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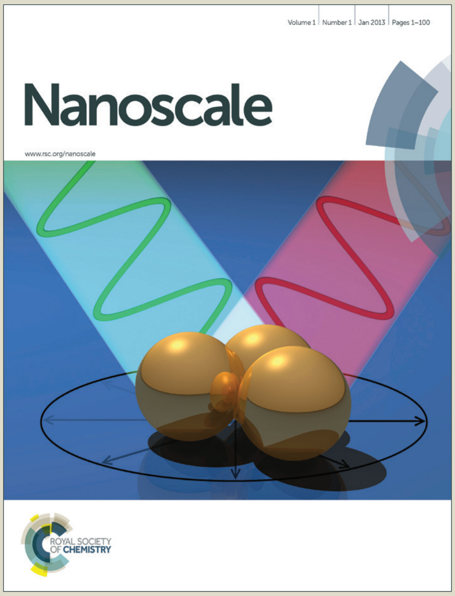
Accepted Manuscript



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# Tunneling Spectroscopy Measurements on Hydrogen-Bonded Supramolecular Polymers

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***Received 27th January 2014, Accepted Xth XXXXXXXXX 20XX***
***First published on the web Xth XXXXXXXXXX 200X***
**DOI: 10.1039/b000000x**

We studied the formation of hydrogen-bonded supramolecular polymers of **E**thyl **H**exyl **U**rea **T**oluene (EHUT) on a gold (111) surface by low temperature scanning tunneling microscopy. Tunneling spectroscopy performed along an individual molecule embedded in a self-assembled layer revealed strong changes in the value of the HOMO-LUMO gap. A variation of the LUMO state is attributed to the effect of space charge accumulation resulting from anisotropic adhesion of the molecule. In addition, for specific tunneling conditions, changes induced through the formation of hydrogen bonds became visible in the differential conductance (dI/dV) maps: isolated molecules, hydrogen bonded dimers and supramolecular polymers of EHUT were distinguishable through their electronic properties.

## Introduction

The ultimate goal of molecular electronics consists in using single molecules or molecularly thin films as electronic devices[1–4]. To this end, one has to contact molecules by metal electrodes and, in particular in the case of thin films, to study how the electronic properties of the investigated molecules, their conformation and consequently the molecular details of charge transfer at the molecule-metal interface are affected by the way molecules are organized within the film[5]. Since the pioneering STM study of charge states of a C60 molecule on a Au(110) surface by C. Joachim *et al.*[6], different strategies have been followed for establishing a double tunneling junction configuration and controlling charge transfer at the molecule-surface interface[7–9]. Up to now these studies where mainly devoted to simple systems like C60 or to small aromatic molecules[10] of known conformation and isotropic interactions. Larger molecules with delocalized electrons such as Phthalocyanine compound were also extensively studied, in particular their interaction with the surface in terms of charging effect and modification of either the band structure of the surface or the HOMO-LUMO gap of the adsorbed molecules. Depending on the tunneling barrier, it was possible to observe shifts of the molecular states under certain conditions.[11,12]

However, long supramolecular polymers formed by directional hydrogen-bonds have not yet been studied extensively by scanning tunneling spectroscopy (STS). Here, we demonstrate how local spectroscopy measurements by STS on hydrogen-bonded supramolecular polymers of **E**thyl **H**exyl **U**rea **T**oluene (EHUT) on a gold (111) surface are affected by conformation and directional molecule-molecule interactions. We present evidence for anisotropic interactions of each individual molecule with the substrate resulting in variations in the measured HOMO-LUMO gap. We also provide an explanation for a spectacular "mirage" effect, i.e. why for specific tunneling conditions a single EHUT molecules is well detectable while a hydrogen-bonded dimer of EHUT becomes invisible in the differential conductance (dI/dV) maps.

