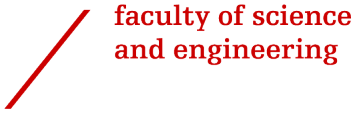

University of Groningen, Groningen

Bachelor Thesis

Faculty of science and engineering

Self-assembly and phase transformation of molecular networks from carboxyl-functionalized triarylamines at the solid 1-nonanol interface

Author:
Stijn Feringa
S3490009

First examiner:
prof. dr. M. A. Stöhr
Second examiner:
prof. dr. G. Palasantzas
Daily supervisor:
B. Jia

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Abstract

In this research the self assembly and switching behavior of a triarylamine derivative is investigated at th solid-liquid interface. The triarylamine derrivative is dissolved in 1-Nonanol and deposited on highly oriented pyrolytic graphite (HOPG). Using an scanning tunneling microscope(STM) operated under ambient conditions the molecular networks of triarylamine were investigated. The STM images showed that the triarylamine molecules formed an open structure at the positive tip bias and a close-packed structure at the negative tip bias. The switching behavior between the open and close-packed network of triarylamine molecules could be initiated by changing the polarity of the tip bias voltage of the STM.

Contents

1 Introduction

In 1986 Gerd Binnig and Heinrich Rohrer were awarded with the Nobel prize for Physics on the development of the scanning tunneling microscope, also known as the STM[1]. The scanning tunneling microscope can detect the tunneling current between a surface and the tip of the microscope. This tunneling current is exponentially dependent on the distance between tip and sample. By this dependence the topography of the sample can be mapped.

Self assembly is described as the assembly of molecular networks without the interference of an outside source[2]. The self assembly of molecular networks at nanoscale can be used in the bottom up approach for a nanomolecular device. The bottom up approach uses the base components, individual molecules and atoms, to form a larger nano-structure.[3] These self assembled molecular networks are therefore the basis for future molecular nano-devices.[4][5][6][7] These self assembled mono-layers can be mapped at a nanoscale with a STM.

A category of these molecular nano-devices use the rearranging of molecular networks at the solid liquid interface. Depending on factors like concentration or applied bias voltage, molecules can arrange in different molecular networks. When applying an external trigger these molecular networks can be switched between different phases. For example light and temperature have been explored.[8][9]. The local electric field under a scanning tunneling microscope can be used to manipulate the arrangement of molecules at nano-scale as well.[10][11][12] As the electric field has an effect on the dipole moment of the carboxylic acid groups. In the molecules studied in this research the the carboxylic acid groups of the molecules create hydrogen bonds to form a stable mono-layer. The electric field can interfere with the dipole moment of these carboxylic acid groups and let them rearrange in different structures. [12]

The transformation of molecular networks is called within this research as switching between the networks. This switching is not due to a switch of the molecule itself. The aim of this research is to study the switching behavior of carboxyl -dimethyl methylene-bridged triphenylamine (Tri-arylamine) within a 1-nonanol solution. The phase transformation between open and close packed structure of the triarylamine derivatives was investigated in dependence of the applied bias voltage applied within a STM setup.

2 Theoretical background

2.1 The scanning tunneling microscope

The scanning tunneling microscope (STM) uses the tunneling current arising between the tip of the STM and a (semi)conducting surfacedue to the quantum mechanical tunneling affect to map the topography of this surface. Tunneling is a quantum mechanical phenomenon where there is a wave function through a classically forbidden potential barrier. In the case of the STM, the potential barrier is the gap between the tip of the scanner and the sample. The tunneling current appears when the distance between the tip and the surface is around 1 nm. A schematic of the STM is given in figure 1. This figure shows the schematic setup of a STM.

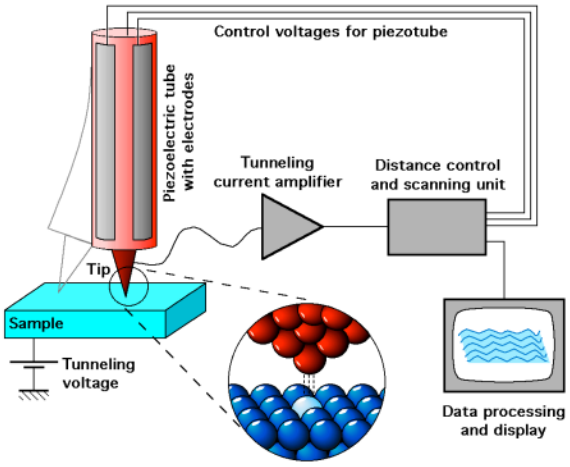

Figure 1: Schematics of a STM [13]

The magnitude of tunneling depends on the applied voltage, and the overlap of the states of the tip and the surface. This will converge into the following equation[14]:

$$I \propto V e^{-\kappa d} \tag{1}$$

Where the tunneling current I is exponentially proportional to the distances d between tip and sample, and linearly dependent on the voltage V. In equation 1, κ is the proportionality constant or decay constant, given by[14]:

$$\kappa = \frac{\sqrt{2m(U-E)}}{\hbar} \tag{2}$$

Where m = electron mass, U = potential of the impenetrable barrier, E = energy for moving in the potential barrier and $\hbar = \frac{h}{2\pi}$.

2.2 Principle of operation

The tip of the STM is most commonly made of tungsten (W) or platinum-iridium (Pt-Ir). This tip scans over a surface. To approach the sample a piezoelectric tube is attached to the scanning tip. An applied voltage will let the piezoelectric tube expand or retract to approach the surface. A different bias voltage is applied between tip and the sample. By this tunneling current occurs. This happens due to the overlap of electron orbital of both the tip and the surface.

