

From Nanofabrication to Self-fabrication – Tailored Chemistry for Control of Single Molecule Electronic Devices

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Abstract: Single molecule electronics is a field of research focused on the use of single molecules as electronics components. During the past 15 years the field has concentrated on development of test beds for measurements on single molecules. Bottom-up approaches to single molecule devices are emerging as alternatives to the dominant top-down nanofabrication techniques. One example is solution-based self-assembly of a molecule enclosed by two gold nanorod electrodes. This article will discuss recent attempts to control the self-assembly process by the use of supramolecular chemistry and how to tailor the electronic properties of a single molecule by chemical design.

Keywords: Electron transport · Molecular electronics · Nanoparticles · Nanorods · Self-assembly



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for the development of new, smaller electronic components – but also for the general understanding of electron transfer in molecular systems such as the photosynthetic reaction center (PSI),^[1] and hetero junctions in organic photovoltaic devices.^[2]

Through the past 15 years of research, it has become evident that an intriguing interplay between the molecule and the electrodes is responsible for the overall properties of a molecular electronic device. In particular the interface between molecule and electrode is important,^[3–5] and it has been shown that the position of a single chemical bond and even the conformation of a single chemical bond^[6–8] can change the electronic properties of a device dramatically.^[9,10]

The key challenge facing researchers today is how to place a single molecule in a controlled fashion between source and drain electrodes. Most research has been focused on the development of test beds with a single molecule in each experimental realization. Typically the methods rely on top-down approaches where macroscopic electrodes are fabricated so that a tiny gap between two electrodes can host a single or a few molecules that are to be studied.^[11,12] Most commonly used are mechanical break junctions^[13] and scanning probe microscopy setups.^[14] An alternative top-down approach is the electromigration method where a thin wire is carefully broken by an electrical current to form a nanosized gap between the two broken parts of the wire.^[15]

All together, these methods have provided new fundamental insight about electron transport at the nanoscale. When considering application aspects – these methods all have one thing in common, the preparation techniques and low functional device yield allow only for one sin-

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Introduction

Electron transport on the nanometer length scale is of general interest – not only

gle molecule to be studied in each experimental realization, prohibitively lowering throughput.

In contrast, modern semiconductor-based microprocessors host billions of active components, all operating at the same time. In order to transform the field of molecular electronics from a playground for the fundamental study of electron transfer processes towards real functional devices, a new paradigm is needed for high throughput fabrication of multiple single molecular devices. Ideally this process should fabricate identical devices in a parallel way.^[12,16]

Self-fabrication is one candidate for a new paradigm.^[17] This paradigm proposes that the chemical design of molecular components should allow for the fabrication of multiple identical devices by self-assembly.

This article will focus on recent attempts to control the properties and assembly of the interface between molecule and electrode by chemical design of the molecular components (Fig. 1 summarizes some of the important parameters). Also, we will present new efforts to synthesize molecular components with the electrodes incorporated and thus use hierarchical self-assembly to bridge the gap between the molecular length scale and the length scale readily accessible by top-down lithographic techniques.

Chemical Control of the Interface Geometry

In a typical experiment, the setup consists of a single molecule between two microscopic electrodes. Two important aspects are: how to fabricate nanogaps comparable to the length of a small molecule (1–2 nm) and how to control the local geometry of the electrodes so that a single molecule can be placed between the two electrodes in a well defined way. Due to the nanometer size of a single molecule it has so far been impractical to place the molecule between the electrodes by mechanical means. Therefore chemical anchoring groups often dubbed ‘alligator clips’ have been used to provide a contact *via* a stable chemical bond.^[18]

Typically electrodes have been prepared from gold, and several functional groups have been tested as chemical anchoring groups, including amines, selenols, thiols and others.^[18–23] Of those, thiols have been the most widely used due to the strong electronic coupling and facile formation of self-assembled monolayers on gold. Due to the reactivity of free thiols, a number of protection group schemes have been applied to mask the thiol and thus allow for the synthesis of a broad range of building blocks for molecular electronic devices.^[24–28]

