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Bias-Induced Conformational Switching of Supramolecular Networks of Trimesic Acid at the Solid-Liquid Interface

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ABSTRACT

Using the tip of a scanning tunneling microscope, an electric field-induced reversible phase transition between two planar porous structures ('chickenwire' and 'flower') of trimesic acid was accomplished at the nonanoic acid/highly oriented pyrolytic graphite interface. The chickenwire structure was exclusively observed for negative sample bias, while for positive sample bias only the more densely packed flower structure was found. We suggest that the slightly negatively charged carboxyl groups of the trimesic acid molecule are the determining factor for this observation: their adsorption behavior varies with the sample bias and thus, is responsible for the switching behavior.

INTRODUCTION

Surfaces that respond to an external stimulus in a specific manner, also known as "smart" surfaces, have aroused great interest due to their myriad of applications as – just to name a few - biosensors, microfluidic devices, intelligent membranes and drug delivery vehicles.[1,2] Most studies aim to achieve reversible control, in which the surface properties are altered when external stimuli are applied and upon removal of the external stimuli the original surface properties are restored. However, non-reversible modifications could also be aimed at in drug delivery systems and surgical implants to facilitate wound healing and regeneration.[3,4]

Physisorbed self-assembled monolayers at the solid-liquid interface have been proven to be a viable approach towards designing such smart surfaces. Due to their relatively weak interaction strength with the supporting surface as compared with chemisorbed systems, the molecular and interfacial interactions governing the assembly provide enough flexibility to ensure good control over the structure formation and switching between different states becomes possible. So far, switching has been achieved through external stimuli such as

light,[5-11] heat,[11-17] pH,[18] surface potential,[19,20] ion triggers[21,22] as well as by an electric field induced between a scanning tunneling microscope (STM) tip and a surface.[14,15,23-27]

Due to their reversibility and high directionality, physisorbed hydrogen-bonded systems at the solid-liquid interfaces are promising candidates for producing smart surfaces. Among others, carboxyl-functionalized molecules are often used to build up H-bonded molecular networks since the carboxyl groups can serve as both hydrogen bond donor and acceptor. In particular, trimesic acid (benzene-1,3,5-tricarboxylic acid, Fig. 1) (TMA), a planar molecule with 3-fold symmetry, which consists of three carboxyl groups (-COOH) attached to a central benzene ring, has been widely-investigated at the solid-liquid interface.[28-35,41] Previous STM experiments at the solid-liquid interface for TMA on highly oriented pyrolitic graphite (HOPG) showed that the type of TMA structure that forms can be controlled by the solvent choice,[30-32,34] by the concentration of TMA in solution[33,36] and by the temperature.[34] Furthermore, it was shown that the structure of TMA networks can be changed by the addition of metal nitrites to the TMA solution[42]. TMA networks were found to arrange themselves in several different configurations. These configurations include densely-packed networks as well as porous configurations. Of these porous configurations, the 'chickenwire' (or 'honeycomb', Fig. 2) and the 'flower' structures (Fig. 3) are the most prevalent ones.

1,3,5-tris(4-carboxyphenyl) benzene (BTB), a larger analogue of TMA with the same functional groups and symmetry, forms similar supramolecular networks as TMA but with a larger lattice constant.[37] A recent paper by Cometto *et al*.[23] showed that the configuration of supramolecular networks of BTB in nonanoic acid on HOPG at the solid-liquid interface can be altered in an STM setup by changing the polarity of the bias applied to the sample. They demonstrated that, upon changing the sample bias from negative to positive, the BTB network could be switched from the chickenwire configuration to the close-packed one.

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Switching the sample bias from positive to negative led to the reverse switching event. However, an unambiguous explanation for the observed switching is not given in [23].

The similarity in molecular structure and formed supramolecular networks on HOPG for TMA and BTB suggests that a comparable bias-dependent switching could occur for TMA as well. So far, however, this switching effect based on changing the sign of the bias voltage has not been investigated for TMA networks. On the other hand, such a comparison study should also add valuable information for deriving a clear explanation for switching of BTB networks. In this paper, we demonstrate that networks of TMA formed at the interface between a nonanoic acid solution and an HOPG substrate can be switched from the chickenwire structure at negative sample bias to the flower structure at positive sample bias by changing the STM sample bias sign *in situ*. Moreover, our results indicate that the switching of TMA networks occurs via a different mechanism as compared to the mechanism suggested for the switching of BTB networks[23].

EXPERIMENTAL SECTION

Solutions of two different concentrations of TMA in nonanoic acid (Sigma-Aldrich, 96%) were prepared. First, a slightly oversaturated solution of TMA in nonanoic acid was prepared. Drops of saturated solution were obtained by drawing liquid from the top of an oversaturated solution kept in a vial. A 66% saturated solution was prepared by taking 1 mL of saturated solution and diluting this with 0.5 mL of nonanoic acid. The 66% saturated solution was used to verify if the switching could also occur at lower concentrations of TMA (see Fig. S3 in the supplementary material). However, we did not perform a systematic test of the effect's concentration dependency.

For each measurement, a drop of TMA solution was placed on a HOPG (Goodfellow) substrate already mounted inside the STM. The HOPG crystal was cleaved using adhesive

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tape before every measurement. All STM images were acquired at the solid-liquid interface under ambient conditions with a Molecular Imaging Keysight N9700C scanner, using mechanically cut Pt/Ir (90:10) wires (Goodfellow, 0.25 mm diameter) as tips. All STM images were analyzed and processed using WSxM 5.0.[38] All bias values are given with respect to a grounded tip. Typcial scanning speeds used were in the range of 480 nm/s. Switching of TMA networks upon changing the bias voltage occurred on the order of seconds.