The STM can operate in 2 modes, the constant height mode and the constant current mode. In the constant height mode the voltage of the z piezo is kept constant. Which means that there will be no change in the piezoelectric material for the distance. In this mode the tunneling current varies due to the exponential dependence on height. For the constant height mode there is no feedback loop. The constant height mode has a probability to crash the tip on the surface if the surface is not sufficiently flat.

In the constant current mode, the tunneling current will be kept constant. In this mode a feedback loop is applied which regulates the voltage for the piezoelectric material and therefore will change the distance between tip and surface to keep the current constant. With the help of a digital program an image of the surface is created translating the height changes into a false color image. The constant current mode is slower with respect to the constant height mode due to the feedback loop. However there is less risk to crash the tip at the surface.

2.3 STM setup

The STM is housed within a wooden isolation box. The inside of the box is covered with acoustic foam which reduces noise from external sources. For example the noise can be created by vibrations from walking next to the STM. The STM itself is mounted on four strings to further reduce any noise. This is necessary as the STM is an extremely sensitive instrument, which can measure atomic resolution with a vertical error within the sub Å regime. In figure 2 a picture of the STM used for this research project is shown. The STM head is mounted above the sample plate. This sample plate is mounted with 3 magnetic rods to the bottom of the STM setup. These magnetic rods are adjustable, such that the height of the sample plate can be changed. One of the magnetic rods is electronically adjustable. This rod lets the sample plate approach the tip. The other two magnetic rods are manually adjustable for greater distance changes. The HOPG surface can be placed on the sample plate for STM measurements. The sample plate is shown in figure 3

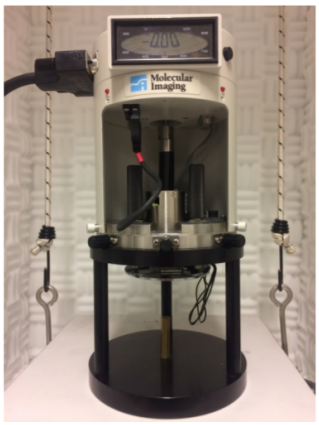

Figure 2: Picture of the STM setup

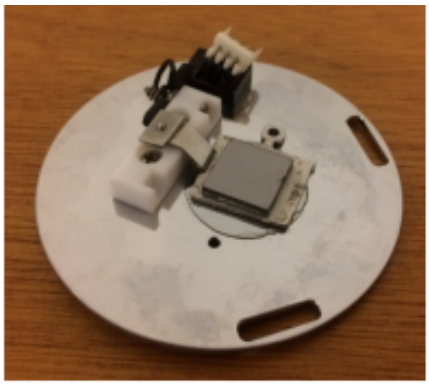

Figure 3: The sample plate and the HOPG sample.

2.4 Solid-liquid interface and switching

The STM can be used in many different conditions, within high temperatures, vacuum or in a liquid. In this research the STM is measuring at the solid-liquid interface under the ambient conditions. The STM tip is within a droplet of a solution containing the molecules we want to deposit on the surface. This surface on which the molecules are deposited is highly oriented pyrolytic graphite, better know as HOPG. The molecules arrange at the solid liquid interface into a crystalline structure. A digital program can visualize the topography of this crystalline structure from the STM data. A conducting solution can create a leaking current. A stable tunneling current can then be found by increasing the set point current of the STM. The set point current is the current that the STM detects. To minimize the leaking current an isolated tip is used. This is a STM tip that has been isolated with nail polish.

2.4.1 The unit cell and switching behaviors.

The unit cell and the switching behavior of molecular networks will be explained using 1,3,5 tris(4-carboxylphenyl) benzene (BTB). Previous research suggests that BTB could be used in functional molecular architectures where it could act as a target site for catalysis or for controllable drugs release.[12] The molecule BTB is shown in figure 4. BTB is a central benzene ring surrounded with 3 benzene rings containing 1 carboxylic acid group each.

This molecule can form stable monolayers due to the formation of hydrogen bonds by the carboxylic acid groups. The structure of the monolayers is dependent on the environment. It is dependent on the substrate, the solvent used, the temperature and the polarity with which we scan. Two of these structures are called the open structure and the close packed structure. The open structure is also know as the honeycomb or chicken wire structure.[12]

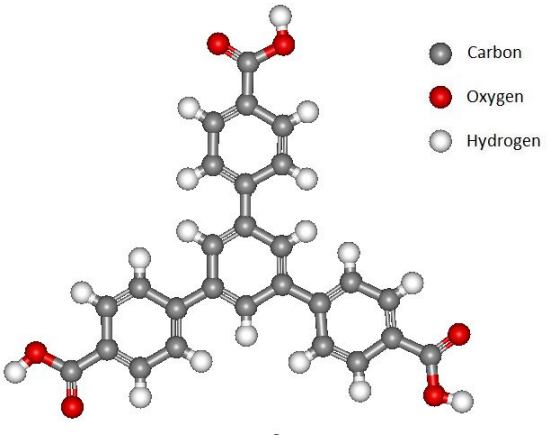

Figure 4: Molecular structure of BTB[15]