## 1 Experimental Section

Bis-urea EHUT ((2-ethylhexyl-3-[3-(3-(2-ethylhexyl)ureido)-4-methylphenyl]urea) was synthesized by addition of racemic 2-ethylhexylamine to 2,4-toluene diisocyanate as previously described[13]. EHUT molecules were evaporated in high-vacuum conditions at a pressure of ca. $10^{-8} mb$ and a temperature of $90°C$ on a clean herringbone reconstruction of Au(111) obtained on gold on Mica layers after flame annealing. STM and STS measurements were performed with a Omicron LT-STM working at $77K$ coupled to a lock-in amplifier to get access to conductance signal, using a bias modulation $V_{mod} = \pm 20mV$ at a frequency of $1kHz$. The phase signal

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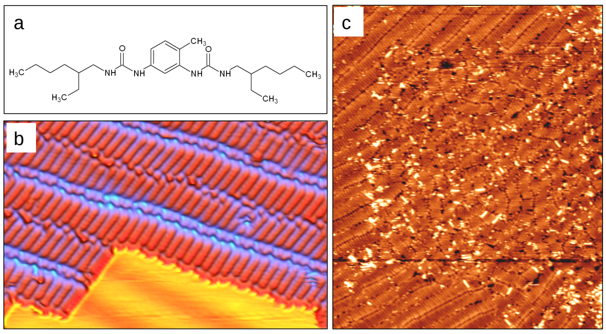

**Fig. 1** a) Scheme of the EHUT molecule. b) $20 \times 12.3 nm^2$ topographic image of an ordered monolayer of EHUT on Au(111) ($V_s = -500mV$, $I_t = 570pA$, $T = 77K$). Every continuous object corresponds to one single molecule. The bare gold substrate underneath the molecules can be seen at the bottom of the image[14]. c) $50 \times 60nm^2$ topographic image of an initially ordered monolayer of EHUT where a $40 \times 40nm^2$ area was disturbed by a previous scan at $-50mV$ and $2nA$. Many bonds in the layers are broken due to the tip interactions leading to sub-units such as short dimer-rows, few assembled molecules and single molecules randomly oriented with various conformations.

was tuned in order to minimize the capacitive crosstalk perturbation in the tunneling current. With these conditions, spectroscopy measurements on molecules embedded in ordered monolayers was performed with an open feedback loop. It was also possible to perturb the well ordered self-assembled monolayers by high electric field from the tip due to pulses of the bias voltage of typically $+3V$ to $+5V$ during 50 to $500ms$, leading to small patches of assembled molecules. Conductive image were performed in constant current mode with a reduced closed feedback loop in order to minimize the contribution of the vertical response of the piezoelectric scanner. Density Functional Theory (DFT) calculations were performed with the Gaussian 09 suite of programs, using the hybrid functional B3LYP, in combination with the $6-31G(d,p)$ basis set for all atoms[26,30]. The 0 value is assigned to the vacuum level and the calculations were done for the molecules in gas phase in order to see the effect of interaction between molecules in energy levels.

## 2 Results and discussion

The here investigated EHUT molecule (see 1a)) belongs to the family of bis-urea molecules only 2.4 nm long, which have been specifically designed for their high power of association through up to four hydrogen-bonds pointing in the same direction. This compound does not present useful intrinsic electronic properties, but is an excellent model to probe the effect of the self-assembly on the electronic properties of a hydrogen bonded supramolecular polymer. The ability of EHUT to form reversible architectures has been extensively studied in solution[15–18]. The sublimation of EHUT powder from a crucible in UHV onto a clean herringbone reconstructed Au(111) surface leads to a very large self-assembled supramolecular layer. An example is depicted in 1b). Hierarchical order results from a combination of multiple interactions at different levels: two molecules combine themselves by four hydrogen-bonds of the urea groups. However, the smallest self-consistent unit cell within the self-assembled monolayer consists of four molecules interdigitated via branched alkyl chains which lead to the formation of a zipper-like structure, as extensively studied previously[20]. Based on STM measurements and ab-initio calculations we concluded that EHUT on Au(111) forms a monolayer built up of close-packed twin-rows. Each molecule is ”edge-on” with the hydrogen-bonds pointing in a direction parallel to the surface. The zippers adopt an ”arch-like” configuration where the alkyl chains at the central zipper line are in direct contact with the substrate[19,20].

