Chapter I

Context and Motivation:
Two-dimensional organic nanostructures

The development of organic devices with nanoscale features is becoming the focus of intense research activity. Organic electronics has the potential to revolutionize the fabrication of computers and other electronic devices. “Electronic newspapers”, smart windows, flexible film solar cell sheets, luminescent wallpaper are only a few examples of future electronic devices based on organic electronics. Thin films of organic molecules and polymers are expected to be used as active layers to replace inorganic materials such as silicon. Engineering efficient organic devices requires selecting organic materials with optimal electronic properties and building optimized organic structures. Therefore the fabrication of next generation of organic devices begins with the understanding and the control of assembly on the molecular scale to produce new devices having advanced properties.

1.1 Supramolecular nanostructures for organic devices

Investigation of supramolecular assembly on various surfaces is motivated by the potential of future organic electronics. In recent times there has been considerable interest in the development of organic solar cells and organic transistors [63]. Fig. 1.1 presents an optimized design for an organic solar cell. The organic active layer is composed of arrays of donor and acceptor molecular columns that form an optimized heterojunction in between two electrodes. The aim of this multi-component organic structure design is to facilitate an effective charge carrier extraction from the device. The performance of the organic solar cell will depend on processes which take place in the organic active layer such as absorption of light, energy transfer, charge separation and transport. The optimization of these processes is a crucial issue in this field. Three aspects have to be considered. First is the choice of the active molecules, because electron donor and acceptor molecules play a key role to enable photon adsorption and subsequent charge separation. Secondly is to form an efficient electric
contact between the organic film and the two electrodes in order to optimize the charge collection. And finally is the morphology of the organic molecular layer, which plays a crucial role in the charge transport within the organic devices.

**Fig. 1.1:** Schematic arrangement of donor and acceptor molecules to give a nano-scale separation of the columnar structures in the organic solar cell. [1]

In this thesis, the engineering of multi-component molecular architectures on a metal substrate will be investigated in order to determine the key parameters driving molecular assembly. The aim of this study is to develop concepts and methods for building organic structures relevant for organic devices, with a design similar to the one presented in Fig. 1.1.

**Fig. 1.2:** Schematic illustration of a top-contact FET based on edge-on arranged organic molecules and uniaxially aligned columns connecting the source–drain contacts. The arrow indicate the direction of the charge carrier transport.[1]
Another promising organic device is the organic field-effect transistor (OFET). OFETs, as opposed to traditional transistors, have shown great potential for a wide range of functional applications where low-cost, light-weight, flexibility and large-area coverage can be achieved. [2,3]. A design of an OFET is presented Fig. 1.2. The transistor is made of a metal gate underneath a combined structure of an organic molecular layer on top of an insulating film. To enhance device performance, the structure of the organic film on the insulating film has to be well controlled in order to increase the charge carrier mobility. Highly ordered molecular films grown on insulating thin films would suit perfectly the design of OFETs as shown in Fig 1.2.

In the case of organic photovoltaic solar cells and in the case of OFETs, engineering organic devices with enhanced properties requires building highly ordered organic films on a preferentially flat substrate, having metal or insulating electronic properties. This means the immobilization of functional building blocks on surfaces has to be controlled at the molecular level. The ultimate goal is to build highly ordered organic layers on surfaces to achieve high efficiency organic devices. Experimentally, **bottom-up** and **top-down** processes are two approaches for the manufacture of devices. Bottom-up approaches seek to have smaller (usually molecular) components building up into more complex assemblies, while top-down approaches seek to create nanoscale devices by using larger, externally-controlled forces to direct their assembly. Further more, bottom-up approaches use the chemical properties of single molecules to lead single molecule components to self-organize or self-assemble into some useful conformation, or to rely on positional assembly. The huge versatility of the bottom-up approach makes it the choice for our experimental procedures.

To summarize, understanding the process of engineering molecular assemblies on metal and insulating surfaces is essential to develop the next generation of organic devices. The supramolecular self-assembly technique is one of the most promising approaches to build sophisticated organic architecture in an molecular scale. Our objective is to tailor the organic structure design by wisely selecting appropriate molecular building blocks and tuning experimental parameters.
1.1.1 Creating molecular networks using molecular self-assembly

Molecular self-assembly is the process by which molecules adopt a certain arrangement without guidance or management from an outside source. Molecular self-assembly is a key concept in supramolecular chemistry [4,5,6] since assembly of the molecules is directed mainly through noncovalent interactions (e.g., hydrogen bonding, metal coordination, van der Waals forces, π-π interactions, and/or electrostatic interaction). Molecular self-assembly is also an important aspect of bottom-up approaches in nanotechnology. Using molecular self-assembly the desired structure is programmed by the shape and the functional groups in the molecules. Formation of micelles, vesicles, liquid crystal phases, and Langmuir films of surfactant molecules [7] has been successfully achieved. Recently developed fabrication processes based on supramolecular assemblies demonstrate that a variety of different shapes and sizes of the supramolecular architecture can be obtained.