RESULTS AND DISCUSSION

Lackinger *et al.*[31] reported that TMA dissolved in alkanoic acid self-assembled into two different types of supramolecular networks at the solution/HOPG interface. They observed that TMA exclusively formed the flower structure at the interface between HOPG and solutions in butanoic, pentanoic and hexanoic acid, while for solutions of TMA in octanoic and nonanoic acid only the chickenwire structure was observed. Both networks were present at the same time when heptanoic acid was used as a solvent. Hietschold *et al.*[33,36] reported that by tuning the molecule concentration by sonication, TMA self-assembled in flower, filled flower and dodeca-rim structures in heptanoic acid while the chickenwire structure was not observed for these conditions. In contrast to Lackinger *et al.*,[31] both chickenwire and flower structures could be observed in octanoic acid. In nonanoic acid, only the chickenwire and the filled chickenwire structures were reported. In a subsequent study, Hietschold *et al.*[34] observed the flower structure in octanoic acid only after the HOPG substrate was heated up to temperatures between 40° – 70° C.

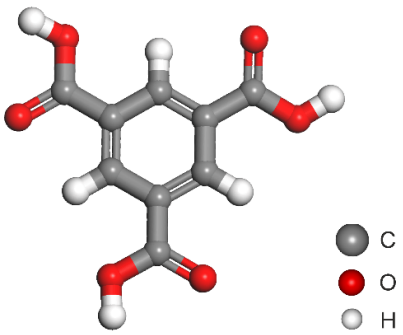

Fig. 1 Schematic representation of benzene-1,3,5-tricarboxylic acid (trimesic acid, TMA).

In our experiments, we used solutions of TMA in nonanoic acid. According to earlier studies, TMA should arrange in the chickenwire structure[31] at the interface between solution and HOPG. Fig. 2a shows an STM image of the chickenwire structure. The STM image was obtained by using a negative sample bias for imaging the interface between saturated TMA solution in nonanoic acid and an HOPG substrate. Fig. 2b shows the molecular model of the TMA chickenwire structure which is stabilized by dimeric O–H···O hydrogen bonds (highlighted in yellow). The unit cell parameters for the chickenwire structure were found to be $a = b = 1.6$ nm and $\theta = 60°$, which closely match the values reported in literature.[28,31] The chickenwire network forms even over scales of hundreds of nanometers with the presence of multiple rotational domains (see Fig. S1 in the supplementary material).

At positive sample bias, however, we found that TMA self-assembles into the flower structure. So far, this structure has never been reported for TMA dissolved in nonanic acid.[31,33] Figures 3a and 3b depict an STM image and a molecular model of the flower structure, respectively. Fig. 3a was obtained - like Fig. 2a - at the interface between saturated TMA solution in nonanoic acid and HOPG, but this time we used a positive sample bias instead of a negative one. The flower structure is stabilized by both dimeric O–H···O (highlighted in yellow) and cyclic trimeric (highlighted in blue) hydrogen bonds. The unit cell parameters for the flower structure are found to be $a = b = 2.5$ nm and $\theta = 60°$, which matches values reported in literature.[28,31,39] The flower structure is more densely packed (0.98 molecules per nm^2) than the chickenwire structure (0.78 molecules per nm^2). Like the chickenwire structure, the flower structure also forms on a larger scale and can have multiple rotational domains (see Fig. S2 in the supplementary material).

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We furthermore found, similar to Cometto *et al.*'s results for BTB networks,[23] that it is possible to switch TMA networks from one configuration to the other by changing the STM bias polarity. Fig. 4 shows switching from the chickenwire to the flower structure and vice versa *in situ*, i. e. during scanning. The first part of the STM image shown in Fig. 4a (the top part) was obtained at a sample bias of -0.5 V. In this part of the image, TMA arranged in the chickenwire configuration. After switching the sample bias to +0.5 V (indicated by the white dotted line in Fig. 4a), the TMA molecules assembled into the flower structure. This switching was also observed for a different concentration of the TMA solution (see Fig. S3 in the supplementary material). As shown in Fig. 4b, we also observed switching back from the flower to the chickenwire structure by switching the sample bias from a positive to a negative value. These results demonstrate that TMA networks can be reversibly switched *in situ*, similar to the switching effect Cometto *et al.* reported for BTB.[23]

