

 \* Electron tunnelling manipulation of selfassembled molecular nanostructures
\* Coronene: A Single Molecule Atom Counter
\* Measuring the conductance of single molecular wires as a function of the electron energy
\* Synthesis of Y-Shaped Polyarenes, Crushed Fullerenes and Nanographene Fragments

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Detailed information about the project, further reading documents and AtMol workshop series contributions could be found at www.atmol.eu.

We would like to thank all the authors who contributed to this issue as well as the European Commission for the financial support (ICT/FET FP7 AtMol project no. 270028).

> Dr. Antonio Correia Editor - Phantoms Foundation

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# Electron tunnelling manipulation of self-assembled molecular nanostructures

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Several methods were developed in the last decades to manipulate molecules using the tip of a scanning tunneling microscope. Single atoms and molecules can be moved on a surface in a controlled way. However, for the development of devices at the nanoscale, it is important to move not only adsorbates one by one, but also structures composed bv several molecules. Therefore. purely а electronic excitation method was recently used for the controlled movement of weakly interacting assemblies of few molecules. The adsorption of Acetylbiphenyl molecules on a Au (111) surface and the formation of nanostructured given by four molecules and stabilized by hydrogen bonding will be described in this article. The electron tunnelling induced manipulation of these presented. nanostructures will be Depending on the polarity and position of the applied voltage, the direction of movement can be selected.

#### Introduction

To develop molecular machines based on single molecules, scanning tunneling microscopy (STM) at low temperature, with its high resolution and stability, is a very convenient technique. Prototypes of molecular machines, which can be controlled at the atomic scale, can be tested by adsorbing specially designed molecules on a surface in ultra clean conditions, imaging and manipulating them using the tip of an STM.

In the last few years, the manipulation of a molecule with the tip apex of a scanning tunneling microscope (STM) has become a well-established technique to study the mechanics of a single molecule on a surface [1-3].



Fig. 1 > Schematic representation of the electron tunnelling manipulation of a windmill nanostructure./

The controlled manipulation of single atoms and molecules on metal surfaces by means of the STM tip was developed during the last two decades [4-6]. In particular. STM has proven to be a versatile tool for the atomic-scale manipulation and the construction of nanostructures [1, 2, 4-7]. Single atoms and molecules can be precisely positioned by lateral [6] or vertical manipulation [8]. Different mechanisms of manipulation were developed on metal [6], ultrathin insulator [9, 10], or semiconductor [11] surfaces. Other manipulation techniques employ electric fields [12], or inelastic tunneling electrons [13]. Voltage pulses were used to desorb or dissociate molecules, to induce conformational changes or chemical reactions [14].

In particular, inelastic electron tunneling induced manipulation is a process where tunneling electrons are injected from the STM tip positioned above the adsorbed molecule, thus moving it. The electron energy is normally transferred through an excited state, leading to excitation (rotational, vibrational, or electronic), the rate of which is controlled by the applied bias and the tunneling current [3].

In an STM experiment, when an electron tunnels through an adsorbate, inelastic electron scattering may induce elementary electronic or vibrational excitations of the adsorbate [2]. The inelastic electrons transfer energy to the adsorbate. Such energy, stored in the electronic or vibrational excitation of the molecule, can movement chemical triaaer or transformation at the atomic scale [2]. Therefore, electron tunnelling induced manipulation might be based on two different excitations depending on the applied bias voltage. At high voltages an electron may transiently occupy an electronic excited level of the adsorbate: at low voltages vibrational modes may be excited.

Experimentally, electron tunnelling induced manipulation is realized by positioning the STM tip above the location of the molecule at a fixed height. The feedback loop can be switched off and the tunnelling current and/or the voltage are increased from imaging to manipulation parameters. The electrons can be injected either from the tip or from the substrate depending on bias polarity. The point in time at which a change in the molecule happens is recorded by monitoring the tunnelling current versus time. A sudden change in current is indicative of the success of the manipulation. These sudden jumps are caused by changes in the apparent height of the molecule either

through a motion of the molecule, or a conformational change, or a modification of the electronic structure [13].





Fig. 2 > Top panel: Molecular structure of the Acetylbiphenyl molecule used in the described experiments. Bottom panel: STM image of a single Acetylbiphenyl molecule on Au (111) stabilized by a defect./

Electron tunneling was recently used to induce the controlled rotational switching of a molecular motor [15]. A molecular motor adsorbed on a gold surface could be rotated in a clockwise or anticlockwise direction by selective inelastic electron tunnelling through different subunits of the motor.

Electron tunnelling induced manipulation has the advantage to be triggered just by electronic excitations and to avoid any direct mechanical interactions of the STM tip apex with the adsorbate. Moreover, being mechanically less destructive than common lateral manipulation, it can be successfully applied to the controlled manipulation of weakly bonded supramolecular assemblies [16]. Recently, it was demonstrated that it is possible to manipulate controlled in а way supramolecular structure by electron tunnelling induced manipulation [16].



In this article, we will describe the adsorption of Acetylbiphenyl molecules on the Au (111) surface and the formation of windmill nanostructures studied by STM at low temperature. In Fig. 1 the voltage pulse manipulation of the windmill structure is schematically shown. By applying voltage pulses just on one selected molecule of the structure, it is possible to move the complete supramolecular assembly to a chosen position on the surface without destroying it.

## **Experimental details**

The 4-Acetylbiphenyl (ABP) molecules (Fig. 2) were studied on the Au (111) surface with a low-temperature STM (5 K) under ultra-high vacuum conditions (<10<sup>-10</sup> mbar). The gold single crystal surface was cleaned by repeated cycles of Ne ion sputtering and subsequent annealing at 720 K. The molecules were deposited from a Knudsen cell at 320 K onto the Au (111) substrate kept at room temperature. After deposition, the sample was cooled down to cryogenic temperatures and transferred to the STM. For topographic imaging, either low voltages (0.1 V) or low currents (25 pA) used to were ensure that no manipulation happens during scanning.

Differential conductance spectroscopy measurements were performed using lock-in detection with a modulation frequency of 833 Hz and a modulation amplitude of 20 mV. To ensure the recording of a stable spectrum, the measurements have been done under closed feedback-loop conditions with a low set-point current (25 pA).