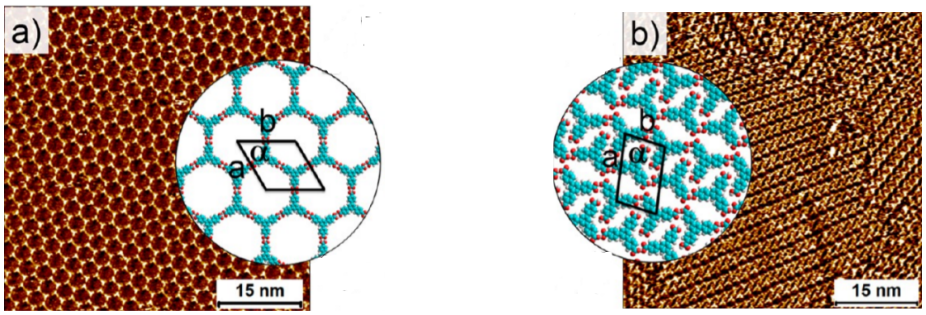

Figure 5: The crystalline structure of BTB formed by a nonanoic acid solution on HOPG sample. (a) The open structure formed by BTB molecules. In the circle the molecular representation with a unit cell is shown. (B) The close packed structure formed by BTB molecules. In the circle the molecular representation with a unit cell is shown. [11]

A periodic structure repeats itself and can be described by a unit cell. The unit cell is the smallest part of a molecular network that can be repeated to form the network again. The open structure has a unit cell given in table 1. The closed packed structures has a different unit cell given also in table 1. Most commonly unit cells are described by the lengths a, b and angle θ. The lattice parameters are shown in table 1

Switching BTB networks can be done by the change of external parameters. A switch of molecular networks is described as the change from a stable mono-layer to another stable mono-layer. This means that when a switch has occurred the unit cell of the crystalline structure has changed. For example the switch can

happen due to a change of polarity of the bias voltage of the STM. Where the bias voltage is applied on the tip and the sample plate is grounded. Changing the polarity of the bias voltage the molecular networks will rearrange.

	a	b	θ
open	$3,1 \pm 0,1$nm	$3,1 \pm 0,1$nm	$60 \pm 1°$
close	$2,5 \pm 0,3$nm	$1,6 \pm 0,2$nm	$78 \pm 3°$

Table 1: The unit cell of the open and close packed structures of the BTB molecule[15][11]

2.4.2 Triarylamine

The second molecule is carboxyl-dimethylmethylene-bridged triphenylamine (triarylamine) with molecular formula: $C_{30}H_{27}O_6N$. This molecule has been shown to form crystalline structures on Au(111) and Cu(111)[16]. The crystalline structure of triarylamine has not been reported at a solid liquid interface on HOPG. The switching behavior of triarylamine has not yet been reported as well.
The ball and stick model of triarylamine is shown in figure 6. The molecule has a central nitrogen atom surrounded with carbon atoms in 3 benzene rings, making a triangular molecule. Triarylamine has three carboxylic acid groups, which can form hydrogen bonds. Also six methyl groups are positioned in pairs on each side of the molecule.

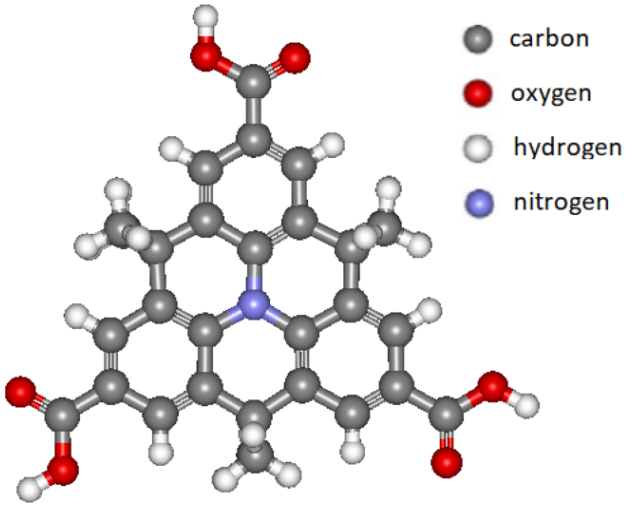

Figure 6: The molecule structure of triarylamine, with grey, red, white and blue being carbon, oxygen, hydrogen and nitrogen respectively.

From earlier research the open structure is found to have a chicken-wire or honeycomb structure, shown in figure 7, similar to the open structure of BTB. However there has been no reports on the close packed structure of triarylamine.

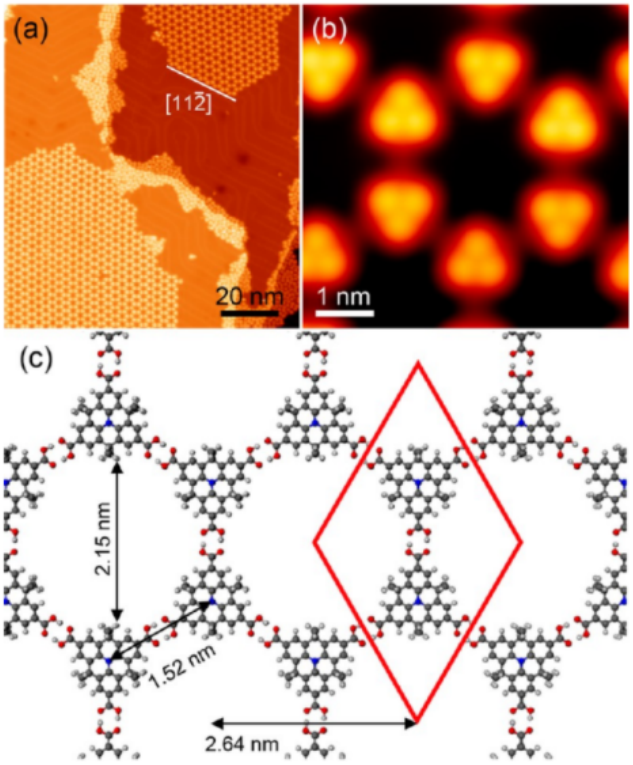

Figure 7: Open structure of triarylamine on Gold (Au(111)), (a) The overview of the STM image, (b) High-resolution STM topogrophy of a single pore, (c) the unit cell depicted in red within the crystalline model.[16]