### 2.1 Spectroscopy of EHUT in perfectly ordered supramolecular layers

The self-assembled monolayer as a whole is rather mobile on the substrate but also quite rigid as it can cross monoatomic steps on the gold substrate without significant disturbances of the layer structure[21]. It was, however, possible to create disorder in such a layer with a STM tip at specific voltage and current conditions. 1c) shows an area of previously ordered molecules after a smaller scan at low voltage ($50mV$): intermolecular interactions were partially broken, one can recognize fragments of zipper-rows, half zipper-rows and individual molecules, resulting in an amorphous layer of densely but randomly packed molecules. It is essential to notice that for lower coverages, small patches or individual molecules are extremely mobile on the surface, making precision measurements impossible since the tip-molecule interaction easily overcomes the substrate-molecule interaction in most of the cases (see ref[21]). Therefore, we performed spectroscopy measurements on molecules embedded in an ordered monolayer, where interactions with neighboring molecules stabilized the position of the molecules. Under these conditions, spectroscopy measurements where highly reproducible and the spatial dependence of the STS spectra were repeatedly measured over 350 times.

In 2a), the colored arrows indicate the position of the STS measurements. $I(V)$ and $dI/dV$ spectra were simultaneously acquired and are shown in 2b) in accordance with the color code of 2a) along the molecules. The central yellow arrow (color on-line) indicates the position of the zipper line. Here, van der Waals interactions between neighboring supramolecular polymers cause that the alkyl chains point partially in the

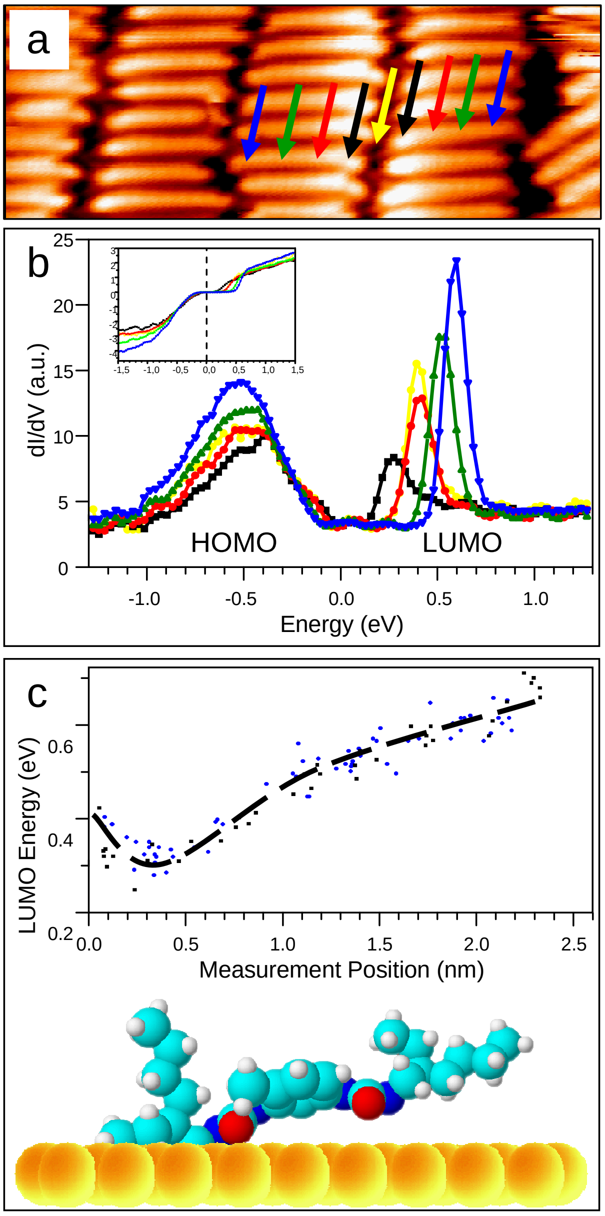

**Fig. 2** a) STM image of a monolayer of EHUT ($3.5 \times 10nm^2$, $V_s = -0.5V$, $I_t = 1.2nA$, 77K). Arrows represents the positions along the EHUT molecules where spectroscopy measurements were taken. Corresponding dI/dV spectra (and I(V) in the inset) according to the color code are represented in b). c) Representation of the energy of the LUMO state along the molecule (conformation calculated in[20]) measured as a function of the distance to the zipper line (yellow arrow in a)). The dashed line was drawn to guide the eye.

direction of the surface normal[20], causing, in turn, stronger adhesion at these points.