Even though thiols do bind to gold surfaces with a binding energy of approxi-

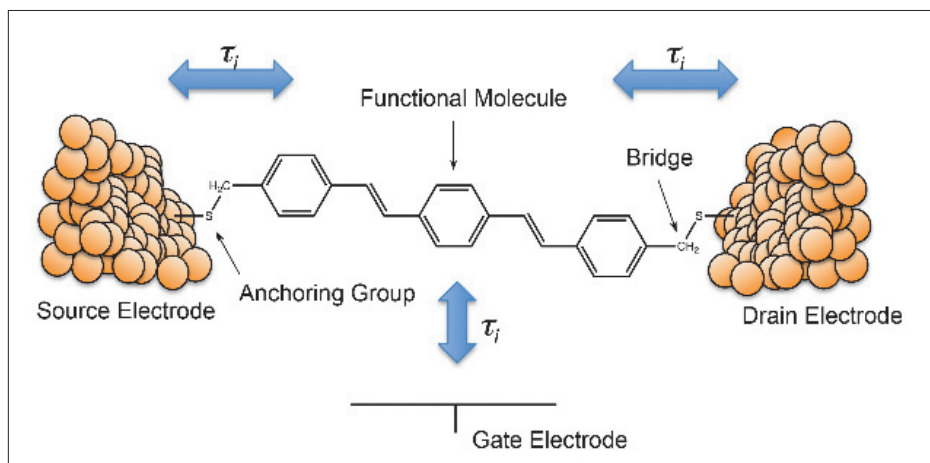


Fig. 1. Illustration of a typical three terminal molecular electronic device. Important design parameters governing the electronic coupling (τ) between different parts of the device are: the anchoring chemical group, the bridging atoms, and the functional part of the molecule with low lying energy levels enabling electron transport.

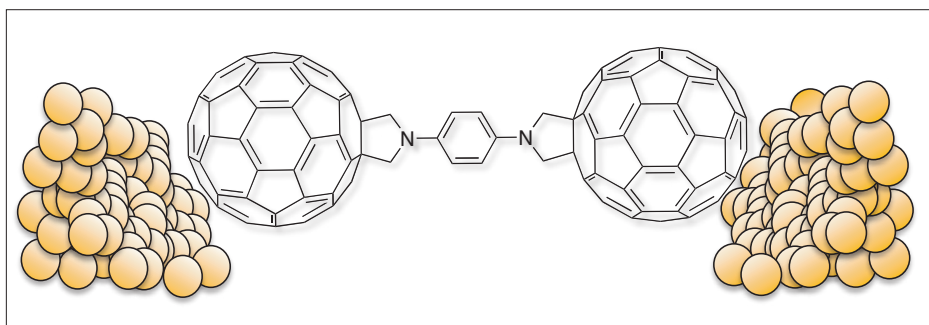


Fig. 2. An example of chemical control of the contact region between molecule and two gold electrodes by the use of fullerene. A schematic representation of 1,4-bis(fullerene)pyrrolidine-1-yl benzene between two gold electrodes.^[34]

mately 40 kcal/mol,^[29] the use of thiols on gold also poses some intrinsic drawbacks. Due to the chemical structure and reactivity of gold surfaces, the position of the thiol on the gold surface might be bonded to different geometrical sites. Though energetically almost identical, the consequence for electronic transport through a molecule placed in these different positions is significant. Recent computational studies of alkane thiols^[30] predict that a difference of a factor of 2.3 from lowest to highest conduction states is achieved by moving a single molecule between two different binding sites on gold – in good correspondence with the variations observed experimentally.^[5,31]

Ideally, the chemical connection between molecule and electrode should be stable at ambient temperature, and the electronic properties should not depend much on the detailed atomic geometry of the electrode surface.

Surprisingly, fullerene (C60) appears to satisfy these requirements. Fullerene binds to metal surfaces^[32] and electronic measurements on the single fullerene molecule shows that under the right conditions there is a strong electronic cou-

pling between the energy levels of fullerene and the energy levels of the metal electrode.^[32,33] In contrast to the single bond binding between thiol and gold – the contact between gold and C60 is most likely shared between several chemical interactions due to the large size of C60. These findings might render C60 a more ideal ‘alligator clip’ since it should be less influenced by small changes in the contact region as opposed to the thiol bond described above.