The parameter of the unit cell of the open structure can be found in table 2.

	a	b	θ
open	$2,64 \pm 0,13nm$	$2,64 \pm 0,13nm$	$60 \pm 1°$

Table 2: The unit cell of the open structures of the triarylamine molecule on Au(111)[16]

3 Experimental

3.1 Solvent and molecule

Due to working at the solid-liquid interface, we needed to prepare a solution which can be applied on a surface for scanning. First a certain amount of solvent is measured. This solvent is placed in a glass bottle. Secondly the molecule is weighed and added to the solvent. The molecule will dissolve into the solvent.It is possible to ultrasonicate the solution to speed up the dissolving process. When enough molecules are added to the solvent an over saturated solution will appear. This is when after ultra sonication still non dissolved molecules are within the solution. For the experiments, we use the transparent solution of the topmost part of the solution, which is the saturated solution. This saturated solution can now be used for experiments as well as the fabrication of any diluted solutions.

3.2 Tip and surface preparation

A platinum iridium (90-10) wire is prepared for scanning with the STM. With tweezers and wire cutters the tip can be prepared. The wire as well as the tweezers and wire cutters are cleaned with acetone and ethanol to remove any contamination of the tools. To create a sharp tip for the STM, the tip needs to be pulled rather than cut. A sharp tip will appear due to metal deformation. This is done by a wire cutter and pliers which will pull on the Pt/Ir wire until it breaks. Figure 8 depicts how a tip is made. This tip can be used for STM measurements. When necessary an isolated tip can be prepared by coating a tip with nail polish and then cleaning the tip of the wire by dipping the tip in acetone.

For this solid-liquid experiment a HOPG surface is used. To prepare the surface for scanning it needs to be cleaned. Scotch tape is applied on the HOPG surface. When removing the scotch tape a layer of the HOPG surface will be removed from the HOPG sample. The HOPG that remains is now without any dirt from the environment.

When a surface is prepared molecules can be pipetted onto the surface. On the surface 1 to 2 droplets of the solution will be placed. The STM scanning tip will now be immersed in a bubble of the solution when approaching the surface.

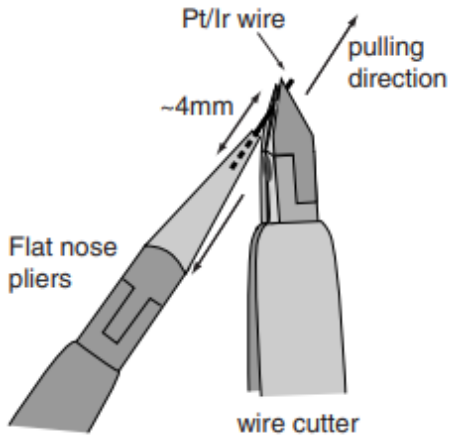

Figure 8: Tip preperation schematics[17]

3.3 Scanning

After the preparations for the STM scanning the sample was approached manually. The sample plate with the desired surface needs to be perpendicular to the scanner head and approaches as close to the tip as possible, without crashing into the tip. From this point the Picoscan 5 software is used to approach the surface until a desired tunneling current is found. The bias voltage is generally set at a +/- 1V. In this research only the constant current mode is used.

When the desired tunneling current has been reached scanning can begin. In order to obtain clear images, the parameters within the program can be adjusted, such as the proportional integral controller for the feedback loop, which reacts on the error between set point current and measured current. The proportional-integral (PI) controller will give a feedback to the piezo tube to withdraw or approach the surface. Other parameters are the set point current, bias voltage and scanning speed. Also the dimensions of the images can be altered. In this report the bias voltage is applied to the tip while the sample is grounded.

4 Results and discussion

The goal is to investigate the switching behavior of the triarylamine in nonanol. For this BTB is studied to get familiar with the switching of molecular networks at the solid-liquid interface. Furthermore, I compare my findings with the ones of the PhD student Baoxin Jia who investigated the triarylamine in nonanoic acid. The switching mechanic is investigated with two different molecules and 2 different solvents. First 1,3,5 tris 4 carboxyphenyl benzene (BTB) within Nonanic acid is investigated, secondly Triaryl amine is investigated within a 1 nonanol solution.
To get familiar with the switching of molecular networks first the research of Fernando P. Cometto[12] was reproduced. Nonanoic acid consists of a chain of 9 carbon atoms, where the last carbon is in a carboxyl group. The nonanoic acid has the molecule formula: $C_9H_{18}O_2$. The structure of the molecule is shown in figure 9.

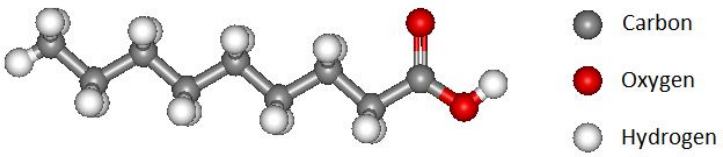

Figure 9: The 3D ball and stick representation of nonanoic acid.

4.1 BTB in Nonanoic acid on HOPG

4.1.1 BTB: open network

The open structure of the BTB networks are shown in figure 10a. This structure was observed for a positive tip bias voltage. In this figure you see each protrusion represents a BTB molecule. The unit cell is given in table 3. When comparing the data with theory shown in table 1, it is found that it is within error boundaries. The difference between the found unit cell and unit cell in table 1 is due to drift. In figure 10b the ball and stick model of the open structure is shown. This shows the hydrogen bonds and the orientation of the molecules. The hydrogen bonds are formed by the carboxylic acid groups of BTB, for the open structure double hydrogen bonds are formed.