For all STS curves, we can distinguish two main peaks being at positive and negative energies, respectively. The structure of the peak observed at ca. $-500$ $meV$ is wide. Its position corresponds to the upper edge of the 2D band of the gold surface and is attributed to the HOMO level. The position of the HOMO level did not depend on the position along the molecule. This suggests pinning of the HOMO level as will be discussed later in the context of dI/dV maps. Starting from the central part of the zipper (yellow curve), the full width at half maximum (FWHM) of this peak first decreased (black curve) and then gradually increased with increasing distance from the zipper line (red → green → blue).

A significantly narrower peak was observed at positive energies, which is attributed to the LUMO level. Moving the position of the tip along the molecule led to spectacular changes in energy. At the position of the zipper line, the peak was found at ca. $+400$ $meV$ (yellow curve). However, as the tip was moved away from the zipper line, the LUMO peak first shifted to lower energies (black curve, peak at ca. $+280$ $meV$) followed by a gradual, almost linear increase to energies as high as ca. $+600$ $meV$ (blue curve) at the opposite extremity of the molecule (2c)). We attribute this shift mainly to a charging effect of the molecule in combination with a variation of the strength of the molecule-substrate interaction (strength of adhesion), i.e. the local fluctuation of the hybridization of the molecular orbitals with the gold atoms. It seems that this charging effect is also suggested in Ref.[12] for fluorinated copper-Phthalocyanines where the electron transfer effect mainly affects unoccupied levels. The variation of conductance of a molecule in contact with a substrate was also discussed by S. Datta[27]. In this paper, he introduced a parameter $\eta$ to describe the fraction of the applied potential which drops, e.g. due to a slight detachment of the molecule from the substrate, between a molecule embedded in a self-assembled monolayer and the substrate. $\eta$ allowed to quantify the shift in energy of the HOMO and LUMO peaks measured at a metal-molecule-STM tip junction. For a perfect contact between molecule and substrate ($\eta = 0$) the energy gap measured with the STM tip is expected to correspond to the actual HOMO-LUMO gap. In contrast, for $0 < \eta < 1$ the gap should appear larger, as depicted in 3. If $E_f$, $E_H$, and $E_L$ define the Fermi energy and the energies of HOMO and LUMO, respectively, the molecule is conducting at positive bias voltage $V_s$ only when:

$$eV_s > \min\left(\frac{E_f - E_H}{\eta}, \frac{E_L - E_f}{1-\eta}\right)$$

Taking into consideration that EHUT molecules are oriented mainly parallel to the substrate and accounting for the pinning of the HOMO state at the edge of the sp band of the