![Fig. 1.3: Supramolecular self-assembly process on a surface: a molecular beam is directed onto a solid substrate. The adsorption (energy $E_{ad}$), thermal migration and rotational motions (barriers $E_m$ and $E_{rot}$), and substrate-mediated and direct lateral interactions (energy $E_s$ and $E_{as}$) are key parameters. A molecule (tecton) self-assembles into the twin chain on the surface. A scheme of how surface atoms (a is the lattice periodicity) can influence the supramolecular characteristics and the noncovalent-bond length $d$ is shown in the inset. [12]](image-url)
Self-assembly processes are one of the most promising methods to engineer complex molecular architectures on various substrates. Adsorption, mobility, and intra- or intermolecular interactions, all of which depend on the substrate crystalline lattice, chemical nature, and symmetry [8, 9, 10, 11] are key parameters that govern the formation of molecular architectures. A balancing of lateral molecular and surface interaction is at the origin of the formation of supramolecular order.

<table>
<thead>
<tr>
<th>Process</th>
<th>Energy range (eV)</th>
<th>Distance (Å)</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>$E_{ad} \approx 0.5$ – $10$</td>
<td>$\approx 1.5$ – $3$</td>
<td>Directional, site selective</td>
</tr>
<tr>
<td>Surface migration</td>
<td>$E_m \approx 0.05$ – $3$</td>
<td>$\approx 2.5$ – $4$</td>
<td>1D / 2D</td>
</tr>
<tr>
<td>Rotational motion</td>
<td>$E_{rot} \approx \text{dim}(E_{ad})$</td>
<td>$S(\text{molecule length})$</td>
<td>2D</td>
</tr>
<tr>
<td>Indirect substrate mediated</td>
<td>$E_s \approx 0.001$ – $0.1$</td>
<td>$0(lattice\ periodicity)$</td>
<td>Periodicity</td>
</tr>
<tr>
<td>Reconstruction mediated</td>
<td>$E_s \approx 0$</td>
<td>Short</td>
<td>Covalent</td>
</tr>
<tr>
<td>van der Waals</td>
<td>$E_{vdW} \approx 0.02$ – $0.1$</td>
<td>$&lt; 1$ nm</td>
<td>Non-selective</td>
</tr>
<tr>
<td>Hydrogen bonding</td>
<td>$E_{hb} \approx 0.05$ – $0.7$</td>
<td>$\approx 1.5$ – $3.5$</td>
<td>Selective, directional</td>
</tr>
<tr>
<td>Electrostatic ionic</td>
<td>$E_{ei} \approx 0.05$ – $2.5$</td>
<td>Long range</td>
<td>Non-selective</td>
</tr>
<tr>
<td>Metal-ligand interactions</td>
<td>$E_{al} \approx 0.5$ – $2$</td>
<td>$\approx 1.5$ – $2.5$</td>
<td>Selective, directional</td>
</tr>
</tbody>
</table>

Table 1: Classification of basic interactions and processes, with associated energy (barrier) and typical distances relevant when functional molecular species are employed to engineer molecular architectures on metal substrates [12].

The self-assembly process (Fig. 1.3) was described by Barth [12, 64, 65 66]. The principle of two dimensional supramolecular self-assembled structure formation is explained by a general molecular growth example. Molecules are directed onto a clean substrate surface. The molecule in the given example is absorbed (energy gain $E_{ad}$) on the surface at specific sites. The molecules migrate and rotate in two dimensions (thermally activated processes associated with energy barriers $E_m$ and $E_{rot}$, respectively). From the point of view of thermodynamics, molecules on the surface try to assemble in an order with minimum free enthalpy. Noncovalent-bond formation between functional groups (energy gain $E_{al}$) allows molecules to adopt low-energy positions that govern the molecular supra-structure. In addition, the indirect substrate-mediated interactions (maximum energy cost $E_s$) also influence the molecular self-assembly process. The addition of all these processes leads to the
self-assembly of molecules into complex molecular architectures which are energetically stable. Table 1 [12] gives an overview of the relevant process and interactions with associated energy ranges and interaction length.

According to the described molecular self-assembly procedure, several parameters play a key role in formation of self-assembled supramolecular networks. Tuning molecule-molecule interaction, molecule-substrate interaction, temperature, and molecular concentration ratio is the key to control the formation of complex supramolecular networks using self-assembly technique.

1.1.1.1 Molecule-molecule interactions

Different types of molecular interactions can drive supramolecular self-assembly.

- **Van der Waals interaction**
  
The Van der Waals interaction is an attractive force between molecules (or between parts of the same molecule) that depends on the distance of the molecules. Van der Waals forces are relatively weak compared with other forces as shown in Table I [12]. The Van de Waals interaction has moderate specificity and directionality. It can exist between the substrate and the deposited molecules or between the molecules on the surfaces.

- **Hydrogen bond**
  
A hydrogen bond is regarded as the attractive interaction between a positively charged hydrogen atom and a long pair of an electro-negative atom, like nitrogen, oxygen or fluorine. The hydrogen bond can be schematically presented as the formation of A-H⋯B, where A and B are electronegative elements and B possesses a long pair of electrons. These bonds can occur between molecules (intermolecular), or within different parts of a single molecule (intramolecular). The hydrogen bond is stronger than a van der Waals interaction, but weaker than covalent, or ionic bonds. Hydrogen bonding is highly directional. The selectivity and directionality of hydrogen bonds stabilizes the formation of supramolecular architectures.
Lucas and co-workers [14] reported adenine growth on the Au(111) surface which gives a good example of how the hydrogen bond mediates self-assembly of adenine molecules to form a highly ordered 2D structure. A molecularly resolved STM image is shown in Fig. 1.4 (a). The lattice vectors of the structure as measured from the STM images are $d_1 = 15.6$ Å, $d_2 = 12.5$ Å and the angle between the two neighbouring unit cells is $\sim 42^\circ$. This structure is formed by two periodically repeated hexagons, each consisting of six molecules as indicated in Fig. 1.4 (b). As is shown clearly in the proposed model in Fig. 1.4(b), the structure is stabilized by two N-H$\cdots$O hydrogen bonds between each of the two adenine molecules.