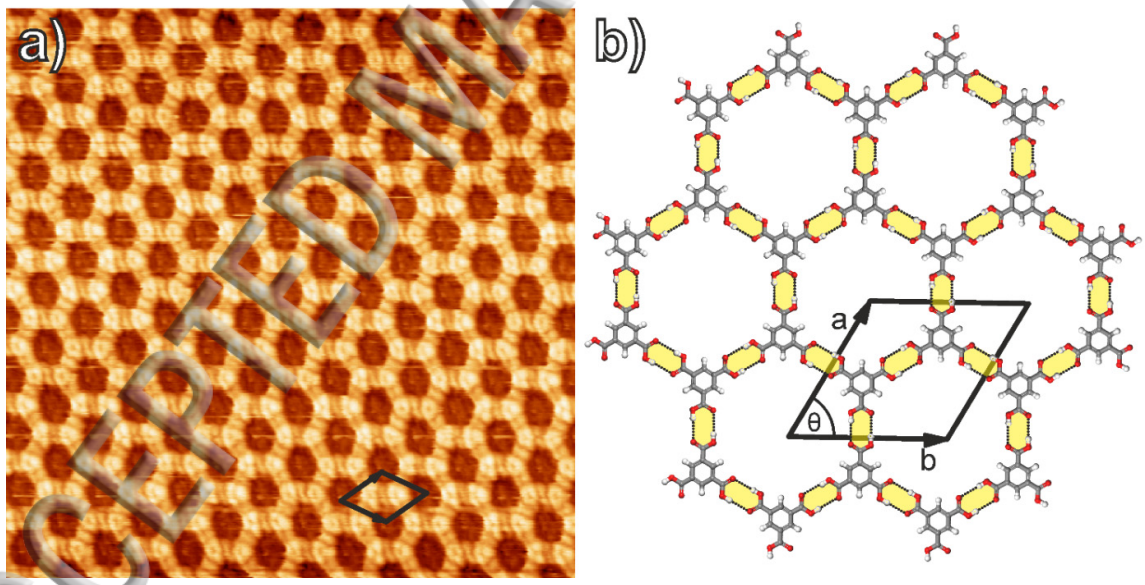

Fig.2 (a) STM image (20 x 20 nm^2, V_{bias}= -1 V, I = 20 pA) showing the chickenwire structure formed by TMA at the interface between nonanoic acid and HOPG. (b) Molecular model of the chickenwire structure. The chickenwire structure is exclusively stabilized by dimeric O–H···O hydrogen bonds (highlighted in yellow and shown by black dotted lines). The unit cell

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parameters for the chickenwire structure are $a = b = 1.6$ nm and $\theta = 60°$. The unit cell is indicated by a black rhombus.

In order to explain the observed switching behavior of TMA, the following three effects have to be looked at in more detail: (i) possible formation of a dipole moment for TMA upon conformational changes, (ii) possible deprotonation of TMA´s carboxyl groups and (iii) thermodynamic considerations.

Cometto *et al.*[23] hypothesized that a possible reason for the structural switching of BTB networks is an out-of-plane dipole moment present for the close-packed BTB networks because in that arrangement the molecules are not completely coplanar with the HOPG surface, in contrast to the chickenwire (also called honeycomb) BTB structure for which the molecules are coplanar with the HOPG surface. These molecular dipole moments would then make the close-packed networks energetically more favorable under a positive sample bias by favorably aligning with the electric field between the STM tip and the HOPG substrate. Theoretical investigations for the adsorption of an individual TMA molecule on graphene reported a highly deformed molecule with its carboxyl groups closest to the graphene.[40] Thereby, TMA gets n-doped and graphene is left p-doped. However, for either the chickenwire or superflower structure TMA was found to be almost planar. This is due to the formation of directional H-bonding within both structures. Based on these earlier findings, we assume that the formation of out-of-plane dipole moments is less pronounced – if at all - for TMA within 2D structures. Therefore, the mechanism proposed by Cometto *et al.*[23] cannot explain the switching of TMA networks. On the other hand, we can deduce that the carboxyl groups are negatively charged and can act as electron acceptors which in turn favors TMA adsorption on a positively charged substrate.

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A partial deprotonation of the carboxyl groups of BTB at positive sample bias (due to water contamination of the organic solvent) was suggested to support the switching mechanism.[23] Under such conditions, the water molecules would act as proton acceptors and drive the transition to the more densely packed structure. Accordingly, partial deprotonation of the TMA molecules at positive sample bias cannot be completely ruled out for the present case. However, in agreement with refs. [23] and [15] we do not favor this interpretation since a well-defined partial deprotonation - exactly one out of three carboxyl groups - would need to happen for each TMA molecule.