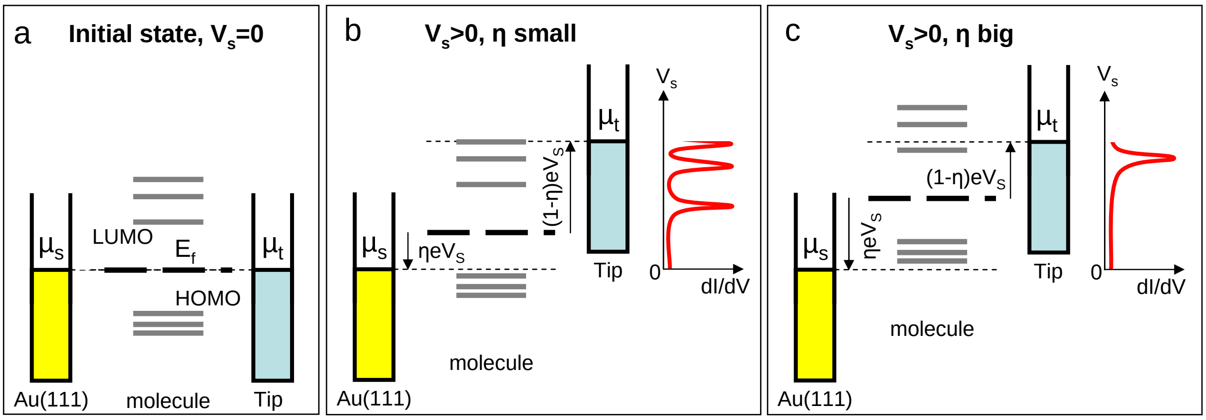

**Fig. 3** Illustration of the charging effect relating the shift of the position of the LUMO peaks to the parameter $\eta$ (see text). a) Bias voltage is zero and the Fermi levels of substrate, molecule and tip are aligned within the junction. In b), $\eta$ is small (close to zero), representing the case of strong hybridization of molecule and substrate. The resulting shift of the Fermi level of the molecule is small too and when increasing the bias voltage the first LUMO peak appears close to the actual value. c) Represents the case of a rather weak adhesion between substrate and molecule corresponding to $\eta$ close to 1. Thus, the charging effect is large and the measured electronic levels appear at higher values of the bias voltage. This apparent shift of the LUMO level is seen in the $dI/dV$ versus $V_s$ curves of 2.

gold substrate, we applied this model to our system. Accordingly, only the LUMO shifted to higher energies when measuring STS spectra along the molecule. 3b),c) depicts the evolution of the position of the first LUMO as a function of $\eta$ compared to the actual position for $V_s = 0$ (3a)). The shift of the HOMO level in 3 describes the general case of the paper of Datta[27].

Let us assume a perfect contact between molecule and substrate ($\eta = 0$). Then, we expect to measure the lowest energy of ca. $+280$ $meV$ for the LUMO peak, as obtained for the black curve in 2. Moving along the molecule, the shift of the LUMO peak to higher energies up to ca. $+600$ $meV$ (red, green, blue curves in 2b) can be attributed to a loosening of the contact between the molecule and the gold substrate. The corresponding increase of the value of $\eta$ along the molecule reflects the progressive detachment of the molecule from the substrate at increasing distances from the tip zipper-line. Thus, considering molecules that are only weakly interacting with the substrate, STS can lead to mis-interpretation in the evaluation of the gap. This effect was also considered in a recent work[22] where the shift of molecular orbitals was investigated by STS on molecules adsorbed on graphene and the opening of a gap in graphene was concluded.

### 2.2 Spectroscopy of EHUT in independant clusters of molecules

In order to characterize fully the electronic behavior of EHUT molecules during the self-assembling process, it was planned to perform spectroscopy measurements on disordered areas as depicted in 1b). However, these weakly bound molecules were rather mobile on the surface, even at low temperature, making measurements difficult. We could not obtain reproducible $dI/dV$ curves showing the HOMO and LUMO peaks of the molecules for small assemblies of a few molecules as they were easily perturbed by the electric field between the tip and the moving molecules. In some cases, however, it was possible to find stable conditions for obtaining acceptable dI/dV maps of patches of a few molecules. In order to get these small patches, initially ordered supramolecular layers were perturbed using high electric fields or mechanical forces applied via the STM tip as described in the experimental section. As one can see in 4a), using pulses of the bias voltage in the vertical z-direction, it was possible to ”unclip” groups of molecules from the supramolecular layer. The resulting small patches consisted mainly of twin-rows of more than thirty hydrogen-bonded molecules with random orientations. Thus, due to weak interactions with the substrate, the orientation of the zipper lines was not guided the substrate[21]. In addition, the fact that the reconstruction of the underlying gold substrate was not perturbed by the applied pulses further corroborates that the supramolecular layer is only weakly interacting with the substrate[19–21]. Through the applied perturbations, it was also possible to separate occasionally individual molecules from the main layer which were still in contact with this layer via their ends, as can be seen in 4a). There, the frames labeled I, II, and V show one single molecule, two molecules linked via hydrogen-bonds and five linked molecules, respectively. These individual molecules did not form twin rows and $\pi$-stacking and hydrogen bonds with other groups of molecules were broken. It was possible to image these out-of equilibrium states because the molecules were stabilized via weak Van der Waals interactions due to contacts via the alkyl chains. We also note that the conformation of these so stabilized individual molecules did not significantly differ from conformations within an ordered monolayer.