- **$\pi$-$\pi$ interaction**

  The $\pi$-$\pi$ interaction is a non-covalent interaction between organic compounds. $\pi$-$\pi$ interactions originate from partial intermolecular overlap of p-orbitals in $\pi$-conjugated systems. In comparison with the hydrogen bond, the $\pi$-$\pi$ interaction is weaker and has no strong directionality, which makes it more difficult to judge its importance [15].

- **Coulomb repulsion and steric effects**

  Other more complex factors in the formation of supramolecular networks are the Coulomb repulsion of equally charged functional groups and steric hindrance. The system will always try to arrange itself in such a way that it minimizes these effects.
1.1.1.2 Molecule-substrate interaction

Physisorption and chemisorption:

Interactions between molecules with the solid substrate or other templates can also play a non negligible role in two dimensional supramolecular assemblies. Chemisorption and physisorption are the two main effects dominating the molecule-substrate interactions.

Chemisorption is an adsorption process characterized by a strong interaction between an adsorbate and the substrate surface. Covalent and ionic interactions are involved in the chemisorption process, leading to the formation of chemical bonds. In comparison, the physisorption is a process in which there is no mixing of the electronic states of the atom or molecule with those of the substrates and the forces involved are mainly weak van der Waals forces. The physisorption does not involve any chemical bonds.

In the case of molecules absorbed on a surface, non-covalent weak forces dominate the molecule-substrate interaction. The molecular self-assembly results from the combination of intermolecular forces and molecule-substrate interaction, where the crystalline structure of the surface plays a key role [16]. In this regard, molecule-substrate interaction usually determines adsorption geometry (epitaxy) and conformation at low coverage.

![Fig. 1.5](image-url)

**Fig.1.5:** (a) STM image of a $2\sqrt{3} \times 2\sqrt{3}$-R30° $C_{60}$ domain on Au(111), 7.3×7.3 nm$^2$, $U_s = -2$ V
(b) image of a $C_{60}$ monolayer on Ag(111) showing three different domains 19 19 nm$^2$, $U_s = -2$ V [13].
Molecule-substrate interactions have been investigated experimentally. Altman and co-workers studied fullerene self-assembly on Au(111) and Ag(111) surfaces [13]. C_{60} molecules diffuse on Au(111) and Ag(111) at room temperature and form close packed structure as shown in Fig. 1.5 (a) and (b). The fact that C_{60} molecules can diffuse on these surfaces after deposition reveals a weak C_{60}–surface interaction.

![Fig.1.5: An STM image of a Si(100)-(2×1) surface after deposition of ~ 0.06 ML of C_{60} molecules at room temperature. At this coverage, the molecules randomly distribute across the surface, remaining mostly isolated. A few small clusters form with two or three molecules.](image)

Quite different are the observations by Sarid et al. [17] who investigated the adsorption of C_{60} molecules on Si(100) surfaces. They observed that post-annealing at 600°C affects C_{60} positioning on the Si(100) substrate [17]. The STM image in Fig. 1.6 (a) shows C_{60} molecules deposited at room temperature on Si(100). The molecules are randomly distributed and mostly isolated. The molecules do not diffuse at room temperature and are predominantly adsorbed in the troughs between Si dimer rows. The authors suggest that the positioning of the molecules results from dipole-induced dipole interaction between C_{60} molecules and the Si(100) surface since the strength of that interaction is of the same order of magnitude as van de Waals interactions.
Fig. 1.6 (b) shows an STM image of the Si(100) after deposition $C_{60}$ at room temperature followed by post annealing at 600°C. The STM image shows now that the $C_{60}$ molecules are not adsorbed in the Si troughs anymore but bonded between two troughs instead, i.e. locations corresponding to the top of the dimer rows. The authors suggest that the bonds of the silicon dimers break at elevated temperature and $C_{60}$ molecules bond to unsaturated Si dangling bonds. In that case $C_{60}$ would be chemisorbed on the surface. The authors hence concluded Our observations suggest a physisorption, which arises from a dipole-induced dipole interaction between $C_{60}$ molecules and the Si(100) surface. The strength of the interaction is on the same order of magnitude as the van der Waals interaction. Annealing the sample to elevated temperatures promotes the transition from physisorption to chemisorption, which is covalent in nature, where the C molecules bond to locations corresponding to the top of the dimer rows.

The influence of surface reconstructions:

**FIG.1.7:** STM images at 50 K of a reconstructed Au(111) surface with adsorbed nitronaphthalene (a) 0.1 ML NN at 65 K. (b) 0.2 ML NN at 50 K.

Inset: 0.2 ML NN at 10 K. [18]

Böhringer et al. reported that the $(22\times\sqrt{3})$ reconstruction of the Au(111) surface is driving the formation of self-assembled supramolecular clusters of nitronaphthalene (NN) molecules [18]. After 0.1 monolayer (ML) deposition, molecular clusters of distinct size and structures first appear at ~ -200°C at the fcc elbows of the Au(111) reconstruction, building
regular molecular arrays, Fig. 1.7(a). Upon further cooling these clusters do not grow in size but identical clusters are observed within the fcc domains at 50 K, Fig. 1.7(b).