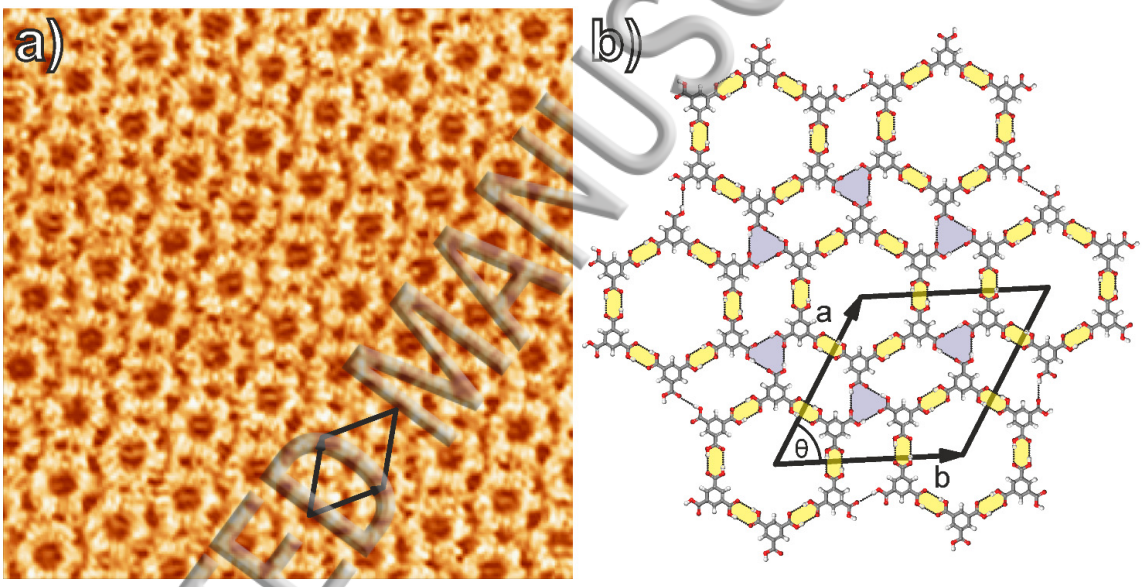

Fig. 3 (a) STM image (20 x 20 nm^2, V_{bias} = +0.5V, I = 20 pA) showing the flower structure formed by TMA at the interface between nonanoic acid and HOPG. (b) Molecular model of the flower structure which is stabilized by dimeric O–H···O (highlighted in yellow) as well as cyclic trimeric (highlighted in blue) hydrogen bonds. The intermolecular O–H···O hydrogen bonds are indicated by black dotted lines. The unit cell parameters for the flower structure are a = b = 2.5 nm and θ=60°. The unit cell is indicated by a black rhombus.

The effect of temperature for the formation of specific structural phases from either TMA or BTB at the liquid/HOPG interface has been studied by several groups. Lackinger et al.[14] investigated the temperature-induced reversible phase transition between the chickenwire and the close-packed structures of BTB in fatty acid solutions from a thermodynamic point of view. Their findings suggest that the presence and stability of the chickenwire structure at room temperature can only be explained by accounting the stabilizing contributions of the solvent molecules co-adsorbed in the BTB pores. Upon increasing the temperature, the co-adsorbed solvent molecules desorb first as they are more weakly bound to the HOPG surface than the BTB molecules. Thus, a destabilization of the porous structure occurs, leading to the formation of the more densely packed structures. De Feyter et al.[15] investigated the switching behavior of the BTB chickenwire structure filled with guest molecules (coronene and nanographene) in fatty acid solutions. They observed that the two-component host-guest system can be reversibly switched between a low (chickenwire) and a high density (close-packed) phase using either a thermal (global) stimulus or the electric field applied between the STM tip and the substrate (local stimulus). They also reported that the self-assembled networks became insensitive to the voltage polarity in a dry environment, emphasizing the fact that the presence of the solvent is vital for the switching behaviour. Furthermore, by adding a droplet of warm solvent on top of the pre-formed BTB-nanographene network held at room temperature, the phase transition of the host-guest system from the porous network to the close-packed one was triggered. Upon cooling down of the sample, the reverse phase transition was observed. For TMA Hietschold et al.[34] reported that annealing the chickenwire structure in octanoic acid solution at temperatures between 40° - 70° C resulted in the formation of the flower structure (images were acquired at positive sample bias and thus, a bias effect can be ruled out). From the above discussion we hypothesize for the present case,

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that the chickenwire structure is stabilized by solvent molecules and the flower structure is preferred over the chickenwire one from a thermodynamical point of view.

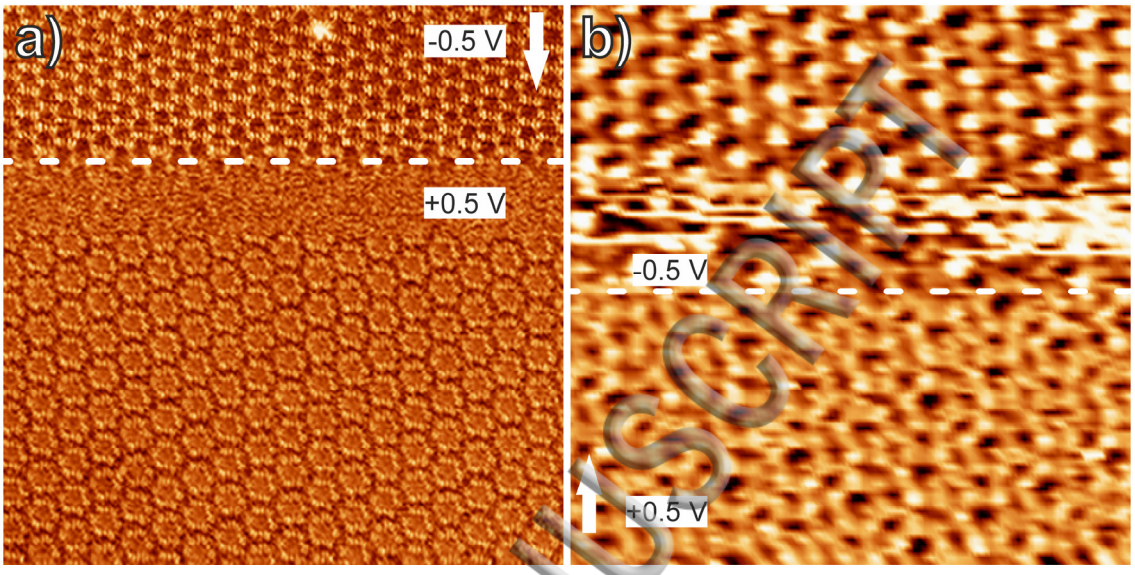

Fig. 4 STM images of TMA formed at the interface between nonanoic acid and HOPG showing the voltage-induced phase transformation from chickenwire to flower structure and vice versa. The white arrows indicate the scan direction. (a) At first, the sample bias was set to -0.5 V. In this part of the STM image (40 x 40 nm^2), TMA forms the chickenwire structure. At the white dashed line, the sample bias was switched to +0.5 V, after which the molecules rearranged into the flower structure. The tunneling current was kept at 20 pA for the entire image. (b) STM image (20 x 20 nm^2) demonstrating the reverse switching, namely from the flower to the chickwire structure. For +0.5 V, the flower structure is present while upon switching the bias to -0.5 V (at the white dashed line), the chickenwire structure appears. However, in the present case, the contrast for the chickenwire structure is inversed.