Manipulation was performed by applying voltage pulses to a single molecular nanostructure. The STM tip was precisely positioned on a nanostructure and a voltage pulse between tip and sample is applied. During the pulse, the feedback loop was kept closed and the



Fig. 3 > Top panel: STM image of an island of disordered ABP molecules on Au (111). Bottom panel: Linescan recorded over one of the island molecule, as indicated by the arrow in the top panel./

tip height was recorded. A jump in the tip height indicates a manipulation event. Typical voltage pulses between 2 V and 2.5 V of both polarities were applied for manipulation.

## **Results and discussion**

#### Adsorption of Acetylbiphenyl on Au (111)

In Fig. 2 the chemical structure and a STM image of a single Acetylbiphenyl molecule are shown.

The molecule is composed of two phenyl rings and an acetyl group. When deposited on Au (111) at submonolayer coverage, the molecules diffuse to step edge and defects or self-assemble in small ordered structures. An STM image of a single molecule adsorbed at a defect is presented in the bottom panel of Fig. 2.

When the coverage increases, island of molecules are formed, where disordered (Fig. 3) and ordered structures (Fig. 4) can be found on the surface.

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Fig. 4 > STM topography image of an island of self-assembled tetramers of ABP on Au(111). Both chirality can be observed in the same island./

As one can see in Fig. 2 and in the linescan at the bottom of Fig. 3, the molecule shows two lobes, one larger and more intense than the other. As confirmed by calculations [16], the more intense lobe corresponds to one phenyl ring connected to the acetyl group, while the other lobe corresponds to the second phenyl ring.

In the ordered islands, the ABP molecules self-assemble into small weakly bonded supramolecular structures formed by ABP tetramers (ABP<sub>4</sub>) and having the form of windmills.

In Fig. 4, a detail of an island composed by ABP windmill nanostructures is shown. The windmills are present on the surface in two mirror symmetric forms as a consequence of the prochiral nature of the single molecules. The islands show windmills of both chiralities. The windmills interact each other only very weakly.

By reducing the molecular coverage, single windmills structures can be observed by STM on the clean Au (111) terraces, with enough space in between to allow manipulation experiments.

The exact adsorption conformation of a windmill structure was determined by calculating the STM image of an ABP<sub>4</sub> molecular windmill on the Au (111) surface. The molecular adsorption

geometry was first optimized using the ASED+ semi-empirical molecular mechanics technique, which is well adapted for such large supramolecular adsorbates [17]. Constant current images of the optimized geometry were then calculated using ESQC (electron-scattering quantum chemistry) [18].

The so obtained calculated geometry is presented in Fig. 5. The calculations confirms that the windmill nanostructures are kept together by a hydrogen bond-like bonding. The calculated structure shows a bond length of 3.1 Å [16], in good agreement with the STM topography measurements shown in Fig. 4.



Fig. 5 > Calculated STM image of a single windmill nanostructure on the Au (111) surface./

To perform electron tunnelling induced manipulation, it is especially important to determine the electronic structure of a windmill structure, as the manipulation can be induced by tunnelling electrons into the electronic resonances of the molecular nanostructure.

Differential conductance spectra (dl/dV spectra) have been recorded over single  $ABP_4$  windmills at several positions. The results are shown in the spectra of Fig. 6. In the inset, the exact position of the STM tip on the windmill during the experiment is shown. The experiment was repeated for three different positions. In all three cases, a resonance at a positive voltage

of about 2.5 V is observed. This peak can be assigned to the lowest electronic excited state of the ABP adsorbate [19]. For negative voltages, the spectra appear flatter. However, a broad resonance at about -2.2 V can be distinguished in the spectrum in all three cases.



Fig. 6 > dI/dV spectra taken on the windmill structure. The inset shows a STM image of the windmill where the exact position of the tip during the measurements is indicated. Corresponding spectra and positions have the same color./

By comparing the spectra taken at the three different position on a single molecule of the windmill (Fig. 6), no differences in the measured features was observed. The large and less intense feature at negative voltage appear unchanged. For positive voltages, the position of the resonance peak is not changed, but its intensity decreases by moving the STM tip from the center of the windmill to the side. The electronic resonance seems therefore localized towards the center of the windmill structure. No differences on either topography or spectroscopy were observed between the four molecules composing the windmill.

## Pulse induced positioning of the windmill structures

The first step towards the development of reliable atomic scale controlled molecular machines is to understand the motion and the intramolecular mechanics of a single molecule on a surface. In the last few years, mechanically driven molecular machines have been demonstrated including molecular gears [20, 21], motors [22-24], wheels [25, 26], and different kinds of nano-vehicles [27, 28]. Moreover, the manipulation of a molecule with the STM tip apex has become a well-established technique to study the mechanics of a single molecule on a surface [1, 2].

On metal surfaces, the standard method for lateral manipulation of single atoms [4], single molecules [1], or small groups of molecules [29] is to bring the tip of the STM close to the adsorbate, thereby increasing the tip adsorbate interaction, and then move the tip to the desired final location on the surface.

Attempts to move the windmills using this conventional lateral manipulation technique resulted in a destruction of the supramolecular nanostructure and the separation of its ABP components. In order to move the individual windmills, voltage pulses of about 2.3 V should be applied on top of or close to one of the ABP molecules of the nanostructure. As a consequence. a controlled collective movement of all ABP molecules of the chosen windmill at the same time could be observed.

By positioning the tip on the center of the windmill, a rotation of the complete structure can be induced. An example of windmill rotation is shown in Fig. 7. The green dot indicates the position of the tip during the voltage pulse and the white lines indicate the position of the windmill structure before the manipulation.

Rotational movements are mainly observed at positive voltage pulses (in more than 40% of the cases in contrast to less than 5% at negative voltages) with rotational angles of 15° (33%) or 30° (66%) in the clockwise or anticlockwise direction.