![Image](image_url)

**FIG. 1.8:** (a,b) Two ML Ag/Pt(111) trigonal network. (a) LT-STM image 60×60 nm² where three types of domains (fcc, hcp1, and hcp2) can be observed. Inset, FFT (Fast Fourier Transform) of the STM image (b) Atomically resolved LT-STM 7.5×7.5 nm². (c,d): Example of a potential application of a well-ordered nanohole pattern: self-organized growth of C₆₀ nanoclusters at RT. (c) Overview RT-STM image 200 × 200 nm² showing long-range order of a molecular nanostructure array replicating the hexagonal symmetry of the nanohole pattern, which is also illustrated by FFT (inset). (d) Close-up RT-STM image 70×60 nm² of the array of C₆₀ nanoclusters trapped inside the nanoholes. [19]

Mansour *et al.* investigated the formation of C₆₀ clusters on a reconstructed Ag/Pt(111) surface [19]. Figs. 1.8(a, b) shows STM images of a Pt(111) surface covered with 2 ML of Ag. A triangular shaped network appears on the surface. With an average period of about 7
nm, the trigonal network can be regarded as a (25×25) superstructure with respect to the underlying Pt(111) atomic lattice. Mansour et al. [19] showed that removing about 0.1 ML of the Ag top layer of this surface structure leads to the formation of nanoholes at specific domains of the trigonal network. Deposition of C$_{60}$ molecules on this surface leads to the long-range ordering of a C$_{60}$ nanostructure arrays replicating the hexagonal symmetry of the nanohole system. Figs. 1.8(c,d).

1.1.1.3 The influence of temperature on molecular self-assembly

On the microscopic scale, the increase of temperature provides necessary energy to allow for the molecules to migrate or rotate around their equilibrium positions. During the annealing process, sufficient energy is provided for the molecular system to change from an initial state to a final state. In the final state, the whole system will have reached thermodynamic equilibrium and the properties of the molecular system will not change in time. In general, the system will reorganize until a minimum free enthalpy is reached. In the case of molecular nanosystem, molecules may form stable and ordered supramolecular structures at specific temperatures. That means that in a wide range of annealing temperatures there may be different spatial supramolecular architectures that are stable in certain limited temperature range. Therefore it may be possible to use the temperature as an external stimulus to manipulate and drive supramolecular self-assembly on surfaces, as discussed with the two examples here below.

Wang et al. [20] investigated the self-assembly of rubrene molecules on Au(111). Their STM measurements reveal that rubrene forms a highly defective organic layer on Au(111) after post-annealing at 353 K, Figure 1.9(a). Annealing at 363 K for 10 min leads to formation of a well ordered monolayer where rubrene forms a complete row-like supramolecular structure, shown in Figure 1.9(b). The few black hole-features in the layer in Fig. 1.9(b) result from missing molecules.
Li et al. examined the temperature-dependent self-assembly of stilbenoid (SD) on graphite [21]. Figure 1.10 (a) presents an STM image of a SD self-assembled network at 20°C. The molecules form an hexagonal structure, as it is outlined in Fig.1.10(a). Figure 1.10 (b) presents an STM image of the molecular assembly after annealing at 65°C. The molecules now adopt an arrangement, having a parallelogram unit cell. In the case of SD molecules on graphite, annealing permits to change the molecular ordering.
1.1.2 Engineering multi-component supramolecular structures using self-assembly

Building multi-component architectures at the molecular level is important in device technology. The molecules must not only have the desired electronic properties but also be able to self-assemble with other molecules in the desired molecular architectures in order to optimize the structure electronic properties and limit the number of defects. This is actually one of the limitations to the development of organic solar cells as in Fig.1.1. Controlling multi-component molecular self-assemblies is therefore essential in order to engineer new supramolecular architectures having enhanced properties. Various factors enter in this process, namely the choice of the molecules which can form a specific type of bond, the temperature and the relative surface concentrations of the different adsorbed species, as we shall illustrate below with several examples

1.1.2.1 Selecting complementary molecules

Otero et al. [22] mixed DNA bases (guanine (G), adenine (A) and cytosine (C)) on an Au(111) surface. C molecules were first deposited at room temperature, (Fig.1.11 A,B). Then either the complementary base (G) or the non complementary base (A) was deposited onto the partially C covered surface (held at room temperature). Then the samples were heated for 10–15 min at a temperature below the lower desorption temperature of the two bases contained in the mixture. STM images of such a sequential co-deposition and heating sequence are shown in Fig.1.11A–C for C+G and Fig.1.11D–F for C+A. [22]

The STM images reveal that hydrogen bonds are locally formed on the surface between C and G molecules (complementary bases) and between C and A molecules (non-complementary bases). However, long-ranged multi-component supramolecular self-assembled networks were not observed using these molecules.
Fig. 1.11: STM images of DNA bases on Au(111). Co-deposition experiments for the complementary DNA bases cytosine and guanine (A–C) and the non-complementary bases cytosine and adenine (D–F) on Au(111). During the first step, similar amounts of cytosine were deposited at room temperature in each case (A, D). After deposition of guanine (B) a sharp increase in the number of fivefold rings is found (indicated by the green shading), which was not observed after deposition of adenine (E). C+G and C+A mix on code position (B, E). After heating, the complementary cytosine and guanine mixture remains disordered (C), while the non-complementary cytosine and adenine mixture segregates into adenine islands and cytosine zigzag branches (F). [22]

1.1.2.2 Selecting molecule functionalities

Forming extended hydrogen-bonding-based supramolecular networks requires to wisely select molecules for their abilities to form hydrogen bonds with each other. However, Fig.1.11 shows that this does not guarantee that long-ranged self-assembled domains will develop. As hydrogen bonding energies can strongly vary (table 1), small variations in the binding energy and the direction of bonding are expected to lead to dramatic changes in the supramolecular self-assembly. By functionalizing the molecules, the molecular binding
energies can be tailored. For example, 3,4,9,10-perylene-tetra carboxylic-dianhydride (PTCDA) and 3,4,9,10-perylene-tetracarboxylic diimide (PTCDI) both have a functionalized perylene skeleton. PTCDI is a PTCDA molecule in which one oxygen atom is replaced by an N-H group (Fig 1.12).