Inspired by these findings, molecular electronics components based on derivatives of C60 have been synthesized (Fig. 2).^[34,35] Initial measurements using the break junction technique found that one of the dominant features of the molecule was extremely high stability of the single molecule junctions – even at room temperature.^[34]

Effect of the Nature of the Chemical Bridge

The nature of the electron transport through single molecule devices depends strongly on the electronic coupling be-

tween molecule and the electrodes. If the coupling is weak, the electron transport is a stepwise process where an electron is first transferred from the source electrode to the molecule and then in a second step transferred from the molecule to the drain electrode. This process is called Coulomb blockade since the Coulomb charging of the electron only allows for one additional electron on the molecule.^[4]

If the coupling is strong, the electrons can tunnel through the molecule in a coherent manner. This type of transport is called coherent transport and the currents observed are typically several orders of magnitude higher than for Coulomb blockade type transport.^[3,4,9]

Interesting from a chemical point of view is that the coupling between molecule and electrode can be controlled by chemical design.

A weakly coupled system can be a system where the molecule is physisorbed and the low lying energy levels of the molecule are prevented from interacting with the electrodes. If the molecule is a π -conjugated system this hindered interaction can be achieved by the use of bulky aliphatic protection groups^[36] or by the use of methylene spacers as intramolecular tunneling barriers (Fig. 3).^[2]

Strong coupling between molecule and electrodes requires overlap between molecular orbitals and the electronic levels of the metal. This can be achieved through chemisorption *via* direct chemical bonds.

Fig. 3 demonstrates the difference in conductance by applying this concept. Fig. 3 left shows the so-called stability diagram of the electron transport through a weakly coupled single molecule. A stability diagram is a representation of the electron transport through a device with variations in source, drain and gate electrode potentials. The x-axis represents the potential of the gate electrode, whereas the y-axis represents the source–drain bias. Areas marked red and yellow are highly conductive whereas in the black areas, no current flows demonstrating the ‘Coulomb Blockade’. In contrast, the strongly coupled molecule (Fig. 3 right) the current flows more freely through the molecule with little or no dependence of the gate potential. Remarkably, the difference in open state conductance between the two molecules are 3–4 orders of magnitude.^[9]

Chemical Fabrication of Electrodes

As a complement to common top–down photolithographic techniques that do not control features on the atomic level, chemical self-assembly is emerging as a powerful tool for the controlled fabrication on the nanoscale.^[37] In particular in the field of molecular electronics, where lithographic tech-

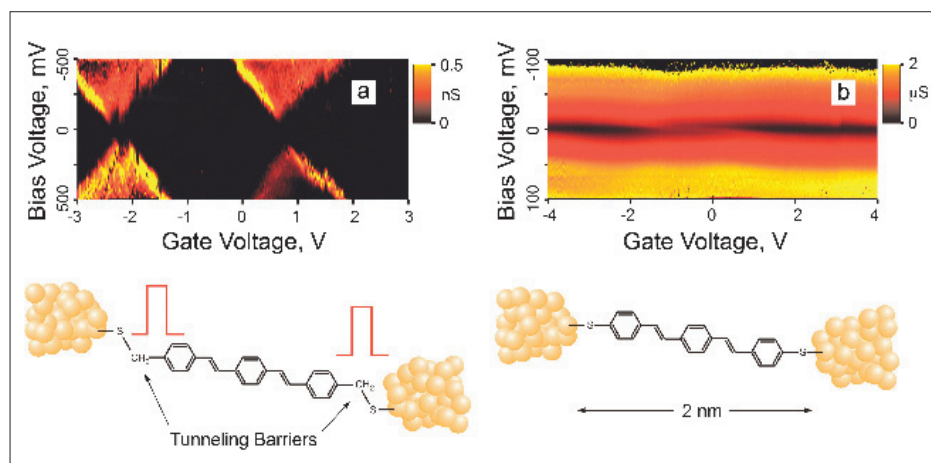


Fig. 3. Tailoring the transport properties by insertion of a methylene spacer as a ‘chemical bridge’. a) Electronic properties of an OPV molecule with methylene spacers resulting in a two step Coulomb Blockade type electron transport. b) Electronic properties of an OPV molecule strongly coupled to gold electrode resulting in a one step coherent electron transport. Reprinted with permission from ref. [9], copyright American Chemical Society.

niques do not provide sufficient resolution for the construction of nanoscale structures small enough to contact single molecules, self-assembly is a method that allows for the parallel assembly of equivalent supramolecular species. Particularly important for single molecule electronics is the formation of nanogaps between two or three electrodes,^[11] and the chemical fabrication of nanogaps has recently been dubbed an important future challenge for nanochemistry.^[38] In this section we will present methods for the chemical self-assembly of nanogaps from gold nanostructures.