Fig. 7 > Rotation of a windmill nanostructure. Top panel: STM image of a windmill before manipulation. The green spot indicates the position of the tip during the application of a voltage pulse of 2.3 V. Bottom panel: STM image of the same windmill after the manipulation. The white lines indicate the position of the windmill before manipulation./

Considering that the windmill nanostructures are chiral, it is interesting to investigate if there is a rotational preference connected to the chirality of the windmill. However, out of the 200 measured rotational events, no significant preference for one or the other rotation direction was observed. If there is a preferential rotation direction due to the chirality of the molecules, as suggested by a recent work on a single chiral molecular rotor [30], it will be rather small. From our measurements, we can give an upper limit for rotation directionality of about 5%. This confirms that molecule-surface chirality is only necessarv condition for а unidirectional rotation of an adsorbate.



Fig. 8 > Translation of a windmill after the application of several voltage pulses on a lateral group. Top panel: STM image of a windmill before manipulation. The green spot indicates the position of the tip during the application of the first voltage pulse of 2.3 V. Bottom panel: STM image of the same windmill after the manipulation. The white lines indicate the position of the windmill before manipulation./

By applying the same kind of voltage pulses outside the center of the windmill. translational motions are induced. An example of such manipulation is shown in Fig. 8. In such case, a series of four voltage pulses was applied, the first of them at the position of the green dot in the figure. The white lines indicate the position of the windmill structure before the manipulation and help to visualize the movement of the windmill. A single voltage pulse induces Å, typically a lateral jump of 3 corresponding to the surface lattice constant of the Au (111) surface. To move the windmill over larger paths, series of voltage pulses are applied consecutively along a predetermined line on the surface.



Importantly, by selecting the molecule to which the voltage pulse is applied, the direction of the manipulation can be chosen. The windmill can be therefore moved in four different directions (up, down, right, left) depending on the position of the tip on the nanostructure during the voltage pulse. In the example of Fig. 8, the windmill moves down because the voltage pulse was applied on the lowest molecule. By selecting the sign of the voltage pulse. it is possible to switch between attractive or repulsive movements. A negative voltage causes a movement of the structure towards the tip, while a positive voltage pulse induces the jump of the windmill away from the tip position.

More in detail, by changing the sign of the applied voltage, different types of motions can be selected. For negative voltages the windmill moves in the direction away from the position of the tip. For positive voltages, two possible movement types could be observed. Most frequently, translational movements are induced. In this case, the direction of the translation is opposite to that for negative voltages; that is, the center of the supramolecular structure moves toward the position of the tip. In some other cases, and only when the tip is positioned exactly in the center of the nanostructure, the windmill rotates around its center when positive voltages are applied.

In order to understand the described manipulation events, the tip height traces taken during the time interval of the voltage pulses can be systematically analyzed and the results compared with the dl/dV spectrum recorded over a windmill at the same position where the voltage pulse has been applied for manipulation. It was observed in this way that the energy onset position of the resonances (Fig. 6) corresponds to the measured quantum yield, indicating the presence of an inelastic input channel on the windmill.

The experiment demonstrate that the localized inelastic excitations of one of the ABP molecules building the windmill arte sufficient to translate or to rotate the complete supramolecular windmill without internal nanostructure any apparent structural change. Therefore, once a threshold voltage has been reached, where tunneling in molecular resonances is possible. the supramolecular structure can be moved.

#### Conclusions

presented The experiment here demonstrates a method to controllably move supramolecular structures on a metal surface by STM and can help in understanding the movements of weakly bound molecules on metal surfaces. It provides a novel procedure to manipulate individual nanostructures gently and purely electronically. The structures can be moved to the chosen positions on the surface without the need for complex intramolecular mechanical mechanisms.

STM at low temperature is at present the only experimental method, which allows both precise sub-molecular imaging of a single molecule and the possibility of manipulation and measurement of the electronic properties in clean and controlled conditions. Such properties can be usefully applied to test molecular machines. In this case, the STM tip supplies the driving forces necessary to power the nano-machine, which can be driven electrically, by means of tunnelling electrons electric fields. or or mechanically, by taking advantage of chemical and Van Der Waals forces between tip and molecule.

The manipulation of hydrogen bonded windmill nanostructures presented in this article is an example of a purely electrically driven nanomachine, where the repositioning of the nanostructure can be driven in a very precise and nondestructive way. This work contributes to understand the mechanics of molecular nanostructures and to the development of nanomachines controlled at the atomic scale.

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## nanoresearch

## Coronene: A Single Molecule Atom Counter

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To contact selected peripheral  $\pi$  bonds of a single Coronene molecule, gold adatoms were manipulated one by one on a Au(111) surface with the tip of a scanning tunnelling microscope to form Aun-Coronene complexes. Tunnelling electron spectroscopy and differential conductance mapping show how the electronic ground state of the Aun-Coronene complexes is shifted in energy concomitantly with the number of gold atoms coordinated to the Coronene molecule. By simply following the linear energy downshift of the Aun-Coronene's ground state the number of interacting atoms can be counted demonstrating that а Coronene molecule can function as a single molecule atom counter.

#### Introduction

Molecules are often considered as potential building blocks to be used in the fabrication of future generations of circuits with electronic components miniaturized down to atomic scale. Molecules can be chemically designed to mimic standard electronic circuits by using chemical groups designed to function like the basic elements of a digital electronic circuit [1-6]. It has also been proposed to abandon classical electronic circuit design and to perfom Boolean logic operations by manipulating the electronic quantum states of a single designed molecule custom [7,8].

Recently it has been demonstrated that a trinaphthylene molecule can function as a NOR logic gate [9,10] by using single Au adatoms as classical logical inputs. The molecule converts the inputs classical on/off information in quantum information leading to a controlled shift of trinaphthylene's electronic quantum states which conforms with the output of a NOR logic gate. The rationale of this approach is that it is better to embed higher level functionalities within one single molecule rather than to pursue the chemical synthesis of large molecules having the shape or functions of single electronic circuit components.

Intramolecular guantum behaviours are also rich enough to implement simple analogue functions inside a single molecule without forcing the molecule to have the shape of an analogue electrical circuit. To demonstrate this, we have selected the Coronene molecule and manipulated its ground electronic state by contacting its  $\pi$  electronic system with single Au atoms. A Coronene molecule is able to count one by one the number of Au atoms interacting with its  $\pi$  system. The output reading of this counter is performed by recording the tunnel current intensity passing through very specific positions on the Coronene  $\pi$ system.