Combining the considerations made above, the following scenario for explaining the switching behavior is brought forward. In agreement with previous studies, we may conclude that in the moment the bias polarity is changed (equal to a voltage pulse), both TMA and the

solvent molecules react to this perturbation by shortly desorbing from the surface into the solution. For a positive sample bias, the thermodynamically favored phase (flower structure) adsorbs. This is reasonable since the adsorption of the negatively charged carboxyl groups (of both TMA and the solvent) is considered favorable at positive sample bias (perhaps also due to the favorable alignment of their dipole moment with the electric field) and thus, their number will be maximized. One now would expect that a close-packed TMA structure, similar to the close-packed BTB structures, should form. However, close-packed TMA arrangements have so far not been reported at the graphite/fatty acid interface whereas the underlying reason could up to now not be identified. For negative sample bias, the kinetically trapped phase (chickenwire structure) forms which is stabilized by the co-adsorption of solvent molecules inside the pores and for which the number of carboxyl groups per unit area is less compared to the flower structure. This may be explained by the unfavorable situation that the negatively charged carboxyl groups have to adsorb on a negatively biased sample.

CONCLUSIONS

Supramolecular networks that can be externally triggered in a controlled manner represent an excellent candidate for a smart surface. In this work, we studied the switching behavior of TMA networks at the interface between an HOPG substrate and a nonanoic acid solution using the electric field in an STM setup. We could successfully switch from the chickenwire structure at negative STM sample bias to the flower structure at positive sample bias. By changing the bias polarity, the energy barrier between the two different supramolecular configurations is reduced, and the switching becomes possible. Our results suggest that the switching of TMA networks occurs via a different mechanism as the one suggested for switching of BTB networks[23]. It is worth mentioning that, up to our knowledge, the flower structure of TMA in nonanoic acid on HOPG was never reported. Furthermore, it was

previously reported that the TMA chickenwire structure in octanoic acid was not affected by an electric field.[27] These results demonstrate that there are still new effects to be observed for a molecule as extensively studied as TMA. The results also give yet another illustration of the inherent invasiveness of using STM for probing surfaces.

SUPPLEMENTARY MATERIAL

See supplementary material for overview STM images of the chickenwire and flower structure and an STM image of the switching of the chickenwire to flower structure.

ACKNOWLEDGEMENTS

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REFERENCES

[1]P. M. Mendes, Chem. Soc. Rev. **37**, 2512 (2008).

[2]J. Rogers, Z. Bao, K. Baldwin, A. Dodabalapur, B. Crone, V. Raju, V. Kuck, H. Katz, K. Amundson, J. Ewing and P. Drzaic, Proc. Natl. Acad. Sci. U. S. A. **98**, 4835 (2001).

[3]H. K. Patra, Y. Sharma, M. M. Islam, M. J. Jafari, N. A. Murugan, H. Kobayashi, A. P. F. Turner and A. Tiwari, Nanoscale **8**, 17213 (2016).

[4]M. Abrigo, S. L. McArthur and P. Kingshott, Macromol. Biosci. **14**, 772 (2014).

[5]D. Bleger, A. Ciesielski, P. Samori and S. Hecht, Chem. -Eur. J. **16**, 14256 (2010).

[6]Y. Shen, L. Guan, X. Zhu, Q. Zeng and C. Wang, J. Am. Chem. Soc. **131**, 6174 (2009).

[7]Y. Shen, K. Deng, X Zhang, W. Feng, Q. Zeng, C. Wang and J. R. Gong, Nano Lett. **11**, 3245 (2011).

[8]K. Tahara, K. Inukai, J. Adisoejoso, H. Yamaga, T. Balandina, M. O. Blunt, S. De Feyter and Y. Tobe, Angew. Chem. -Int. Edit. **52**, 8373 (2013).

[9]L. Xu and L. Wan, J. Phys. Chem. B **110**, 3185 (2006).

[10]X. Zhang, S. Wang, Y. Shen, Y. Guo, Q. Zeng and C. Wang, Nanoscale **4**, 5039 (2012).

[11]X. Zhang, Q. Zeng and C. Wang, Chem. -Asian J. **8**, 2330 (2013).

[12]A. Bellec, C. Arrigoni, G. Schull, L. Douillard, C. Fiorini-Debuisschert, F. Mathevet, D. Kreher, A. Attias and F. Charra, J. Chem. Phys. **134**, 124702 (2011).

[13]M. O. Blunt, J. Adisoejoso, K. Tahara, K. Katayama, M. Van der Auweraer, Y. Tobe and S. De Feyter, J. Am. Chem. Soc. **135**, 12068 (2013).

[14]R. Gutzler, T. Sirtl, J. F. Dienstmaier, K. Mahata, W. M. Heckl, M. Schmittel and M. Lackinger, J. Am. Chem. Soc. **132**, 5084 (2010).

[15]S. Lee, Y. Fang, G. Velpula, F. R. Cometto, M. Lingenfelder, K. Muellen, Mali, K. S. Mali and S. De Feyter, ACS Nano **9**, 11608 (2015).

[16]C. Marie, F. Silly, L. Tortech, K. Muellen and D. Fichou, ACS Nano **4,** 1288 (2010).

[17]J. Saiz-Poseu, J. Faraudo, A. Figueras, R. Alibes, F. Busque and D. Ruiz-Molina, Chem. -Eur. J. **18**, 3056 (2012).

