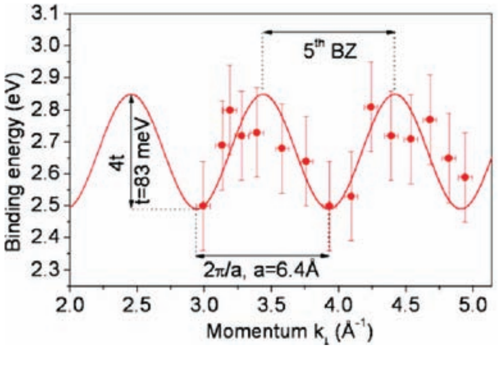

Figure 3. Experimental peak positions of the spectral feature related to the guanine HOMO (●) as a function of the out-of-plane electron momentum, $k_\perp$, and a fit of the dispersion around the 5th Brillouin zone (BZ) using a one-dimensional tight-binding model (—).

The curvature of the band at the center of the Brillouin zone provides a very small effective mass of a positive charge carrier m_h of 1.11 times that of a free charge suggesting the occurrence of band-like charge transport and of a high but anisotropic intrinsic hole mobility μ_h at room temperature (of >18 cm^2/(V s) using the relation $\mu_h > (e/m_h) \times (\hbar/4t)$).[15,16] Values that can be derived for the mobility may depend to some extent on the model employed but may even be larger than that calculated for guanine stacks[9] and as high as the best values for pentacene thin films.[17] Given the likely strong temperature dependence of t, an intermolecular bandwidth of more than 300 meV at 298 K compares well with predictions of up to more than 1.0 eV for favorable structures of guanine assemblies.[6,9] Note that such configurations are not provided by the helical arrangement of the DNA backbones. In this case, the orbital overlap vanishes even in polyguanine sequences.[7,9]

With guanine as *the* prototype, hydrogen-bound, self-assembled thin films made of relatively small heterocyclic molecules emerge as a new class of materials with excellent and highly anisotropic transport properties. Even more, the promise of combining the use of suitable, low-dimensional templates and solution processing of genetic matter may create the field of “Biological Electronics”. In this vision, electronic properties may be programmed and self-replicated using the power of supramolecular chemistry and genetic engineering.

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Supporting Information Available: (1) Details of experimental conditions; (2) Topographic (a) and phase-contrast (b) AFM images of a hydrated guanine multilayer on HOPG(0001); (3) Remark on the choice of V_0 and on the evaluation of the peak positions. This material is available free of charge via the Internet at http://pubs.acs.org.

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