In this article, this counting effect is demonstrated experimentally using a low temperature STM, single atom and molecule STM manipulations, differential conductance (dl/dV) constant current imaging and dl/dV spectroscopy. All the images were calculated using the Elastic Scattering Quantum Chemistry technique in the framework of the Extended Hückel Molecular Orbitals approximation (EHMO-ESQC) [12].

#### Model System

To count classically using a quantum system, let us consider a model system with two non degenerate electronic states, |g> being the ground state of the counter and |i> the state corresponding to one input. When |i> and |g> are electronically coupled each state undergoes an energy shift, |g> shifts down and |i> shifts up, with  $\Delta$  being the initial energy difference between those 2 states. For a small coupling  $\alpha$  as compared to  $\Delta$ , |q> still keeps its ground state characteristics and becomes |G> with an energy shift downwards of  $-\alpha^2/\Delta$  likewise |i> becomes ||> with a  $\alpha^2/\Delta$  upward energy shift. When N identical li> states are coupled to la>. the resulting new |G> ground state is shifted by  $(\Delta - \sqrt{(\Delta^2 + 4N\alpha^2)})/2$ . The ground state |G> will be linearly shifted down in energy by  $N\alpha^2/\Delta\alpha$  as a function of N and for  $\alpha << \Delta$ . Therefore, the |G> energy position can be used to count the number of identically coupled li> states. Notice that this counter can saturate when  $2\sqrt{(N)\alpha}$  is not negligible compared to  $\Delta$ . But this limitation depends on how each i> state is spatially coupled to |G> as discussed below.

Τo demonstrate experimentally this counting effect, we have manipulated the ground state (HOMO) of a Coronene molecule by bringing single Au atoms in interaction with Coronene's  $\pi$  system. A Coronene molecule has six peripheral phenyl rings (see Coronene's model in Fig. 1), then there are six equivalent sites accessible for contacting one Au atom. different There are three possible configurations to contact two atoms: they could be bind to two nearest neighbouring phenyl rings like (1,2) or (2,3), interact with non-adjacent phenyl rings like (1,3) or (1.5) or be in diametrical opposite positions like (1,4), here each of the numbers in parenthesis indicates the external Coronene phenyl each single Au atom is contacted to (see Fig. 2). For three Au atoms, there are three fully equivalent interacting configurations possible e.g. (1,3,5). Once a given phenyl is selected for the first Au input, the other atoms must be contacted respecting specific input positions for the Coronene to work as a counter. The output reading position around the Coronene external phenyl crown must also be selected depending on this initial input choice.



Fig. 1 > (Top) Characteristic dI/dV spectra recorded on a Coronene molecule (in black) and on a Au<sub>1</sub>-Coronene complex (in red). The energy shift of Au<sub>1</sub>-Coronene ground state resonance (HOMO) with respect to Coronene's HOMO is clearly observed. (Bottom) Images corresponding to the STM topography, dI/dV map and ESQC calculated conductance map of Coronene and Au<sub>1</sub>-Coronene respectively (image size: 2 nm x 2 nm). The ESQC dI/dV maps were both calculated at the energy corresponding to the HOMO resonances of Coronene and Au<sub>1</sub>-Coronene./

## **Results and Discussion**

A sub-monolayer of Coronene molecules  $(C_{24}H_{12}, Sigma-Aldrich 99.99\% purity)$  was deposited on the surface of a Au(111) mono-crystal using free evaporation. During the evaporation, the substrate temperature was kept below 80°C. After the molecules sublimation the sample was cooled down using liquid helium and transferred to the STM chamber. All STM imaging, manipulation and spectroscopy measurements were done at ~7 K.

Prior to any experiment an oxide free electrochemically etched Tungsten tip is gold coated by indenting it in the Au(111) substrate following the method described by Hla *et al* [13]. Spectra are taken to test whether the tips are in fact metallic and fit for obtaining spectroscopic data. Only tips whose spectra taken on a clean Au terrace showed the resonance corresponding to the surface state of Au(111) were used in our experiments.

Constant current STM images taken after depositing Coronene molecules show that the molecules adsorbed both on Au(111) terraces and at step edges. the characteristic herringbone reconstruction of Au(111) can also be observed. In the topographic STM images. sinale Coronene molecules are imaged like a 6 branched star as presented in Fig.1. Characteristic dl/dV spectra of single Coronene molecules were obtained by positioning the STM tip over a molecule's center and over any of its 6 outer lobes. The main features of dI/dV spectra taken from outer lobes are a resonance peak at -1.4 V and a broad tail at positive bias showing no distinctive resonance. Furthermore dI/dV spectra taken at the molecule center appear featureless. On a constant current dI/dV image recorded at -1.4 V, the central Coronene phenyl ring appears featureless while six external lobes are clearly imaged. ESQC

constant current images calculated at the HOMO resonance match perfectly the experimental images, also shown in Fig. 1. The calculated images enable to identify the 6 lobes observed on the experimental dl/dV images, these lobes correspond to the outer phenyls of Coronene.

To form the Aun-Coronene complexes the Au adatoms and the Coronene molecule were brought together into electronic interaction using STM manipulation in constant current mode. Atom manipulations done to form atommolecule contacts show that manipulated single gold atoms arrange selectively in a conformation in which a gold atom is always underneath an outer phenyl ring. Attempts to obtain single atom contacts at other positions of Coronene's external phenyl rings as well as underneath Coronene's center resulted in unstable conformations and it was not possible to investigate their effect in the Au atom counting process.

The energy shifts of Coronene's ground state as a function of the number N of interacting Au atoms were tracked by systematically recording dl/dV spectra on lobes away from the contacted outer phenyls. After contacting one Au atom to any of Coronene's six outer phenyl rings its dI/dV spectrum presents a shift of the HOMO (ground state) resonance by nearly 200 mV with respect to a bare Coronene's HOMO (see Fig. 1). The ESQC experimental and calculated constant current dl/dV images of a Au1-Coronene complex match perfectly indicating that the interaction of a single Au atom with the Coronene has broken the HOMO symmetry through the local deformation of the Coronene skeleton at interaction location. the Au This deformation was already observed for the interaction of a trinaphthylene molecule with a single Au atom [9,10].