Gold nanoparticles are interesting building block for nanoscale structures due to their chemical stability and their facile preparation.^[39] Examples of nanoscale assemblies of gold nanoparticles are numerous and have been reviewed elsewhere.^[40] Following are examples of the use of gold nanoparticles as building blocks for molecular electronics.

In an effort to construct gold nanowires by self-assembly – gold nanoparticles were spread on a water surface in a Langmuir-Blodgett trough. When co-spread with a suitable surfactant, such as DPPC^[41] or ambipolar polymers^[42] the gold nanoparticles are organized into wires or maze structures (Fig. 4). By tuning the chemical nature of the self-assembled monolayer, the 2D assembly directed by lipid films allows for precise control of the gap size between gold nanoparticle segments. The size of the assembled nanogaps could be controlled by adjusting the length of the stabilizing alkyl thiol monolayer.^[43]

The detailed structural and electronic properties of the nanogaps was probed by transferring the wires to a solid support. By subjecting the assembled wire structures to solutions of oligo(phenylene-vinylene)s (OPVs) of different lengths, the method

allows for electronic characterization, and therefore an estimate of the single molecule conductance.^[43] The conductivity of the self-assembled material depended on the length of the bridging OPV molecules and whether the molecule was able to fully bridge the gap between two nanoparticle segments.^[43] By reaction with OPV3 molecules that were long enough to bridge the gap between gold nanoparticle segments the conductance was enhanced from 0.05 S/m to 18 S/m – more than 2 orders of magnitude.^[43]

By employing gold nanoparticle assemblies, van der Molen *et al.* and Ikeda *et al.* were able to demonstrate optical induced switching.^[44,45] In their systems they used gold nanoparticles bridged by a π -conjugated and thiol end-capped diarylethene molecule as the active component. The diarylethene molecule switches from a cross-conjugated state to a fully conjugated state when exposed to 270–370 nm photons. The back reaction was reversibly induced by photons in the visible 570 nm range – the difference in conductivity between the two states was about five times, thus demonstrating the importance of the molecular conformation on the electron transport in such structures.^[44,45]

The DNA molecule, ubiquitous in nature, has been used for a large variety of self-assembled systems. The high selectivity, facile synthesis and programmability render DNA unequalled for programmed self-assembly applications. The use of molecular origami^[46] and self-assembled boxes^[47] are some recent impressive examples of DNA programmed self-assembly.

DNA has been used for programmed assembly of gold nanoparticle structures.^[48] By meticulous control of the synthesis, gold nanoparticles were first functionalized with DNA strands, then assembled on function-

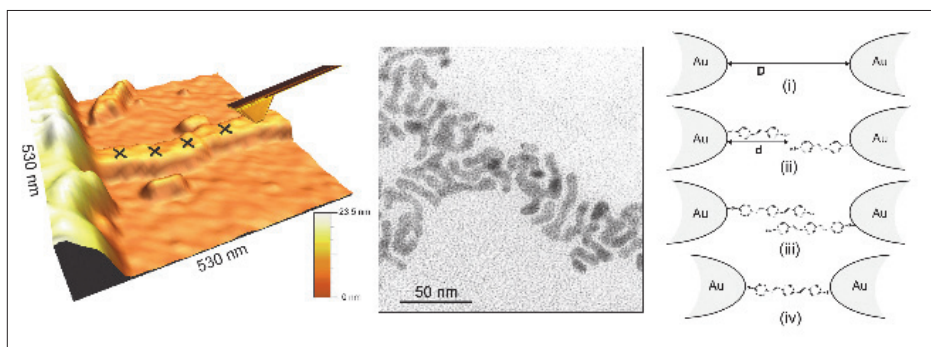


Fig. 4. Left: 3D representation of an AFM image of the device consisting of a microscopic gold wire (left side of picture) and a self assembled nanowire of gold nanoparticles (marked with crosses). A conductive AFM probe was used to measure the conductivity. Middle: TEM micrograph of a nanowire consisting of fused gold nanoparticles. The nanowires are on average separated by 1.7 or 3.0 nm nanogaps controlled by the length of the stabilizing alkyl thiols. Right: Schematic description of the molecules in the nanogaps. The conductivity of the different materials was measured to be i) less than 0.05 S/m, ii) 0.4 S/m iii) 1.5 S/m and iv) 18 S/m. Reprinted with permission from ref. [43], copyright 2004 American Chemical Society.