![Fig 1.12: Chemical structure of melamine (a), PTCDI (b) and PTCDA (c). Red, blue, grey and white balls are oxygen, nitrogen, carbon and hydrogen atoms.]

When PTCDI and melamine are mixed together, one expects these molecules to form 3 hydrogen bonds (2×N-H···O, 1×N···H-N). In the case of a PTCDA and melamine mixture, one assumes that these molecules form 2 hydrogen bonds (2×N-H···O), if the repulsive interaction between melamine N and PTCDA O is neglected. In theory in that case the PTCDI-melamine and PTCDA-melamine would be identical but the binding energy would be different. However, predicting multi-component binding is far from being an easy task because various binding schemes may occur at will be illustrated in the following.

Fig. 1.13 shows an experimental observation of melamine-PTCDA self-assembly on Au(111) [23]. The PTCDA-melamine ratio is 1:2. The molecules form long-ranged domains of molecular stripes. Each stripe is composed of a single PTCDA molecular row and a double row of melamine molecules. The unit cell outlined in Fig.1.13(b) in blue has a parallelogram shape, with an angle of 85° and lengths of the lattice vectors 10.0 Å (the periodicity along the PTCDA rows) and 19.9 Å (PTCDA PTCDA separation across two melamine rows). Fig.1.13(b) shows the molecular arrangement as observed in Fig.1.13(a). This network is stabilized by various single PTCDA-melamine hydrogen bonds.
PTCDI mixed with melamine on the same Au(111)-(22×√3) surface at the sample temperature forms a completely different supramolecular structure [24]. Fig. 1.14 shows the PTCDI-melamine self-assembly at room temperature on Au(111). The molecules form a chiral structure having a pattern called “pinwheel”. The network is hexagonal with a 37.8 Å lattice parameter. The model of this supramolecular network is presented in Fig. 1.13b. In this configuration the centre of the pinwheel is composed of a melamine arrangement, where six melamine molecules form a chiral hexagon. This hexagon is surrounded by PTCDI pairs (side by side).
In this structure PTCDI and melamine can be connected through triple hydrogen bonds or single hydrogen bonds.

The two examples presented above in Fig.1.13 and 1.14 indicate that, just by changing two N-H into two O in a perylene based molecules dramatically changes the multi-component self-assembly of this molecules with melamine. This highlights that the formation of molecular architecture is very sensitive to molecular functionalities that allow for hydrogen bonding. This indicates that there are countless opportunities to control multi-component self-assemblies by wisely selecting molecular design.

1.1.2.3 Selecting molecular ordering using temperature

As for single component ordering (section 1.1.1.3), temperature is a key parameter driving multi-component self-assembly.

Fig. 1.15: PTCDI-melamine networks on Au(111) after post-annealing at 100°C (a,b,c) and after post-annealing at 120°C (d,e) [25]
Fig. 1.15a shows the molecular superstructure formed by deposition of PTCDI and melamine on Au(111) followed by post annealing at 100°C for 10 h [25]. This domain has a honeycomb structure. The molecules assemble into a hydrogen bonded honeycomb network in which PTCDI molecules are located at the edges of the hexagonal unit and melamine molecules form the vertices, Fig. 1.15b,c. Fig. 1.15d shows the molecular superstructure formed after post-annealing at 150°C for 10 h. The PTCDI-melamine network has now a parallelogram unit cell, Fig. 1.15e. The first multi-component network is made of PTCDI and melamine blocks connected through three hydrogen bonds, Fig. 1.15c. In the second network, in addition to this bonding, PTCDI-PTCDI double hydrogen bonding and PTCDI-melamine single hydrogen bonding are conserved. This example shows that a small temperature increase (20°C) can affect the number and directionality of the molecular hydrogen bonds involved in the supramolecular self-assembly and dramatically modify the resulting multi-component architecture.

### 1.1.2.4 Tuning molecular concentration ratio

In the case of multi-component molecular networks, molecular concentration ratio is also expected to influence supramolecular ordering. For example PTCDI and melamine molecules can form different molecular networks having different molecular ratio. Theobald et al. reported the formation of a honeycomb networks having a 3:2 ratio [26], whereas the PTCDI-melamine “pinwheel” structure (Fig. 1.14) has a 3:4 ratio. [24].