Fig. 2 > Spectra recorded on a Coronene molecule and on each of the Aun-Coronene complexes investigated (n: 1, 2, 3). These spectra show how each additionally contacted gold atom resulting in a Aun-Coronene produces a further spectral shift with respect to Au(n-1)-Coronene. At the top: STM topographic images (2 nm x 2 nm) of each Aun-Coronene complex the spectra were taken from, the exact location each spectrum is taken on the complexes is indicated in the images. The hexagons with numbered circles at the top of each STM image represent Coronene's outer phenyl rings. These diagrams represent each of the input conformations, their corresponding spectrum is indicated each with an arrow. The highlighted circles indicate the phenyl rings the gold atoms were coordinated to./

The calculations enable to identify the origin of the deformation which arises from the two carbon atoms at the end of the phenyl ring directly interacting with the Au atom, due to their interaction the two carbon atoms are pushed up together with their corresponding hydrogen atoms. This deformation breaks the delocalization of Coronene's system explaining how both the π experimental and the calculated images are showing only 4 lobes instead of the 6 lobes imaged for a bare non deformed physisorbed Coronene.

The downshift in energy relative to the native Coronene's HOMO is observed for each subsequent addition of single Au atoms. As presented in Fig. 2, the dl/dV spectra recorded for the different Au<sub>2</sub>-Coronene complexes (1,2), (1.3), (1.4) show its negative resonance peak shifted by 400 mV relative to the HOMO of a bare Coronene. The (1.3.5) Au<sub>3</sub>-Coronene complex shows а resonance peak shifted also by nearly 200 mV as compared to the Au<sub>2</sub>-Coronene complexes HOMO. that is a 600 mV spectral shift from Coronene's HOMO (See Fig. 2).

The electronic structure and molecular orbitals of Au<sub>n</sub>-Coronene have been calculated as a function of N using the MOPAC2009 semi-empirical quantum chemistry code in the framework of the Potential Model-parametrization-6 Self Consistent Field approach (PM6-SCF) [11]. Electronic structure diagrams of the Au<sub>n</sub>-Coronene complexes clearly show the incremental energy shifts of their electronic ground states concomitantly with each additional aold atom contacted.

Molecular orbital calculations done for all Au<sub>n</sub>-Coronene complexes reveal that the Single Occupied Molecular Orbital (SOMO) of a bare Au<sub>1</sub>-Coronene complex is nearly a pure Au 6s atomic orbital. The location of this 6s Au orbital in the Coronene HOMO-LUMO energy gap is responsible for the stabilization of the Coronene HOMO. When Coronene interacts with two Au atoms, the HOMO and LUMO of the Au<sub>2</sub>-Coronene complex are essentially the symmetric and antisymmetric superposition of the two Au 6s orbitals. In this input conformation Coronene's native HOMO is shifted down further in energy as compared to

the Au<sub>1</sub>-Coronene complex and becomes Au<sub>2</sub>-Coronene's HOMO-1. For the Au<sub>3</sub>-Coronene complex, the three Au 6s orbitals give rise to three molecular orbitals HOMO, SOMO, and LUMO. These states are also located within the bare Coronene HOMO-LUMO energy gap and stabilized even more Coronene's native HOMO which is again the HOMO-1 of the Au<sub>3</sub>-Coronene complex. With a good selection of the metal atom inputs and of their location relative to the Coronene  $\pi$  system, the initial HOMO of the Coronene can be pushed down in energy following a linear law as given by the simple model described above.



Fig. 3 > Plots showing the linear spectral downshift of Aun-Coronene's HOMO peak as function of the contacted n gold atoms. The electronic structure of Aun-Coronene complexes in free space calculated using PM6-SCF show the same spectral shifts observed in the experimental spectra. The corresponding  $\Delta E$ shift for each complex is plotted. Both experimentally measured (in blue) and calculated shifts (in red) follow the same spectral behaviour dependency with respect to the number of gold atoms input. /

The recorded dl/dV spectral shifts of selected input conformations for all Au<sub>n</sub>-Coronene complexes showing the counting function of Coronene are plotted in the Fig. 3 and compared with the spectral shifts extracted from electronic structure diagrams calculated

using PM6-SCF. There is an excellent agreement between the experimental and the calculated shifts as a function of the number of Au atoms interacting with a Coronene molecule. This confirms that the presence of an Au 6s orbital in the region of the HOMO-LUMO energy gap stabilizes linearly the Coronene HOMO.

#### Conclusions

Herein we have demonstrated that STM manipulated Au adatoms contacted to selected phenyl rings of a single Coronene molecule result in an energy shift of the ground state of the Au<sub>n</sub>-Coronene complexes. This energy shift is linear as a function of the number of contacted Au atoms and therefore can be used to count the number of atoms input, hence demonstrating that Coronene can function as a single molecule atom counter.

We have also calculated how the counting stands using larger effect а Au<sub>n</sub>circumcoronene series where 6 outer phenvls are available on the circumcoronene external phenyl crown. Indeed the circumcoronene HOMO is downshifted in energy as a function of the number of Au atoms interacting with its  $\pi$ system. Even if the number of interacting Au reaches a maximum of 6, the shift is with apparent linear no saturation because in the HOMO state, the orbital weight of the outer phenyl decreases due to this around state quantum normalization. For even larger circular  $\pi$ conjugated systems corresponding to a nano-graphene like macromolecule disk, the HOMO normalization will stabilize the counting effect since the number of central phenyl rings will increase faster than the number of available phenyls on the last outer crown of the disk. It remains to be determined how fast this effect occurs as a function of the disk diameter to estimate the maximum number of Au atoms a nano-graphene disk can count.