[18]L. Piot, R. M. Meudtner, T. El Malah, S. Hecht and P. Samori, Chem. -Eur. J. **15**, 4788 (2009).

[19]K. Cui, K. S. Mali, O. Ivasenko, D. Wu, X. Feng, M. Walter, K. Muellen, S. De Feyter and S. F. L. Mertens, Angew. Chem. -Int. Edit. **53**, 12951 (2014).

[20]S. Yoshimoto, T. Sawaguchi, W. Su, J. Jiang and N. Kobayashi, Angew. Chem. -Int. Edit. **46**, 1071 (2007).

[21]A. Ciesielski, S. Lena, S. Masiero, G. P. Spada and P. Samori, Angew. Chem. -Int. Edit. **49**, 1963 (2010).

[22]B. E. Hirsch, K. P. McDonald, B. Qiao, A. H. Flood and S. L. Tait, ACS Nano **8**, 10858 (2014).

[23]F. P. Cometto, K. Kern and M. Lingenfelder, ACS Nano **9**, 5544 (2015).

[24]S. Lee, Y. Hsu, H. Wu, H. Lin, H. Hsu and C. Chen, Chem. Commun. **48**, 11748 (2012).

[25]S. Lei, K. Deng, Y. Yang, Q. Zeng, C. Wang and J. Jiang, Nano Lett. **8**, 1836 (2008).

[26]K. S. Mali, D. Wu, X. Feng, K. Muellen and M. Van der Auweraer, S. De Feyter, J. Am. Chem. Soc. **133**, 5686 (2011).

[27]Q. Zheng, X.-H. Liu, X.-R. Liu, T. Chen, H.-J. Yan, Y.-Wu, Zhong, D. Wang and L.-J. Wan, Angew. Chem. -Int. Edit. **53**, 13395 (2014).

[28]S. Griessl, M. Lackinger, M. Edelwirth, M. Hietschold and W. M. Heckl, Single Mol. **3**, 25 (2002).

[29]S. Griessl, M. Lackinger, F. Jamitzky, T. Markert, M. Hietschold and W. Heckl, J Phys Chem B **108**, 11556 (2004).

[30]T. N. H. Nguyen, T. G. Gopakumar, R. Gutzler, M. Lackinger, H. Tang and M. Hietschold, J. Phys. Chem. C **114**, 3531 (2010).

[31]M. Lackinger, S. Griessl, W. M. Heckl, M. Hietschold and G. W. Flynn, Langmuir **21**, 4984 (2005).

[32]M. Lackinger and W. M. Heckl, Langmuir **25**, 11307 (2009).

[33]T. N. H. Nguyen, T. G. Gopakumar and W. M. Hietschold, J. Phys. Chem. C **115**, 21743 (2011).

[34]D. C. Y. Nguyen, L. Smykalla, T. N. H. Nguyen, T. Rueffer and W. M. Hietschold, J. Phys. Chem. C **120**, 11027 (2016).

[35]L. Zhu, X. Xu, Y. Wang, S. Liu, J. Ling, L. Liu, S. Wei, F. Cai, Z. Wang, X. Liu and L. Wang, Surf. Rev. Lett. **21**, 1450035 (2014).

[36]T. N. H. Nguyen, T. G. Gopakumar and M. Hietschold, Surf. Sci. **607**, 68 (2013).

[37]L. Kampschulte, M. Lackinger, A. Maier, R. Kishore, S. Griessl, M. Schmittel and W. M. Heckl, J. Phys. Chem. B **110**, 10829 (2006).

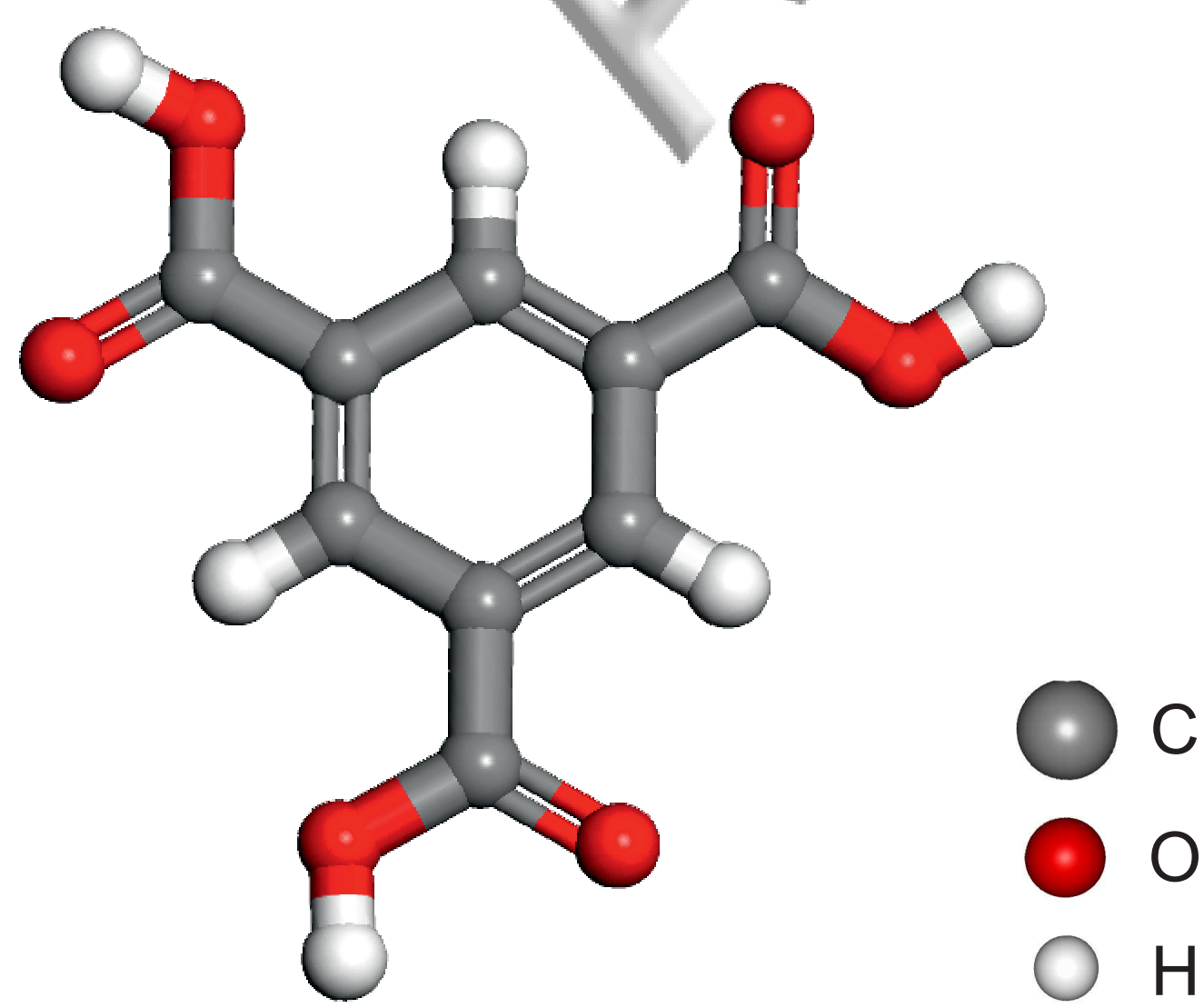
[38]I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero and A. M. Baro, Rev. Sci. Instrum. **78**, 013705 (2007).