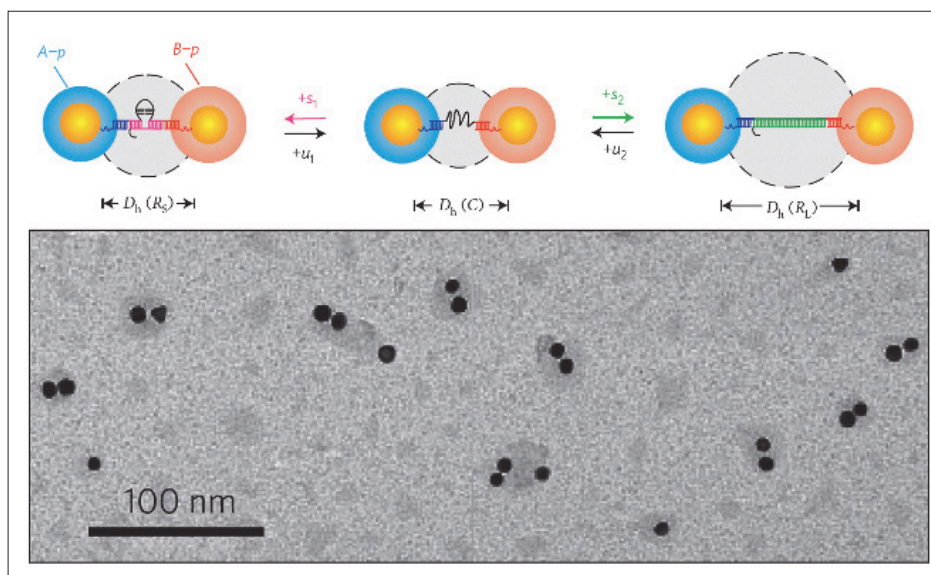


Fig. 5. Pair-wise assembly of DNA functionalized gold nanoparticles with the reversible control of the nanoparticle to nanoparticle distance by a self-assembled DNA loop. Reprinted with permission from ref. [50].

alized surfaces and finally released to react with a complimentary set of functionalized nanoparticles.^[49] The nanoparticle to nanoparticle distance could be controlled the length of the linking DNA strands and further modified by incorporating a loop in the DNA bridge that allowed for reversible particle to particle distance switching by the addition of a complimentary DNA strand (marked in green, Fig. 5).^[50]

The concept of assembling two gold nanoparticles around a single molecule and using the formed nanoparticle–molecule–nanoparticle entity as a building block for single molecule devices has been exploited by Dadosh *et al.*^[51] First, gold nanoparticle pairs bridged by a single conjugated molecule were assembled. Second, the pairs were trapped by electrostatic interactions between two lithographically prepared electrodes thus allowing for electronic charac-

terization of the molecule. One interesting feature of this approach is the use of chemical self-assembly to bridge the gap between the molecular length scale and the length scale accessible by top–down lithographic techniques.

In an attempt to explore this concept further, Jain and co-workers developed a method to grow gold nanorods around a single molecule.^[52] First gold nanoparticle seeds were assembled pair-wise by reaction with a thiol end-capped polyethylene glycol polymer (MW \approx 3500), thereafter the seeds were exposed to an aqueous growth solution containing gold(III)chloride, a surfactant, and a mild reduction agent. Under these conditions, the paired gold nanoparticle seeds grew to form up to 500 nm long crystalline gold nanorods. Fig. 6 right depicts a TEM micrograph of the nanogap with clearly visible crystal planes. The TEM pic-

ture is overlaid by an artist's impression of a molecule in the nanogap.

In another study, gold nanorods were used to contact a single molecule by hierarchical self-assembly.^[53] First gold nanorods were self-assembled to gold nanoparticle-coated tin oxide nanowires. Second, the electronic properties of the OPV molecule were probed by conducting atomic force microscopy (C-AFM). The conductive AFM tip was placed directly on the gold nanorod as one electrode, while the much larger tin oxide nanowire acted as the second electrode. I-V characteristics revealed signatures similar to those previously obtained for OPV molecules, thus confirming that gold nanorods may be promising candidates for bridging the gap between the molecular and micrometer length scale (Fig. 7).^[53]

Conclusion

Single molecule electronics is a fundamental research field that studies the electron transport of the single molecule. One of the present challenges of the field is the control of the interface between molecule and electrode with atomic precision. New attempts to control the structure of the interface by functionalized C60 molecules are emerging. Both molecular bond structure and conformation is important for single molecule devices and chemical design and synthesis of new molecular species are therefore important for the future development of molecular devices with well-defined geometries.