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## Measuring the conductance of single molecular wires as a function of the electron energy

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We have measured the conductance of single graphene nanoribbons as a continuous function of their length, thus determining the current decay along the molecular wire, in combination with theoretical calculations. After onsurface polymerization of the nanoribbons on a Au(111) surface, the tip of a scanning tunneling microscope is used to pull single polymers off the surface at cryogenic temperatures. In this way, individual molecular chains are electrically contacted between two electrodes, the tip and the surface. By systematically changing the bias voltage between the electrodes, the conductance is investigated as а function of the electron energy and the charge transport properties are directly correlated with the electronic structure of the molecular wires, in agreement with theory. In a very particular configuration, the nanoribbons adapt an almost straight shape and experimental evidence for a pseudo-ballistic transport regime is found at the single-molecule level, as predicted by theory.

#### Introduction

Graphene fascinates scientists all over the world because of its unique

electronic and mechanical properties. It consists of sp<sup>2</sup>-hybridized carbon atoms arranged in a honeycomb lattice [1]. Due to the massless propagation of the electrons through the graphene flake they mimic relativistic particles and can be described by the Dirac equation and not by the Schrödinger equation. The electrons lose their mass at the Dirac points and their carrier mobility can be as  $cm^2V^{-1}s^{-1}$ . high as 100,000 Onedimensional graphene stripes, so-called nanoribbons, are therefore of particular interest as molecular wires. Specifically, their electronic structure. and consequently charge transport properties, depends on the precise atomic structure of the graphene nanoribbon [2, 3]. Here we present conductance measurements of a single narrow graphene nanoribbon by pulling it metal surface. Detailed from а understanding charge transport of through a single molecule requires not only such length-dependent conductance measurements, but also a systematic variation of the electrode potentials relative to the molecular electronic states. We show for the first time how the conductance properties of a single molecule are correlated with its states which are spatially electronic mapped via scanning tunnelina spectroscopy before the conductance measurement. The tunnelina decav length is measured over a wide bias voltage range from the localized Tamm states over the gap up to the delocalized occupied and unoccupied electronic states of the nanoribbon. The major part of our results has been published recently. We furthermore show how the conductance depends on the precise

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atomic structure and on the bending of the molecule in the junction, revealing the importance of the edge states and a planar geometry [4]. Finally, we provide experimental evidence for pseudoballistic transport through single molecules, i.e. an ideal transport regime where the current does not decay with the molecular wire length.

Electron transport through a molecule is fundamental in chemical and biological processes [5]. It depends on various parameters: the electronic structure of the molecule, its interaction with the junction electrodes and the energy position of the molecular electronic states with respect to the electrodes. The relation between the molecular electronic structure and the exponential decay of the electron transfer rate with length has been studied experimentally in solution [6]. Charge transport has also been lengths investigated for various of molecular wires when contacting their termini electrodes, either to by comparing different molecules [7-10] or by continuously changing the electrode distance along the molecule [11, 12]. In one study [13] the electrodes bias voltage has been varied, but the electron energy remained always at low voltages in the gap between the ground state (i.e. HOMO) and the first excited states (i.e. LUMO) of the molecular wire, while several thousands of molecules were present in the junction at the same time. However, the conductance of a single molecule can differ significantly compared to the conductance per molecule in an ensemble. Therefore. measurements are necessary at the level of a single and well characterized molecule.

The conductance G of a molecular wire decays exponentially with its length d and can be described by  $G(d) = G_o e^{-\beta d}$ , where  $G_o$  is the contact conductance and

 $\beta$  is the inverse decay length. The inverse decay length depends on the position of the HOMO and LUMO relative to the Fermi level E<sub>F</sub> as well as on their energy difference  $E_q$  and on the effective mass of the electron in the tunnelling junction. A large  $E_q$  leads to high  $\beta$ values and consequently to a low junction conductance, for instance for alkane chains. If the molecule in the junction exhibits electronic states that are located at E<sub>F.</sub> another transport regime is active. In such a case,  $\beta$  becomes very small, for example with the d states of an organo-metallic compound [10] or the  $\pi$ states of a short organic molecular wire [14]. Consequently, a pseudo-ballistic transport regime with still  $G < 2e^2/h$  (i.e. the quantum of conductance) occurs, since the electronic structure of the molecular wire differs from that of the metallic electrodes.

We investigate graphene nanoribbons (GNRs) as their electronic structure can be controlled via their width [2] and edge structure (zig-zag or armchair) [3]. In contrast to top-down fabrication of GNRs, which lack control over the ribbon width and/or edge structure at the atomic scale. bottom-up on-surface polymerization [15. 16] produces precisely defined molecular structures. A chemical well-defined structure is reauired for charge transport measurements as structural defects modify the electronic structure and reduce the conductance [17].

## **Experimental details**

To produce GNRs with an armchair edge structure we have used 10,10'-Dibromo-9,9'-bianthryl molecules (Fig.1a). For the fabrication two heating steps are required: On-surface polymerization takes place at 200°C, where non-planar anthracene oligomers are formed (Fig.1b) and cyclodehydrogenation at 400°C (Fig.1c).



Fig. 1 > Chemical structure of the 10,10'-Dibromo-9,9'-bianthryl molecules (a) which are connected to oligomers (b) after the first heating step and to graphene nanoribbons (c) after the second heating step. STM images ( $3 \times 7 \text{ nm}^2$ ) of a single graphene nanoribbon at different bias voltages: -1.55 V (d), +0.05 V (e). STM image ( $3 \times 7 \text{ nm}^2$ ) (f) and corresponding dl/dV curves (g) taken at different positions (1–10) along a single nanoribbon, revealing the presence of a peak at the ribbon termini that decays within 10–15 Å along the ribbon./

Experiments were carried out under ultrahigh vacuum conditions with a base pressure of 10<sup>-10</sup> mbar. Before depositing the molecules the Au(111) sample was cleaned by Ne ion sputtering (E = 1.5 keV) and subsequent annealing to 750 K. A Knudsen cell with a temperature of about 470 K was used to evaporate the 10,10'-Dibromo-9,9'-bianthryl (DBDA) molecules, controlling the temperature by а thermocouple. The sample was typically at 470 K during deposition (deposition at room temperature results in sinale molecules), Br dissociates and anthracene oligomers are produced, according to the on-surface polymerization process by dehalogenation [15]. Annealing the Au(111) sample further for 5 min to 670 K initiates cyclodehydrogenation [18] and fully aromatic graphene nanoribbons are

created. A modified low temperature STM from Createc was used and all measurements were taken at about 10 K.