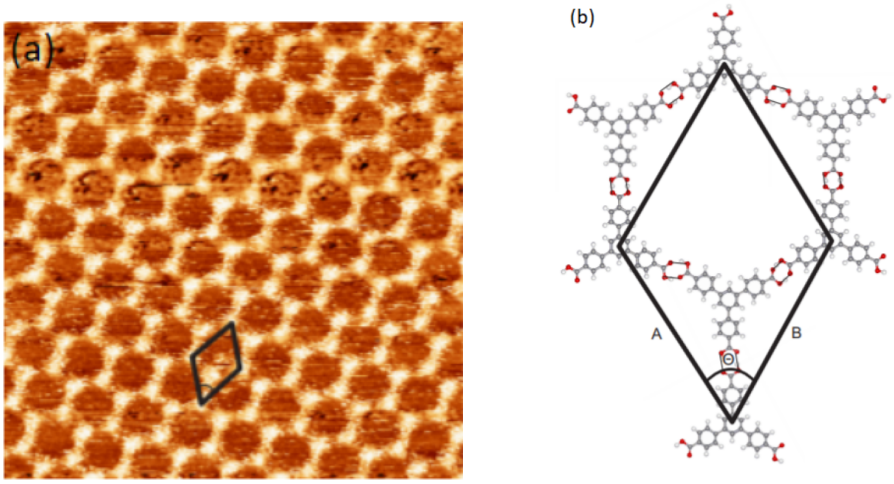

Figure 10: The open structure of BTB networks (a) STM image (30 nm by 30 nm V = 1.0v and I = 50pA) of BTB at nonanoic acid-HOPG interface with unit cell. (b) A ball and stick model of the open BTB structure

	a	b	θ
Unit cell from data	$3.28 \pm 0.26nm$	$3.30 \pm 0.26nm$	$62.7 \pm 4.3°$

Table 3: The unit cell of the open packed structures of the BTB molecule from data

4.1.2 BTB: close packed network

When approaching with a negative tip bias voltage the close packed structure appears, seen in figure 11a. The structure of the close packed network is a compact ribbon like structure. From this structure a molecular model has been made to show the pattern of the crystalline structure, which can be found in figure 11b. The carboxylic acid groups form hydrogen bonds between BTB molecules. The unit cell of the close packed structure is given in table 4. When

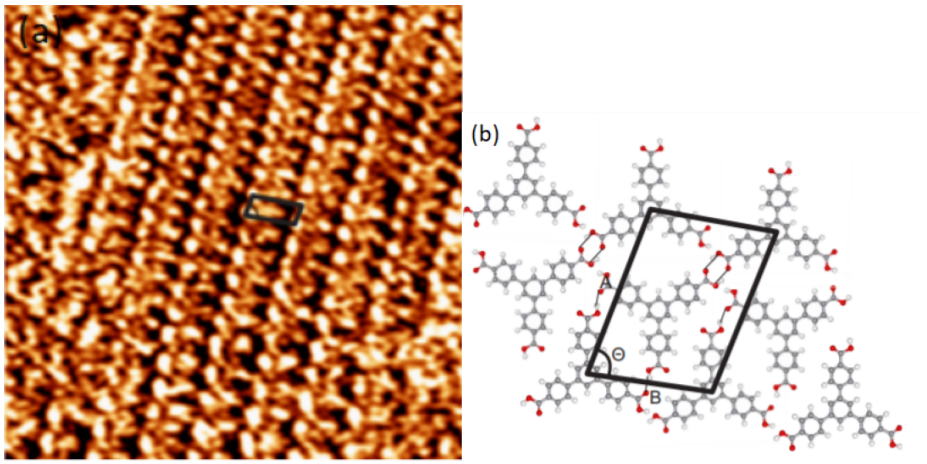

Figure 11: The close packed structure of BTB (a) STM image (35 nm by 35 nm V = -0.8 V and I = 150 pA) of BTB at nonanoic acid-HOPG interface with an unit cell. (b) A ball and stick model of the close packed BTB network

comparing this data with the data given by table 1, it is found that the data is within the error margin of the unit cell shown in table 1. The difference between the found unit cell and known unit cell from data is due to the drift while scanning. The drift is due to the interference of temperature and the piezo drift while scanning. It can be minimized by reducing background vibrations of the STM.

	a	b	θ
Unit cell from data	2.78 ± 0.12nm	1.69 ± 0.18nm	$80.5 \pm 2.5°$

Table 4: The unit cell of the close packed structures of the BTB molecule from data

4.1.3 Switching behavior BTB

BTB has a switching behavior between the open structure and the closed structure when changing the polarity of the bias voltage[12]. To investigate this we approached the surface with a bias voltage of ±0.850 V and a set point current of 150 pA. A clear open or close packed structure is needed to start measurements on the switching behavior. Then by changing the polarity of the tip bias voltage the rearranging into a new structure begins, as shown in figure 12. When changing the polarity of the bias voltage the open structure of BTB will immediately disappear. However the forming of a close packed structure is not instant. This is due to the fact that a oblique structure can be formed while switching[12]. This structure does not appear when approaching with a negative bias voltage. The oblique structure will disintegrate within the close packed network over time. This structure can be seen in figure 13.