[39]M. Lackinger, S. Griessl, L. Kampschulte, F. Jamitzky and W. M. Heckl, Small **1**, 532 (2005).

[40]F. Shayeganfar and A. Rochefort, Langmuir **30**, 9707 (2014).

[41]K. G. Nath, O. Ivasenko, J. M. MacLeod, J. A. Miwa, J. D. Wuest, A. Nanci, D. F. Perepichka and F. Rosei, J. Phys. Chem. C **111**, 16996 (2007).

[42] W. Li, J. Jin, X. Leng, Y. Lu, X. Liu and L. Wang, J. Phys. Chem. C, **120**, 12605 (2016).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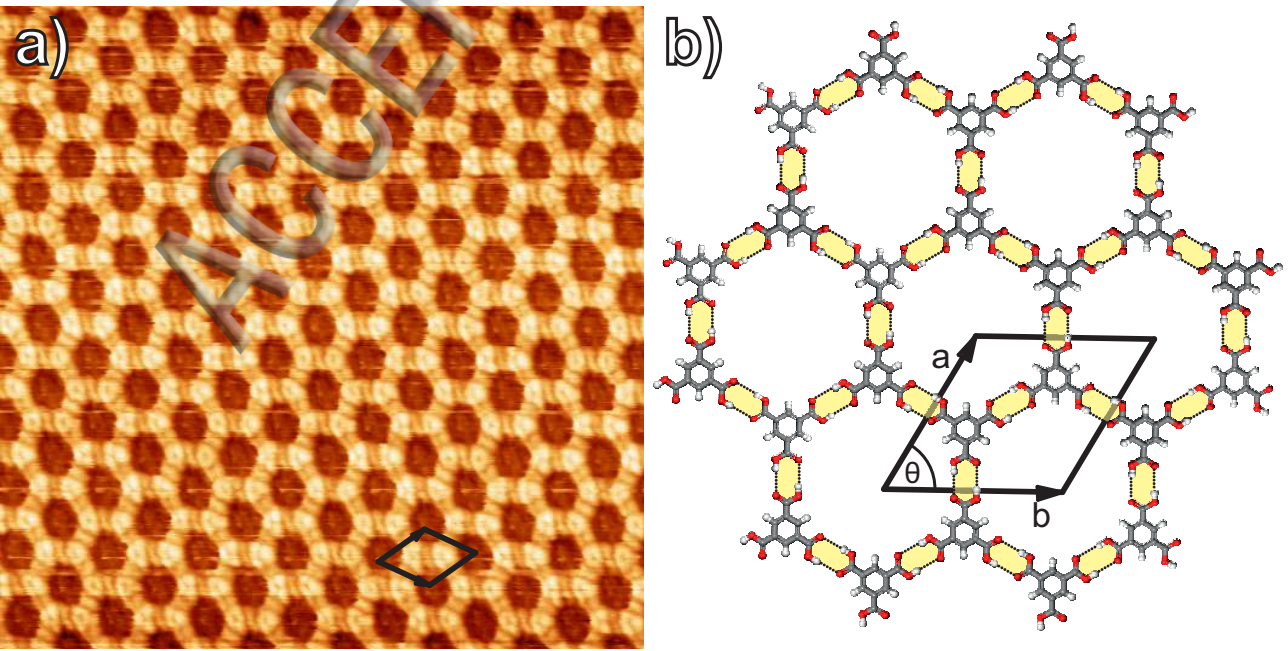
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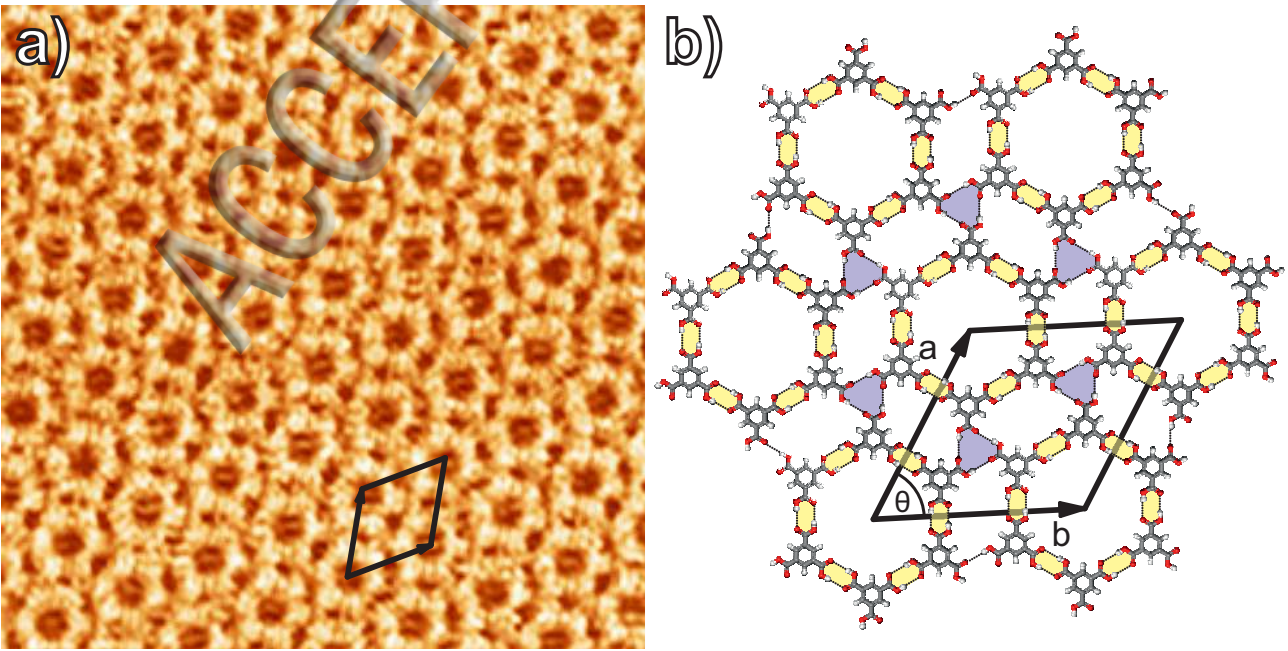
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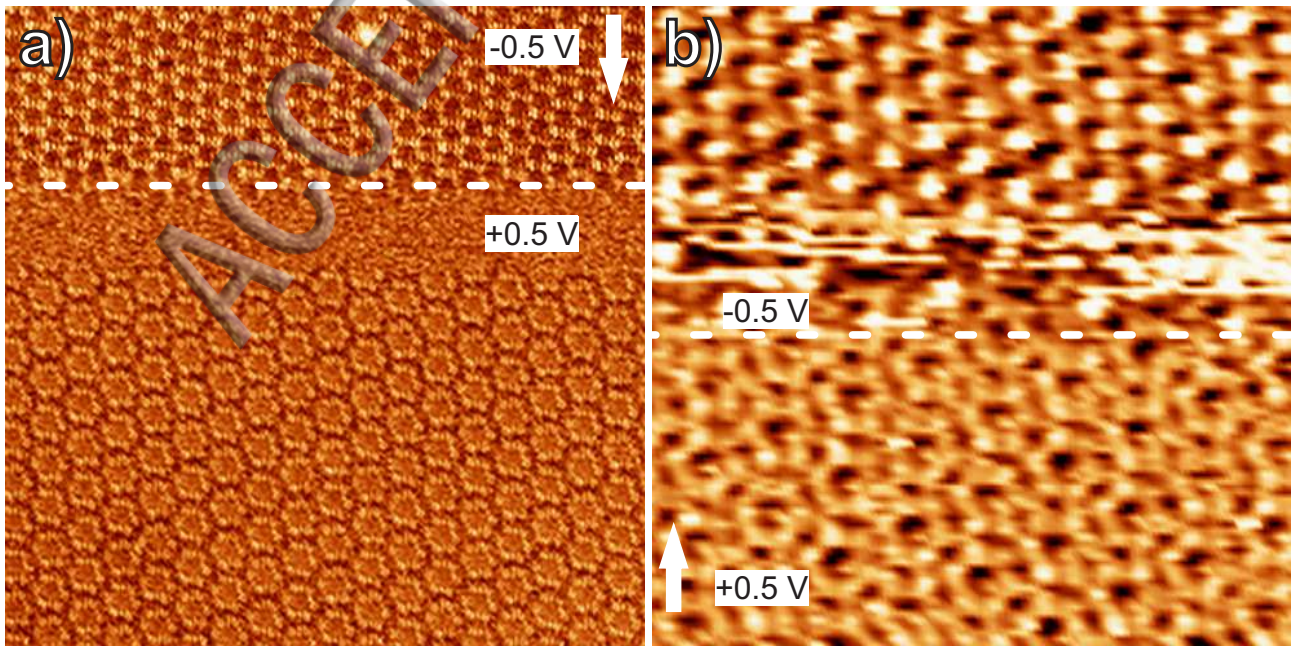
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