#### **Results and Discussion**

The graphene nanoribbons appear as straight stripes with an apparent height of  $1.85 \pm 0.12$  Å (Fig.1d). Their contour is rather homogeneous with characteristic finger-like lobes at both termini (Fig.1e), independent of the ribbon length, if small bias voltages are used. These features are typical for the intact molecule when the Br atoms have already

been dissociated. To study the electronic origin of the bias-dependent appearance, dI/dV spectra, which are known to reflect electronic transparency of the the junction[19], were recorded as a function of the voltage. At the termini a peak at about 30 meV above the Fermi level is resolved, which completely vanishes at the centre of the ribbon (Fig.1f-g). The main difference of these two areas is the structure of the ribbon edge, which is zigat the termini and armchair zad sideways. We assign this feature to the theoretically predicted Tamm states [20], which originate from the specific arrangement of the carbon atoms at zigzag edges and are absent at armchair edges.

To measure the conductance of a single GNR, it was lifted off the surface by pulling controlled STM [12] after attaching one end of the ribbon to the tip. Before and after a pulling experiment the GNR is characterized by imaging and spectroscopy. While the tip is retracted, the effective transport length through the ribbon (indicated by an arrow in Fig.2a) is modified, because the current is only passing through the part of the GNR that does not interact with the surface. If the molecule is successfully lifted from the surface, the slope of the measured STM



Fig. 2 > a) Schematic of the STM pulling experiment (arrow indicates tunneling current). A characteristic current signal during the pulling sequence is shown in the right panel. b) Current as a function of tip height for different experiments (zero tip height refers to tip-surface contact). Different ribbon lengths were used in the experiments, resulting in equivalent conductance properties./

current signal I(z) (i.e. higher conductance) is smaller than for the vacuum junction. From the linear curve in the logarithmic plot (and thus exponential decay), we find that electron transport occurs in the tunnelling regime and obtain a  $\beta$  value of  $0.45 \pm 0.06$  Å<sup>-1</sup> for a low bias voltage of around 0.4 V (Fig.2b). In comparison, a steeper curve and thus larger  $\beta$  value of  $0.76 \pm 0.04$  Å<sup>-1</sup> is found for the anthracene oligomer (Fig.2b: taken at 50 mV bias voltage), i.e. the same molecules before planarization (Fig.1b), due to their lower electron delocalization and larger Eq value. The electrode electron energies are shifted with respect to the GNR depending on the applied bias voltage. At a bias voltage of -1.4 V and +1.8 V the slope

(Fig.2b) decreases and hence the conductance rises. The decay of the current for both polarities is in the same range which points to a similar charge transport mechanism. Moreover, all pulling curves in Fig.2b are very smooth, in contrast to the local bending of a chainlike polyfluorene that causes characteristic oscillations in the current curve [12]. These constant slopes are an evidence for a continuous bending of the ribbon in the junction, this is confirmed by calculations.

The change in conductance is related to the electronic states of the GNR. Therefore, we measured dl/dV spectra of a single ribbon (Fig.3a), similar to Fig.1g but for a larger voltage range. We find two intense peaks at -1.1 V and +1.6 V, which

are assigned to the ground and to the first excited state (approximately HOMO and LUMO) of the molecule, indicating  $E_{\alpha} = 2.7$  eV. In order to correlate the electronic states to the charge transport mechanisms conductance measurements were done for bias voltages between -1.8 V and +2.4 V, hence covering all relevant electronic states (HOMO. LUMO and Tamm states). Independent of the bias voltage the current decays exponentially with respect to the tip height (as in Fig.2b). This provides evidence that tunnelling is always the charge transport and allows us to extract the inverse decay length  $\beta$  as a function of the bias voltage (Fig.3a). Three different regimes can be distinguished: At low bias voltages (up to



about 1.6 V),  $\beta$  values around 0.45  $\pm$ 0.06 Å<sup>-1</sup> are found. According to our calculations, efficient charge transport takes only place in this regime if the Tamm states at opposite ends overlap and thus contribute to the current (Fig.4a). This is only the case for short ribbons with a length of around 2-3 nm. In contrast to the armchair edge structure here, a zig-zag edge strongly improves the conductance, because the Tamm states cause electron delocalization along the ribbon and thus no current decay is observed with the distance (Fig.4a).

The conductance improves if the electron energy coincides with the position of the molecular electronic resonances in the dl/dV spectrum (at -1.1 eV and +1.6 eV, respectively), resulting in lower  $\beta$  values of 0.18 ± 0.03 Å<sup>-1</sup> (at 1.8 V to 2.4 V) and a continuous reduction down to about



0.1 Å<sup>-1</sup> at negative bias voltages. This is in gualitative agreement with calculations (Fig.3b) as the decrease in the  $\beta$  value matches with the onset of the HOMO LUMO molecular and orbitals. Experimental dI/dV conductance maps show that the HOMO as well as the LUMO are delocalized along the ribbon edges (Fig.4c and d). In a tunnelling transport regime, the inverse decay length depends on the electron energy, the molecular energy levels (E<sub>h</sub> and E<sub>l</sub> are the positions of HOMO and LUMO, respectively) and the effective mass m\* of the electrons [21]

$$\beta(E) = \sqrt{\frac{2m^{*}(E)}{\hbar^{2}} \frac{(E - E_{h})(E_{l} - E)}{E_{g}}}$$
(1)

 $\beta$  is therefore expected to decrease as soon as the electron energy matches a molecular energy level.