Palma et al. build in Fig. 1.16 the ratio-dependent phase diagram of supramolecular self-assemblies based on melamine molecules and different ditopic imidic linkers. This diagram based on experimental observation shows that bi-components supramolecular ordering are highly sensitive to molecular ratio and molecule characteristics. Variation of the molecular ratio can leads to different multi-component supramolecular networks as well as phase segregation.
Fig. 1.16: Phase diagram of segregation in bicomponent networks made of melamine (MEL) molecules (red triangles) and four different ditopic imidic linkers (1-4) (blue rectangles).[61]

1.1.2.5 Forming guest-host multi-component structures

Two-dimensional supramolecular architectures can be exploited to trap molecular species into specific sites to form long range multi-component structures. It is becoming a very useful strategy to control the ordering of molecules which cannot form directional bonds, like fullerenes for example. This is also interesting in order to build multi component number architectures.

• 2-component architectures

Fig1.17: (a) TSB35 and HBC molecules. (b) Model for the supramolecular assembly of the TSB35 host-matrix. (c) STM image of the TSB35 host and HBC guest structure. [27]
Schull et al. successfully formed a TSB35-HBC guest host network on graphite [27]. TSB35 self-assemble into a honeycomb structure, leaving empty cavities as illustrated by the model, Fig.1.17b. Addition of HBC leads to formation of a HBC-TSB35 (Fig.1.17c). The HBC are trapped inside the cavities of the TSB35 molecular host template network. HBC appears as circle in the STM image, Fig.1.17, whereas TSB35 appears as star.

Fig.1.18: (a) NN4A and Sc$_3$N@C$_{80}$ molecules. (b) STM image (68×68 nm$^2$) of the Sc$_3$N@C$_{80}$–NN4A host–guest architecture on graphite. (c) High-resolution STM image of the Sc$_3$N@C$_{80}$–NN4A structure. The green arrows indicate individual cavities missing one Sc$_3$N@C$_{80}$ molecule. (d) Plan view of the proposed structural model. (e) Side view of the model. [28].

Li et al. reported the formation of a NN4A-Sc$_3$N@C$_{80}$ Guest-host network. NN4A forms a well-ordered open network with a Kagomé structure on graphite [28]. Two kinds of cavities are created, having different size and shape: large hexagonal cavities and small triangular cavities. Sc$_3$N@C$_{80}$ molecules are then deposited onto the molecular networks, and a network of single fullerene molecules appear as observed in the STM images Figs.1.18b,c. The STM image reveals that one fullerene is trapped in the large hexagonal cavity of the NN4A Kagomé network, whereas the triangular cavity remains empty, Fig.1.18c. The model of the 2-component structure is presented Fig.1.18d,e.
• **3-component architectures**

Theobald *et al.* reported the formation of a 3-component PTCDI-melamine-C\textsubscript{60} supramolecular networks on Ag/Si(111)-(\sqrt{3}×\sqrt{3})-R30° surface. PTCDI and melamine form a honeycomb network having large hexagonal cavities. C\textsubscript{60} molecules are then deposited onto this structure. STM image Fig. 1.19b reveals that heptameric C\textsubscript{60} clusters having a compact hexagonal arrangement are formed within the pores. The model of the structure is presented Fig.1.19c. The symmetry of the PTCDI-melamine structure permits to align the C\textsubscript{60} clusters.

![Fig.1.19](image)

Fig.1.19: (a) C\textsubscript{60}, PTCDI and melamine. (b) STM image of C\textsubscript{60} heptamers on a PTCDI–melamine network. Inset, high-resolution view showing an individual cluster. (c) Schematic diagram of a C\textsubscript{60} heptamer. [26]

• **4-component architectures**

Adisoejoso *et al.* [29] successfully formed a 4-component guest-host structure mixing bisDBA-C\textsubscript{12}, COR, ISA, and TRI molecules, Fig.1.20a. A filled Kagomé structure is formed using these molecules, Figs.1.20b,c. The bisDBA-C\textsubscript{12} form the Kagomé structure. Each hexagonal void is filled with a COR\textsubscript{1}-ISA\textsubscript{6} cluster, whereas the triangular voids are filled
with single TRI molecules. The unit cell \((a = b = 5.5 \text{ nm}, \alpha = 61^\circ)\) consists of 12 molecules: three bisDBA-C12, one COR, six ISA, and two TRI.

Fig. 1.20: (a) Chemical structures of bisDBA-C\(_n\), isophthalic acid (ISA), coronene (COR), and triphenylene (TRI). (b) STM image of a mixture of bisDBA-C\(_{12}\), COR, ISA), and TRI. (c) Tentative network model showing the Kagomé structure of bisDBA-C\(_{12}\) hosting the COR\(_1\)-ISA\(_6\) cluster and TRI in the hexagonal and triangular voids, respectively.[29]

1.1.2.6 Using molecular surface nanotemplate

Another strategy to build multi-component architectures consists to take advantage of molecular surface nanotemplate. Chen et al. showed that \(\text{C}_{60}\) molecules form well ordered nano junction arrays on face-on+edge-on p-sexiphenyl (6P) nanotripe structures [30]. The STM image in Fig. 1.21(b) shows that successive deposition of 6P molecules on an Ag(111) surface leads to the formation of face-on+edge-on 6P structure. The model of this structure is presented Fig. 1.21(b). Post deposition of \(\text{C}_{60}\) molecules onto this organic template results in a fairly ordered 2D array of \(\text{C}_{60}\) triplets, as shown in Fig.1.21(c). The corresponding detailed 20 x 20 nm\(^2\) STM image of the \(\text{C}_{60}\) triplet array is displayed in Fig.1.21(d). These triplets
assemble along the underlying 6P nanostripe packing direction with a separation of about 3.3 nm, as highlighted in Fig.1.21(d). In this 2-component architecture, the C$_{60}$ triplets predominantly nucleate on the edge-on 6P molecules of the 6P nano stripe array. In contrary to the guest host structure, the C$_{60}$ molecules are not in contact with the substrate.