We now analyze the patches of isolated molecules indicated by the frames I,II and V depicted in 4a) more closely by STS. The upper row of 4b-d) exhibits the topography signal while the lower row shows the corresponding differential conductance images (dI/dV maps) acquired simultaneously. STM measurements in the constant current mode with a closed feedback loop represent a convolution of the electronic density of states (DOS) and topography and thus interpretation of the resulting images may be difficult or even erroneous. Thus, we have minimized the vertical response of the piezo scanner, assuming only small height variations, in order to obtain signals as close as possible to the real DOS (see ref[23–25]). In column b), we observe one single EHUT molecule (blue arrow) in contact with two neighboring patches of twin-rows. This molecule exhibited a much higher contrast in the dI/dV map compared to the other molecules in this frame. In column c), the pair of molecules seen in the topography image (dashed circle) was not visible in the conductance image with a contrast close to the gold substrate. Finally, column d) depicts five linked molecules with a contrast for both topography and dI/dV map similar to the one of the surrounding patches of twin-rows. One can also notice a strong contrast for the first molecule of the patch of five molecules which is attributed to a break of hydrogen bonding, leading to a different contrast at both extremities. This variation of contrast in the dI/dV maps clearly demonstrates a change in the density of states of the molecules which depends on the interactions with other molecules in the close vicinity and/or the substrate. We think that this can be an exemplary experimental illustration of the energy level splitting in the formation of a bond. In the case of the single molecule, the electronic states of the molecule correspond to the bias voltage used for imaging. When linking molecules via hydrogen-bonds or $\pi$-interactions, according to fundamental solid state physics of binding of two single atoms, the degeneracy of the electronic orbitals of the system is removed by splitting up the energy levels. For our system, we suggest that one single molecule would exhibit a HOMO and a LUMO state as depicted in 5a). As indicated by the STS measurement in the case of a full monolayer coverage, the HOMO level is pinned at the edge of the 2D band associated to the Shockley state of the gold surface which corresponds to the energy of $-500\ meV$. Here we cannot state that the observed level for a single molecule exactly corresponds to the HOMO level and is pinned at $-500 meV$. However, the electrons tunnel from the substrate to the STM tip through one level which we assume can be attributed to a filled state and