Fig. 3 > Conductance dI/dV spectra (top, a and b; all in a pulling geometry) of a graphene nanoribbon and its inverse decay length b (bottom, a and b) for different bias voltages from various nanoribbons used in the experiment (a) and ESQC calculations (b). a) Top: dI/dV spectrum for a nanoribbon in a pulling geometry. Bottom: Error bars reflect the precision in b determination in each individual I(z) curve (at a constant bias voltage and contributing as one data point); a dashed line is drawn to guide the eye. The experimental  $\beta$  values, determined from many nanoribbons, need to be reduced (by 10-15%) to obtain the real values, because the STM tip height is slightly smaller than the effective molecular length in the junction. b) Top: The calculated dI/dV curve (in a pulling geometry) shows the Tamm states resonance doublet, split due to the nanoribbon curvature during pulling. Bottom: The ideal planar b curve (red) is presented for comparison with the curve in an STM pulling geometry (black)./

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It is important to note that ideal (pseudoballistic) electron transport at high bias voltages, where the current does not decay with the length of the molecular wire (i.e.  $\beta = 0 \text{ Å}^{-1}$ ), takes only place for a planar ribbon (red curve in Fig.3b). However, values of around 0.1 Å<sup>-1</sup> are calculated for a pulling configuration (black curve), in agreement with the experimental values between 0.1 and 0.2 Å<sup>-1</sup> at high bias voltages (Fig.3a). Our calculations show that this is due to the non-planar configuration of the ribbon during the pulling process because such a deformation perturbs the electronic delocalization along the molecule (Fig.3b). On the other hand, we also find evidence for this particular charge transport regime in our experiments if the tip-nanoribbon contact holds

up to very large pulling heights. In such a particular case, the curvature of the nanoribbon must be reduced for geometrical reasons and therefore а more planar configuration achieved. is Although the exact ribbon geometry cannot be determined from the STM experiments, a comparison of the nanoribbon length on the surface and the pulling height of the STM tip gives some insight: The ideal straight nanoribbon configuration should be reached if these two values are equal (not taking into account the small error in the determination of

the tip height, while the nanoribbon length can be measured very precisely from the STM images before pulling). In agreement with these considerations, we indeed observe a reduction of  $\beta$  for very large tip heights that approach the values of the nanoribbon length. This is shown in Fig.4b for two nanoribbons of different lengths where the  $\beta$  value is strongly reduced. The 48 Å nanoribbon has been pulled up twice, revealing the same result in both cases. This reproducibility of the reduction of  $\beta$  for very large tip heights supports our interpretation. The two curves do not only become flat (i.e. no current decay), but also slightly increase at the end. This behaviour is expected as the  $\beta$  value of approximately 0 Å<sup>-1</sup> for a planar nanoribbons leads, in combination with the considerable contact conductance values Go (towards the tip and towards the surface), to a current value that exceeds the one for a curved ribbon at these large tip heights. Accordingly, the current curve can even increase in such a configuration as observed in Fig.4b.



Fig. 4 > Calculated pulling curves for low bias voltages of a GNR with arm chair (Case I) and zig-zag edges (Case II). b) Three pulling curves of two different graphene nanoribbons. The length of the nanoribbons is 98 Å and 48 Å. In both cases a bias voltage of +1.8 V is applied. c,d) Experimental dI/dV conductance maps (all 5×5 nm<sup>2</sup> in size) of a defect free nanoribbon terminus at different bias voltages: (c) -1.15 V (HOMO level) and (d) +1.6 V (LUMO level)./

#### Conclusions

Our results reveal the importance of having control over the precise chemical structure of a molecular wire. Depending on the edge structure, pseudo-ballistic transport is predicted for zig-zag edges at low electron energy while tunnelling transport is dominant - and experimentally characterized - for GNRs with armchair edges sideways. In the latter case, even pseudo-ballistic transport is present at a bias energy that coincides with the molecular resonances if the nanoribbon is in a planar geometry. On the other hand, a non-planar configuration of the ribbon in the junction leads to a perturbation of the electronic delocalization along the molecule and, therefore. tunnelling transport with a small inverse decay length as charge transport mechanism.

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## Synthesis of Y-Shaped Polyarenes, Crushed Fullerenes and Nanographene Fragments

P. Calleja, R. Dorel, P. McGonigal, P. de Mendoza, and A. M. Echavarren\*

Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona (Spain) at strategic positions can also be carried out by a triple Au(I)-catalyzed hydroarylation [6] of substrates **3a-b** to give 3,9,15-triaryldiacenaphtho[1,2-j:1',2'-I]fluoranthenes **4a-b** (Scheme 1) [7].

#### aechavarren@iciq.es

As part of a program on the synthesis of large polyarenes for their application in molecular electronics [1]. our group is developina new strategies for the rational synthesis of Yshaped polyarenes and well-defined molecularsections sized of graphite single layers (nanographenes).

One of the objectives of our work in last few years has been the development of methods based on Pd-chemistry for the synthesis of polyarenes [2], and the study of mechanistic aspects of the Pd-catalyzed arylation [3]. Thus, as part of a program on the synthesis of bowl-shaped polyarenes [4], we have reported the synthesis of fullerene C<sub>60</sub> and triazafullerene bv cyclodehydrogenation of the corresponding planar 1 precursors ("crushed fullerene") and 2 ("crushed triazafullerene"), respectively (Figure 1) [5].



The synthesis of other related planar polyarenes with OMe and X substituents



Recently, we have prepared Y-shaped acenes such as 6 and 8 for molecular electronic applications (Scheme 2) [1]. Trinaphthylene (6) was prepared by the trimerization reaction of orthosilvlarvltriflate 5 in the presence of a palladium(0) catalyst [8]. On the other hand, decastarphene-(3.3.3) (8) was obtained bv а based-catalvzed trimerization of 1,4-anthraguinone (7), followed by reduction under forcing conditions [9].



Scheme 2

33



Similar strategies are currently being examined in our group for the synthesis of other Y-shaped molecules such as 12 from dimethyl pentaphene-6,7dicarboxylate (9) (Scheme 3). Thus, naphtho[2,3-*b*]trinaphthylene (12) was prepared by a Diels-Alder reaction of 10 with 1,4-anthraquinone (7) to form 11, followed by reduction.

We also studying strategies for the synthesis of linear acenes **14** (such as tetracene, pentacene, hexacene) by cyclization of the appropriate precursors **13** using a gold(I)-catalyzed [4+2]

cycloaddition of 1,7-enynes as a kew step, a powerful synthetic method developed in our group (Scheme 4) [10]. We also pursue the synthesis of larger polyarenes such as planar C54 derivative **15** by Legotype approaches.

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