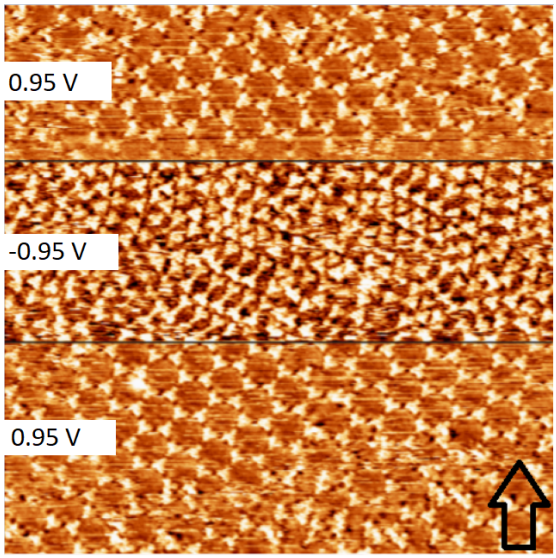

Figure 12: STM image (50.5 nm by 50.5 nm V = ±0.95 V and I = 150 pA) of the switching of BTB networks from open structure to close packed structure and then back to open structure, with the arrow indicating the scanning direction.

The molecular network reacts to the external stimulus of the electric field. This electric field is created by the bias voltage and is dependent on the polarity of this bias voltage. The molecular network releases from the surface when the polarity of the bias voltage is changed. It rearranges to a stable molecular network dependent on the electrical field. This is due to the carboxylic group having a dipole moment which interferes with the external electrical field created by the applied bias voltage.[18]

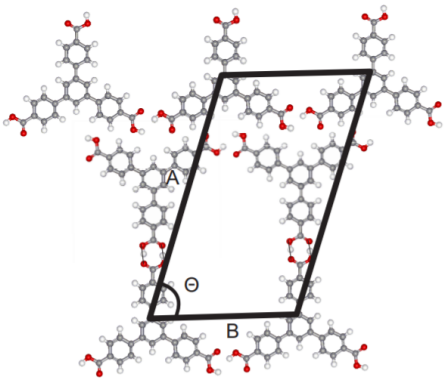

Figure 13: Molecular model of the oblique BTB structure.

4.2 The self assembly of triarylamine molecules

Triarylamine molecules are dissolved in 1-nonanol. This is a carbon chain ending in a hydroxyl group, as shown in figure 14. The molecule has a polar hydroxyl group and a nonpolar carbon chain. Due to the polar and nonpolar part of this molecule the triarylamine can dissolve in the solvent. When dissolving triarylamine in 1-nonanol we found that 1-nonanol can dissolve more molecules than nonanoic acid. This is due to the fact that the 1-nonanol is more nonpolar than its acid counterpart nonanoic acid. To make sure we have an over-saturated solution for scanning, the solution had one hour of sonication and was checked before it could be meassured.

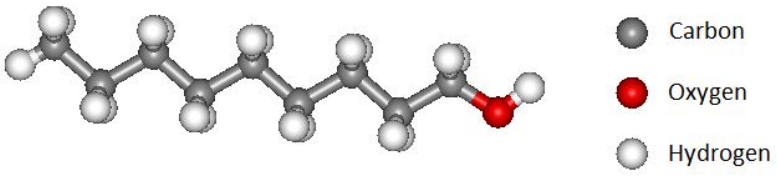

Figure 14: The 3D ball and stick model of 1-nonanol

4.2.1 The self assembly of triarylamine networks at a positive tip bias voltage

To get clear STM images of the triarylamine molecules within 1-nonanol a higher ”approaching” current is desired. This is due to the leakage current. To find the images the set point current was within 200 - 650 pA and the bias voltage was 0.8 V. The triarylamine molecules formed an open structure at the positive tip bias. The open structure is shown in figure 15a. This shows a hexagonal pattern made of triangular molecules. Within this figure a unit cell is drawn to

show the repeating pattern of the triarylamine networks. The STM detects to a large part the surface topography. This means that the methyl groups of the triarylamine molecule give a brighter contrast in the STM images, because these groups are pointing outwards of the 2D triangular triarylamine structure. The carboxyl groups yield a comparatively weak contrast and are difficult to identify in the STM images. This means that the STM image will show the position of the methyl groups. The ball and stick model of this network is shown in figure 15b, where the parameters of the unit cell are given in table 5. In this figure it is also visible how hydrogen bonds are formed between the carboxylic acid groups of the molecules and the orientation of the molecules is shown.

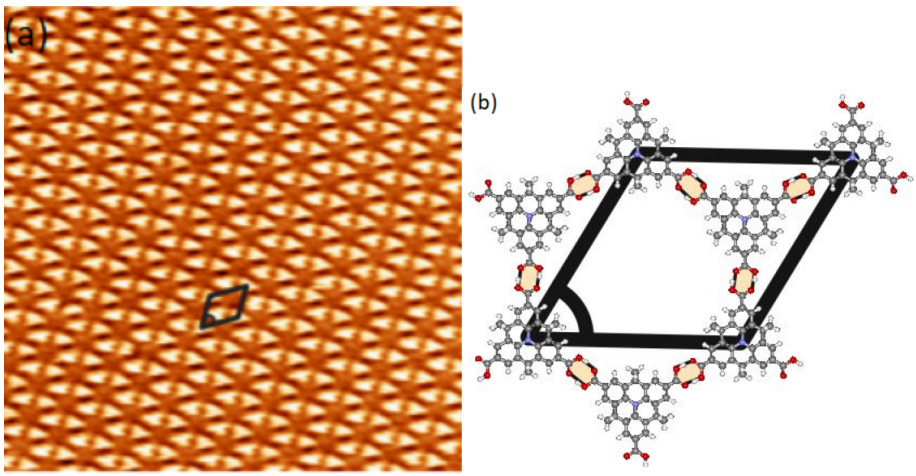

Figure 15: The open structure of triarylamine networks (a) STM image (35 nm by 35 nm V = 0.8 V and I = 600 pA) of triarylamine at the 1-nonanol-HOPG interface with a unit cell. (b) A ball and stick model of the open triarylamine network.

	a	b	θ
Unit cell from data	$2.69 \pm 0.12nm$	$2.73 \pm 0,11nm$	$55.9 \pm 5.1°$

Table 5: The unit cell of the open structure of the triarylamine networks.