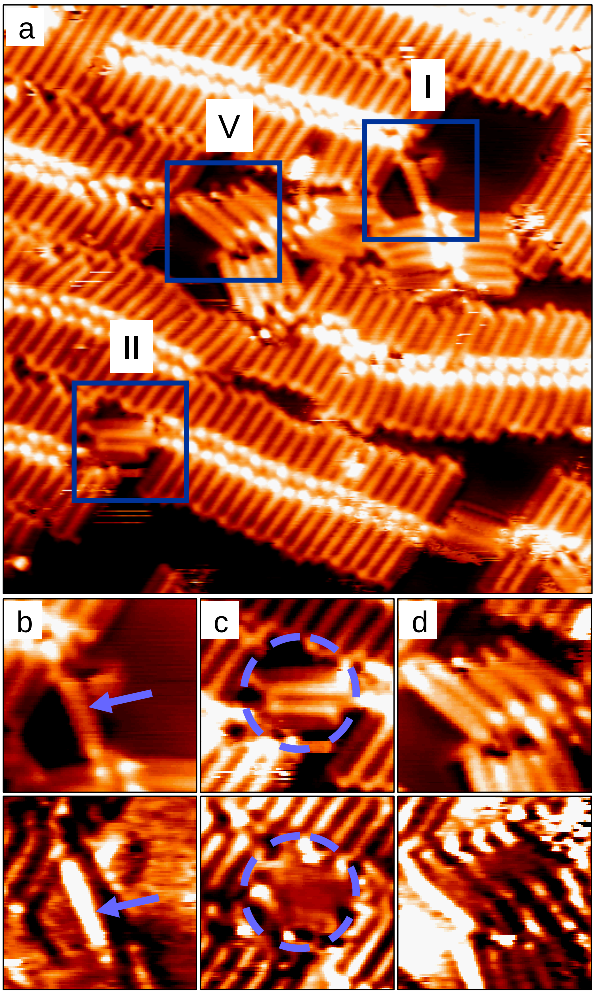

**Fig. 4** a) The supramolecular monolayer was disturbed by z-distance and voltage pulses resulting in a few isolated molecules and patches of molecules disconnected from the main layer ($20x20nm^2$, $V_s = -500mV$, $I_t = 380pA$). Three different regions are highlighted. b), c), d): zoom of STM images ($4x4nm^2$) of isolated patches of 1, 2 and 5 EHUT molecules corresponding to the frames I, II and V in a). The upper row exhibits the topography images while the lower row shows the corresponding differential conductance images (dI/dV maps).

which is represented as HOMO level in 5a) and may move in energy as a function of the number of molecules in interaction for small patches. Thus, the contrast is enhanced in the dI/dV map because of the localized tunneling energy of $V = -500\ meV \pm 20meV$ as opposed to the topography in which the energy is integrated starting from the Fermi level. In the case of two interacting molecules, one can expect that the HOMO level splits up in two sub-levels, due to the coupling of the molecules via hydrogen-bonds and/or the Jahn-Teller effect[28] caused by the distortion of the molecules reported previously[20]. This splitting results in two sub-levels separated by a gap which under these conditions is centered at $-500\ meV$. Therefore, although the pair of molecules is visible in the topography image, it disappears in the dI/dV map. In the energy range of $500 \pm 20meV$ the electrons tunnel from the gold substrate to the tip without tunneling through electronic states of the molecules. This gap can be roughly minimized as it is larger than the convolution of the bias modulation and the temperature effects, which allow us to estimate an order of magnitude of the splitting gap of more than $100meV$. Linking more than two molecules (4d and 5a) leads to further splitting of the energy levels resulting in gaps that are smaller than the modulation amplitude of the bias voltage $V_{mod}$. Thus, electrons can tunnel through these orbitals and produce a contrast in the conductance image which is similar to the contrast obtained for any molecule being part of a compact self-assembled monolayer.

In order to check if this interpretation is realistic, we have performed density functional theory (DFT) calculations with the Gaussian 09 suite of programs, using the hybrid functional B3LYP, in combination with the $6-31G(d,p)$ basis set for all atoms[26,30]. 5b) presents the calculated occupied molecular levels for 1, 2 and 5 molecules in vacuum. For the calculation we considered the conformation of molecules on gold surface which had been determined previously[20]. The similar molecular levels splitting also were obtained for the optimized conformation of molecules in vacuum where molecule showed a tendency to form a helical structure (See Figure 9a of reference[31]). In the latter case, geometry optimizations were carried out with symmetry restrictions by considering hydrogen bonding as semi-bonds between bis-urea sub-units of neighboring molecules. These results indicate that the energy levels splitting is independent of the molecular conformation. The energy values as expressed relatively to the vacuum level, therefore the HOMO and LUMO values appear as negative. This calculation does not reflect the exact reality of the experiment as the gold substrate reconstruction is not taken into account due to its huge unit cell. However, for two molecules connected via H-bonding, a splitting of ca. $550meV$ is found. This value is higher than the bias voltage modulation used for the lock-in detection during measurement. Moreover, for 5-molecules patches, the energy levels are aligned with