For the field to mature towards applications and integrated devices, a new paradigm for the parallel construction of multiple single molecule devices is necessary. Self-fabrication based on supramolecular chemistry is the chemical approach to do just that. The examples described above for self-assembly of molecules attached to gold nanorod electrodes and methods for positioning of gold nanoparticles by DNA and self-assembly of nanogaps might be considered as increments in that direction.

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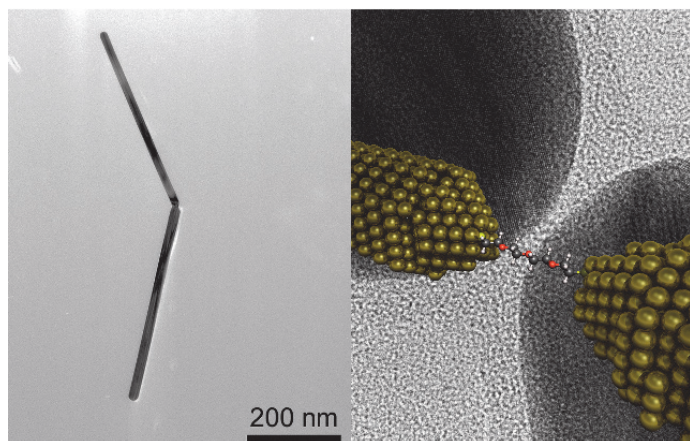


Fig. 6. Gold nanorod dimers. Left: TEM micrograph of gold nanorod dimers grown from linked gold nanoparticle seeds. Right: high resolution TEM micrograph of the nanogap between two gold nanorods revealing the crystalline nature of the gold nanorods. The picture is overlaid by an artist's impression of a molecule in the nanogap between two gold rods. Reprinted with permission from ref. [52], copyright American Chemical Society.

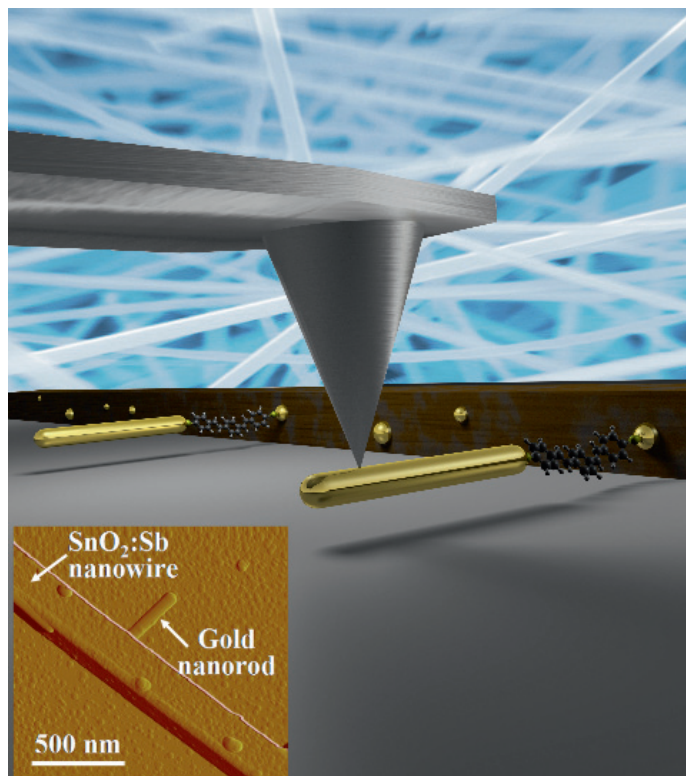


Fig. 7. Hierarchical self-assembly of molecular electronic devices. Left: an artist's impression of the experimental setup consisting of a molecule contacted between a gold nanorod and a $\text{SnO}_2\text{:Sb}$ nanowire, the conductive properties were probed by a conducting AFM tip. Insert an AFM picture of the self assembled device.^[53]

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