![Fig.1.21: 15×15 nm$^2$ STM images of (a) “face-on_edge-on” 6P monolayer nanotripe on Ag(111) (b) Schematic drawings of molecular structure for face-on_edge-on 6P layers . (c) 80×80 nm$^2$ STM images of 0.5 ML C$_{60}$ on face-on_edge-on 6P layer on Ag(111), showing the formation of a well-ordered vertical C$_{60}$/6P nanojunction array, (d) the corresponding detailed 20×20 nm$^2$ STM image of panel (c).[30]](image)

1.1.2.7 Taking advantage of surface reconstructions

As was observed in the case of single-component two-dimensional supramolecular structures (see section 1.1.1.2), surface reconstructions are expected to affect multi-component supramolecular self-assemblies.
The STM image in Fig. 1.22(a) reveals that the reconstructed Au(111)-(22×√3) surface influences PTCDI-melamine supramolecular self-assembly. This PTCDI-melamine network does not correspond to the honeycomb networks presented Fig. 1.15a and Fig. 1.19a. In this multi-component structure, the bright lines of Au(111), corresponding to bridge site atoms, pass through the center of the hexagonal PTCDI-melamine cavities. The PTCDI molecules on these lines are aligned in the (1 1 0) direction, so that the PTCDI molecules are perpendicular to the bright lines of the Au(111) substrate. A model of surface reconstruction-driven PTCDI-melamine supramolecular network is presented in Fig. 1.22(b). In this structure, rows of paired hexagonal cavities are connected through melamine-melamine bonds. This leads to the appearance of parallelogram cavities in addition to the hexagonal cavities.

As was presented in this section, various parameters play a key role in the formation of multi-component supramolecular self-assemblies. The resulting architecture will be governed by the molecular shape and the subtle balance between molecule-molecule interaction and molecule-substrate interaction. Therefore, engineering supramolecular self-assemblies can be tuned by wisely selecting the molecules on the basis of their design and functionalities, by choosing adequate surface and adjusting the relative ratio of the deposited molecular species and the temperature.
1.2 Oxide surfaces and insulating thin films on metal surfaces

The engineering of organic devices like OFETs (Fig. 1.2) requires to grow or to form molecular layers on insulating thin films in order to electronically decouple the molecule from the metal electrode. The interest of nanoscience in using insulating thin films as a nanostructure support is also motivated by the prospect of decoupling nanostructure electronic states from its support, which is a prerequisite to address individual and non-perturbed nanostructure properties. Insulating thin films have been successfully employed to reduce the coupling between the substrates and the absorbates [31] and to explore properties of nanostructures: for example it has been possible to probe the electronic states of single molecules [32] and single metal particles [33], to control the charge state of single adatoms [34]. It has also been possible to observe on insulating thin films the interactions between spins in individual nanostructures [35] and to flip the spin of a single adsorbed atom [36]. In addition to their electronic properties, interest in oxide and insulating surfaces comes from the possibility to use surface reconstruction or structure to control the growth of fcc metal nano crystals [37] and five-fold twinned structures [38, 39]. This is particularly appealing in the aim to develop nanocatalysts having enhanced catalytic activity [40].

Various insulating thin films based on oxides and insulating materials have been studied during recent years. Silica [41, 42], vanadium oxide [43], alumina [32, 42], ceria [44], iron oxide [45, 46], magnesium oxide [47], titania [40], strontium titanate [48, 49, 50] and sodium chloride [51, 52, 53, 54, 55, 56, 57] are some of the most promising insulating materials for nanoscience and nanotechnology. The “ideal” candidate for technological application (such as OFET) is the insulating thin film forming flat and defect free crystalline layers on metal surfaces. In addition it would be advantageous if the insulating thin film was easy to prepare and its thickness easy to control.

In the following section we shall give an overview of the most promising insulating thin films grown on metal surfaces that are currently used in nanoscience.
1.2.1 Magnesium Oxide: MgO

Schintke et al. [58] investigate the growth of MgO on Ag(001) surface. Mg was deposited in oxygen gas on Ag(001). The deposition of 0.3 ML MgO, leads to the formation of two-dimensional square islands of 10–15 nm size nucleated homogeneously on the Ag(001) surface, Fig (1.23). [58] STM images are showing that the islands are crystalline. Scanning tunneling spectroscopy showed that MgO thin films with a thickness of more than 3 ML have electronic properties similar to those of the MgO bulk.

1.2.2 Copper Nitride: CuN

Ruggiero et al. investigated the growth of CuN films on Cu(100) surfaces [59]. A Cu atomic beam is directed onto a Cu(100) substrate in a nitrogen atmosphere in UHV. The authors observed that atomic nitrogen adsorbs in hollow sites between Cu atoms on Cu(100). Figure 1.24(a) shows an atomically resolved STM image of a CuN island. The island is crystalline and appears as 0.18 nm depressions in STM images at low voltage. This is consistent with the expected decrease in local state density within the gap of an insulator. As the coverage increases, the islands become more rectangular in shape and self-organize into an array (Fig. 1.24b), which is well suited for nano scale templating.
FIG. 1.24 STM images of CuN on Cu(100). (a) Atomic resolution image of a CuN island (scale bar=2 nm). The image has been Laplace and Gaussian filtered to emphasize the local contrast. The lattice is shown of Cu (black) and N (white). At higher coverage, islands coalescence into a grid separated by ridges of Cu (Scale bar=5 nm). [59]

1.2.3 Iron oxide: FeO

Ritter et al. [60] characterized the formation of FeO films on Pt(111). Iron is deposited onto a clean platinum surface at room temperature.