4.2.2 The self assembly of triarylamine networks at a negative tip bias voltage

The close packed structure of triarylamine is given in figure 16a. This structure appears to have a chain/ribbon like structure with a unit cell the shape of a parallelogram. The unit cell and the molecular model of the close packed structure is given in figure 16b. This image shows the carboxylic acid groups forming hydrogen bonds between the molecules. The unit cell within figure 16b is the unit cell of the close packed structure using the average of all STM images of the close packed structure. The parameters of the unit cell are given in table 6.

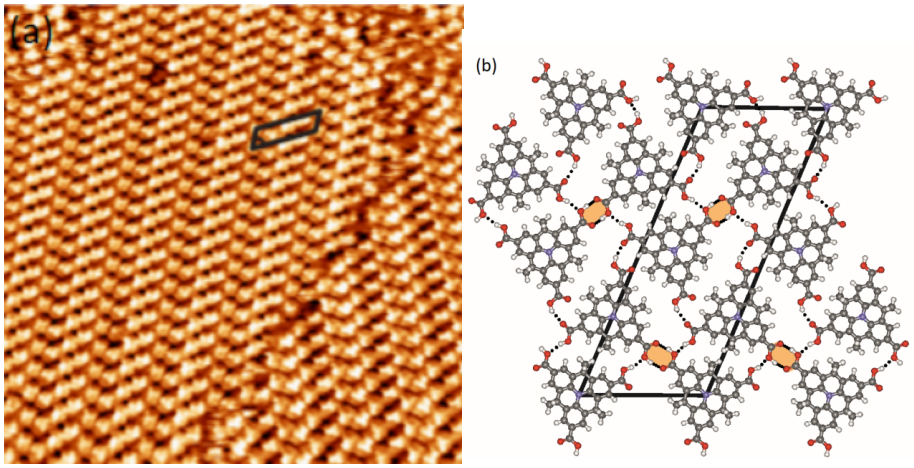

Figure 16: The close packed structure of triarylamine (a) STM image (30 nm by 30 nm V= -0.8 V and I= 650 pA) of triarylamine at the 1-nonanol-HOPG interface with a unit cell. (b) A ball and stick model of the close packed triarylamine network.

	a	b	θ
Unit cell from data	1.45 ± 0.13nm	3.96 ± 0.07nm	$84.1 \pm 3.8°$

Table 6: The unit cell of the close packed structure of the triarylamine molecule.

4.2.3 Switching behavior triarylamine

The switching behavior of triarylamine is accomplished by changing the polarity of the bias voltage. In figure 17 it is shown that the open structure appears for a positive bias voltage and after switching the polarity of the bias voltage the close packed structure will appear. In this figure the scanning direction is downwards. It shows a clear open structure with the hexagonal network. However the close packed structure is not entirely clear and needs time to form. This is due to the Ostwald ripening effect.[19]. This is the effect in which crystal structures grow in area over time. In the figure it is shown that the switching the polarity of the bias voltage will not directly give a clear transformation. In figure 17 the outlined areas represent the time it takes, with a reduced scanning speed, to let the new structure appear. We reduced the scanning speed significantly to make sure that the new structure appears. This is independent of the structure from which you switch.
When switching the tunneling current increases to 3000 pA and after sometime it will reduce to 600 pA after which the molecules reappear. This phenomenon is due to the leakage current. When the bias voltage is changed the molecules leave the surface to reassemble for the new structure. The solution will first mix and therefore create a higher amount of leakage current. After around 60 seconds, consistent molecular networks will appear on the STM image.
The switching behavior of triarylamine at the 1-nonanol-HOPG interface is quite dependent on the properties of the STM tip. An isolated sharp tip will improve the quality of the images of this switching behavior. The switch itself seems to react immediatly on the change in polarity of the bias voltage, however we can not discuss this due to the high current at the switch. The 1-nonanol is interfering with the switching behavior due to the conductivity of this solvent.

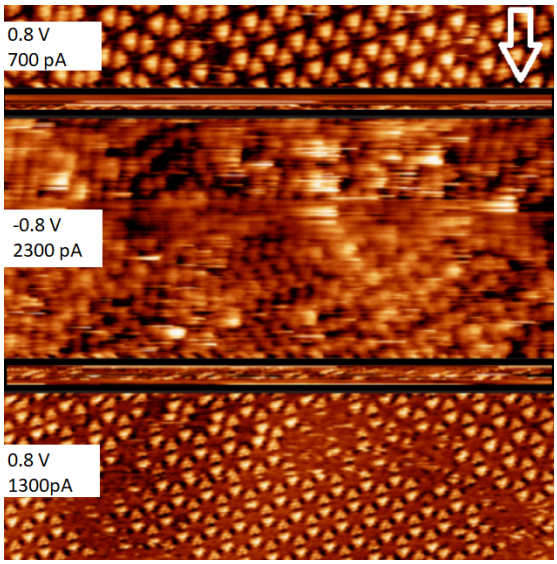

Figure 17: STM image (50 nm by 50 nm V =±0.8 V) of the switching of triarylamine networks from open structure to close packed structure and then back to open structure.