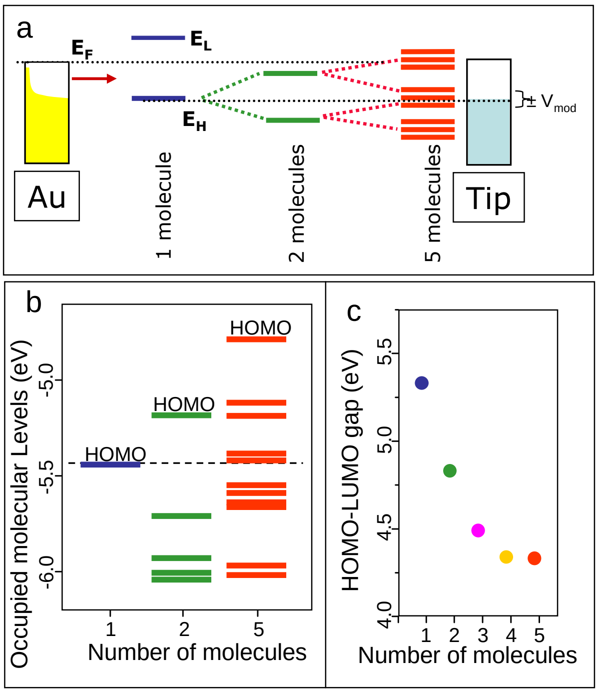

**Fig. 5** a) Illustration of the possible interpretation of the bright and dark contrast seen in the dI/dV maps of 4 showing a variation of the HOMO-LUMO gap as a function of coupled molecules. b) Gaussian calculation of the splitting of the HOMO level of EHUT as a function of the number of molecules associated together via H-bonding. The scale is related to the vacuum level. c) Evolution of the HOMO-LUMO gap for the same configuration of molecules. For more than 4 molecules, the gap remains almost constant.

the initial HOMO state of individual molecules, quenching the ”mirage” effect observed experimentally with a molecular dimer. From this calculation, one has to draw two essential messages : the energy differences such as HOMO-LUMO gap follow the tendency of the experimental observations, i.e. the gap reaches an asymptotic value as the number of molecules in interaction is increasing as depicted in 5c. An analogy may be drawn, for example, with the evolution of the shift of the ground state in 2D copper clusters as a function of the number of atoms in the clusters[32]. However, contrary to that work where the asymptotic behavior appears after a cluster size of more than 30 atoms covalently bound, in our work, the gap value is almost constant after only 4 molecules assembled via H-bonding. This also supports the cooperative behavior of these molecules as reported previously. The second result concerns the energy splitting which can be explained through the interaction of molecules via H-bonding. The molecular conformation used for the calculations was the one obtained in Ref.[20] and the distances between hydrogen and oxygen atoms of neighbouring molecules were fixed, leading to a constraint H-bonding. As the calculation was performed in a gas phase and not on the surface, the molecules showed a tendency to form a helical structure because they were not hindered by the surface. This may also explain the discrepancy between the experimental result and the calculated values which differ from more than $1eV$. However, the general tendency remains in agreement with our conclusions, i.e. the splitting of the energy levels upon the formation of H-bonding between EHUT molecules. Thus, the calculations support our experimental observation and interpretation.

The formation of layers of supramolecular assemblies through hydrogen-bonds have been reported previously (see ref.[29] and references therein). In addition, in our work we provide direct evidence for the splitting of molecular energy levels caused by the formation of hydrogen-bonds during the process of supramolecular self-assembly. The special behavior of the dimer with respect to larger number of linked molecules is reminiscent of the different association constants for dimers and larger supramolecular assemblies in solution[18].

## Conclusions

In summary, using low temperature STM and STS we have investigated the electronic structure of EHUT molecules. The molecules were studied either in supramolecular monolayers or smaller assemblies ranging from a single molecule to patches of few molecules. We were also able to show the evolution of the LUMO position as a function of the strength of interaction between the molecule and the substrate, related to the charging effect induced in the molecule during measurement. This demonstrates that the value of the HOMO-LUMO gap of organic systems may be varying in space as soon as molecule-substrate interactions vary along or across a sufficiently large molecule. This may open new routes for molecular electronics as one may be able to control different conduction channels depending on the interaction strength along the molecule. In addition, we identified a change of contrast in conductance images attributed to the formation of intermolecular hydrogen-bonding and the possible formation of band structures. An asymptotic value for the HOMO-LUMO gap was observed for patches containing more than four hydrogen-bonded molecules, corroborating the cooperative effect involved in the self-assembly process.

## Acknowledgements

The authors acknowledge funding support from the Région Alsace, the CNRS (ACI-Nanoscience) and the German Science Foundation (DFG).

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