FIG. 1.25: (a) 100 100 nm<sup>2</sup> STM image of a 0.9 ML FeO film on Pt(111). (b) 55 55 Å<sup>2</sup> STM image of a sub-monolayer FeO film grown onto Pt(111). A Moiré superstructure with a unit cell of 3×25 Å<sup>2</sup> is created. The direction of this superstructure indicated by the marked atoms is rotated by about 11° against the small FeO(111)-(1×1) unit cell that is also indicated. [60]
Context and Motivation

After the deposition the iron is oxidized for 2 min at temperatures between 870 and 1000 K in 1026 mbar oxygen partial pressure to achieve highly ordered FeO film. The atomically resolved STM images display that FeO form a flat and crystalline film on Pt(111), Fig.1.25. It exhibits a hexagonal surface structure with an atomic periodicity of 3.11 Å. This atomic periodicity is modulated by a larger periodicity of about 25 Å, which creates a moiré superstructure visible in the STM image, Fig.1.25. The large hexagonal unit cell of this moiré structure can be defined by the brightest atomic features in the STM image and is rotated by about 11° with respect to the small (1×1) surface unit cell on the oxide film. This is indicated by the marked atoms with equal brightness in Fig.1.25b which do not line up with the atom rows of the FeO(111) surface.

1.2.4 Sodium Chloride: NaCl

1.2.4.1 NaCl on Cu(111)

Fig. 1.26: (a) DFM images of one monolayer NaCl on Cu(111) The NaCl clusters decorating steps extend about 1 nm above the upper terrace. (b) DFM images of monatomic NaCl islands grown on top of a continuous NaCl film which covers a step of the Cu(111): topography image showing a ‘carpet’-like NaCl film over a substrate step. [62]

NaCl thin films have been successfully grown on Cu(111) surface by Bennewitz et al. [62]. NaCl was evaporated from a Knudsen cell at 675 K. NaCl forms rectangular islands on Cu(111) as observed in the dynamic force Microscopy (DFM) images, Fig.1.26. They also observed that the NaCl layer on Cu(111) is crystalline having a (100) oriented surface [52].
1.2.4.2 NaCl on Ag(100)

Pivetta et al. investigated the growth of NaCl on Ag(100) [54]. Fig.1.27 shows a typical $400 \times 400$ nm$^2$ STM image of the Ag(100) surface after NaCl deposition. At a 1 ML coverage, NaCl forms (100) crystalline island on the Ag(100) substrate. This is confirmed by atomically resolved STM images of the NaCl island, Figs. 1.27(b,c). The islands have an average size of 50 nm and a typical thickness of 1 ML (most have a partial second layer). The Ag steps seem to act as a preferential nucleation sites for the first and for the following layers, Fig.1.27. The STM images also revealed that there are two different epitaxial relationship between the NaCl(100) layer and the Ag(100). The crystalline axis of the NaCl(100) layer can be aligned with the crystalline axis of Ag(100), Fig.1.27(b), or it can be at $45^\circ$, as shown in Fig.1.27(c).

Growing insulating thin films on metal surfaces requires optimizing depositing flux, substrate temperature and gas atmosphere pressure in some systems. As shown above, crystalline and flat MgO, CuN, FeO and NaCl thin films have been successfully grown on
various metal surfaces. For these reasons they are of great interest for nanotechnology and application like organic transistor (Fig.1.2). However the preparation of MgO, CuN and FeO requires to precisely control the metal flux and gas pressure during the insulating thin film growth. If the right balance is not respected, the thin film growth will fail. In comparison, NaCl film can be grown using a convenient one-step process: NaCl can be directly sublimated in UHV onto a room temperature metal surface. NaCl crystalline islands have been indeed successfully grown on numerous crystalline metal surfaces, such as Cu(111) [24, 51, 52], Cu(110) [24, 51], Cu(311) [51], Ag(111) [53], Ag(100) [54], Ge(100) [55], Al(111) [56], Al(100) [57]. However, NaCl has not been systematically investigated on Au(111) surface until this PhD project\(^1\).

1.3 Outline of the thesis

In chapter II we shall present the experimental characterization techniques and setups used during this research project. Scanning tunnelling microscopy (STM) will be presented and discussed in detail. Vacuum and deposition systems will be shown. The preparation of Au(111) thin films on mica and the Au(111)-(22×√3) superstructure will be shown.

In Chapter III, we shall investigate the formation of self-assembled multi-component supramolecular nano-architectures on metal surfaces. The building blocks we shall use are PTCDA, melamine, adenine and C\(_{60}\). We shall especially focus our attention on the influence of temperature, molecule ratio and molecular interaction on multi-component self-assemblies.

In Chapter IV, we shall report on the growth of NaCl thin films on Au(111)-(22×√3). The NaCl film crystalline structure and epitaxy have been characterized. We shall also discuss the study of the growth of organic nanostructures on the NaCl insulation thin film.

\(^1\) We were the first to published a detailed STM investigation of NaCl thin film grown on Au(111)-(22×√3) in 2008 [67]. In 2009, Bombis et al. [68] and Canas-Ventura et al. [69] also investigated this system.
1.4 References

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