4.2.4 Comparison triarylamine in 1-nonanol with nonanoic acid solution

The Switching behavior of triarylamine is also found within a nonanoic acid solution on HOPG. This was done by Baoxin Jia, Ph.D. candidate. In his findings he shows that the switching behavior of triarylamine networks in nonanoic acid is instantaneous. The switching of triarylamine in nonanoic acid is shown in figure 18. This differs from the results of triarylamine networks in 1-nonanol. This tells us that the switching of triarylamine is dependent on the solution in which we scan.
The open and close structure are the same with respect to the structures found with a 1-nonanol solution. The unit cell of triarylamine is independent of the solvents when comparing nonanoic acid with 1-nonanol. However triarylamine seems to switch due to the electrical field of the applied bias voltage. This acts on the dipole moment of the carboxylic acid groups of triarylamine. Changing the polarity of the bias voltage releases the molecules of the surface and rearranges into a new structure. This seems to be the same for BTB as well as triarylamine.

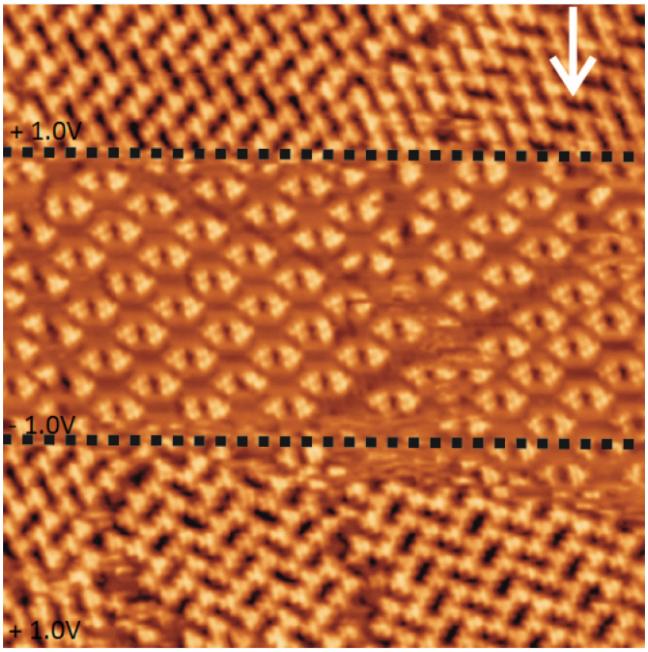

Figure 18: STM image (30 nm by 30 nm, V =±1.0 V, I = 20 pA)showing the phase transformation of triarylamine derivatives at the nonanoic acid-HOPG interface with the close packed structure switching to the open packed structure and back.

5 Conclusion

The aim of this research was to find the switching behavior of BTB and triarylamine at a solid-liquid interface. For this a solution with nonanoic acid or 1-nonanol is used. From STM investigations, the crystalline structure and the switching behavior of BTB and triarylamine were shown. The unit cell parameters of BTB within nonanoic acid was found to be a = $3,28 \pm 0.26$nm, b= $3,30 \pm 0,26$nm and an angle of $62.7 \pm 4.3°$ for the open structure. This unit cell is within the error margin of the unit cell found by L. Kampschulte [15]. For the close packed structure a = $2.78 \pm 0.12nm$, b= $1.69 \pm 0,18nm$ and an angle of $80.5 \pm 2.5°$ were determined. The unit cell is within the error margin found by S. Lee [11]. BTB showed a switching behavior when the bias voltage was changed.
The unit cell of open structure of triarylamine within 1-nonanol was found to be a = $2.69 \pm 0.12nm$, b= $2.73 \pm 0,11nm$ and an angle of $55.9 \pm 5.1°$. The unit cell of the close packed structure of triarylamine is found to be a = $1.45 \pm 0.13nm$, b= $3.96 \pm 0,07nm$ and an angle of $84.1 \pm 3.8°$. The unit cell of the close packed structure has to our knowledge not been reported in literature yet. However it is compared with the research done by B. Jia who has done switching of tri-

arylamine within nonanoic acid. The unit cell of a close packed structure of triarylamine is the same for 1-nonanol and nonanoic acid.
For 1-nonanol as a solvent a leaking current was found. The leakage current was minimized with an isolated tip. Also 1-nonanol appeared to have a higher dissolvability for the triarylamine derivatives compared to nonanoic acid. The dissolvability is due to the polarity of both molecules. 1-nonanol is more non-polar then nonanoic acid. This means that more non-polar molecules can dissolve in 1-nonanol.
The switching behavior of triarylamine at 1-nonanol-HOPG is dependent on the polarity of the tip bias voltage. If the bias voltage is changed the molecules will rearrange to a different structure. The rearranging to a new molecular network is instant for the open structure. However after switching to a close packed structure the molecular network needs time to form a complete close packed network.
For further research on the switching in the solid-liquid interface, the dissolvability of 1-nonanol could be investigated. Due to having a high dissolvability, different molecules which can not dissolve in nonanoic acid could be investigated with 1-nonanol as a solvent. Furthermore, to see if deprotonation is happening while switching an electrolyte could be added to the solvent to see if a new structure appears. This would disprove the theory that switching is due to deprotonation. To conclude if the triarylamine is dependent on the substrate, an investigation on Gold: Au(111) or Copper: Cu(111) could be done.

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