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Exploring charge transport properties and functionality of molecule-nanoparticle ensembles

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Summary

For more than 65 years, scientists have been fascinated by the idea to miniaturize electrical circuits toward the smallest length scales. One particular way is inspired by nature itself, specifically to assemble electrical components and switches from atoms and molecules. After all, it is through such building blocks that life itself is possible. In particular the functionality of our brain is based on organic molecules. The scientific research area that represents the study of electrical currents through molecules is called "molecular charge transport" or "molecular electronics". This research field is strongly stimulated by the developments in organic chemistry to design and synthesize molecules that contain different functionalities. For instance there are relatively well-conducting (conjugated) types of molecules, badly conducting (non-conjugated) type of molecules and even switchable molecules. The molecules typically used have dimensions of the scale of a few nanometers (1 nanometer = 0,000000001 meter). Hence the field of molecular charge transport is part of the larger area of nanoscience and nanotechnology.

To make a working molecular circuit based on a single molecule or a few molecules is challenging. There is a large gap in the length scales of molecules and macroscopic electrodes. Also a so-called "molecular device" needs to be stable enough to function at room temperatures and atmospheric pressures. In this thesis, I have performed fundamental research on charge transport through various molecules. Specifically, I have investigated a special type of molecule that has the ability to change its spin state. To test these functional molecules, I have used a more robust type of molecular device that enables me to bridge the size gap mentioned above.

The concept behind these molecular devices is as follows. First, alkanethiol organic molecules are used to functionalize a gold nanoparticle (~8.5 nm in diameter), forming a molecular monolayer on the gold surface via a Au-S bond. Second, these functionalized gold nanoparticles are self-assembled into a two-dimensional (2D) molecule-gold nanoparticle ensemble. During this process, the functionalized nanoparticles order themselves into an array that can be printed on different types of substrates via a transfer method called microcontact printing. A 2D molecule-gold nanoparticle array can thus be transferred to a device with pre-patterned gold electrodes. The gold electrodes are made via a series of lithographic techniques and they are typically separated by a trench of nanoscopic dimensions. Using the resulting device, the charge transport properties of a molecular-gold nanoparticle network can be measured and analyzed (see Figure 1).

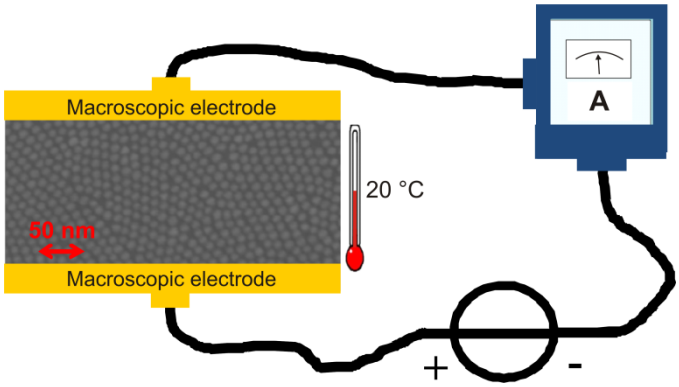

Figure 1: Schematic representation of an electrical circuit based on a 2D molecular-gold nanoparticle array (in this drawing the image of a real molecule-gold nanoparticle array made via a scanning electron microscope is inserted, with a scale bar of 50 nm). This array is contacted to the macroscopic electrodes to measure the charge transport properties of the molecules.

Basically, a molecule-gold nanoparticle array is a collective of multiple gold nanoparticle-molecules-gold nanoparticle junctions. Near room temperature, the conductance of this array is dominated by the molecules, because under these conditions the gold nanoparticles will behave like tiny electrodes with a low electrical resistance. In that case, the electrical resistance of a molecular-gold nanoparticle array is a spatial average of all the gold nanoparticle-molecules-gold nanoparticle junctions. Another advantage of this molecular device is the possibility to perform additional (optical) control experiments on the chemical and physical properties of all the molecules. For a single molecular device these additional analyses are not possible or at least very challenging. The open structure of molecular-gold nanoparticle ensembles makes it also easy to influence the properties of both the molecule and the nanoparticle via external stimuli (i.e. temperature, light).

This thesis comprises six chapters. In Chapter 1, I elaborate on the motivation and history of molecular charge transport. Also I will explain the role of organic molecules in molecular junctions and introduce the experimental techniques used nowadays to study the charge transport through single or multiple metal-molecule(s)-metal junction(s). Here, I motivate my choice to use 2D molecular-nanoparticle ensembles as an experimental technique. In addition, I introduce a special category of compounds, called the spin crossover molecules. This intriguing type of complex molecules possesses the ability to reversible undergo a spin transition (i.e. a change of spin state under the influence of external stimuli (temperature, light, pressure, magnetic fields)). The measurements of molecular devices containing spin crossover molecules are further described in Chapter 6.
Chapter 2 describes the fact that the electrical conductance through molecules on a nanoscopic scale behaves differently compared with bulk matter on the macroscopic

scale. The conduction of current in macroscopic matter behaves according to the classical laws of Ohm and Drude. On a nanoscopic scale, conduction of current is dominated by quantum mechanics. Chapter 2 also describes how the conductance of a molecular device changes as the chemical/physical conditions change, or "switches".
Chapter 3 describes the techniques used to synthesize 2D molecular-gold nanoparticle arrays via self-assembly processes and to microcontact print these arrays on macroscopic electrodes devices. Also other (optical) techniques are explained that are used to determine the properties of my molecules and gold nanoparticles in a 2D molecular-gold nanoparticle array.
Chapter 4 explains my research on the charge transport mechanisms in molecular-gold nanoparticle ensembles as a function of temperature. At low temperatures, the gold nanoparticles demonstrate a special behaviour. Each gold nanoparticle possesses a small electrical capacitance. This capacitance causes the need for an additional energy (also called the charging energy) to allow an electron to hop onto a gold nanoparticle. Hence, when the thermal energy is lower than the charging energy, the gold nanoparticles in the molecular-gold nanoparticle ensemble will not behave as perfectly conducting electrodes anymore. The consequence of this is that the electrical resistance of the molecular-gold nanoparticle ensemble increases dramatically with decreasing temperature. This phenomenon is called Coulomb blockade. Still, limited conduction is possible in the Coulomb-blockade regime. This form of conduction is driven by a charge transport mechanism called multiple inelastic cotunneling, which actually follows from the uncertainty principles of Heisenberg. Simply put, during a multiple inelastic cotunneling event, electrons can be simultaneously transported over multiple gold nanoparticle-molecules-gold nanoparticle junctions.
Here, we first study the charge transport regimes for octanethiol (C8)-gold nanoparticle networks. Through a process called molecular exchange we subsequently insert better-conducting (conjugated) molecules in the same molecular-gold nanoparticle network and study transport behaviour again. We show that the resistance ratio between a conductive network and a non-conductive network increases enormously at low temperatures. This ratio grows with an exponent that is directly related to the number of simultaneous cotunneling events. The fascinating consequence of this is that the on/off ratio of a switchable molecular-gold nanoparticle network could be dramatically enhanced by entering the multiple cotunneling regime. The results of Chapter 4 thus introduce a totally new concept to artificially enhance the properties of switchable molecular devices.
In Chapter 5, I describe my research toward a new type of molecular-gold nanoparticle ensembles. Here, a special type of conjugated molecule is used, called a ligand. A ligand is a molecule that can bond in a distinctive way with (metal)ion(s) to form a "complex" molecule. These new ligand-gold nanoparticle ensembles are also synthesized via a self-assembly process. By using multiple analysis techniques on these ligand-gold nanoparticle ensembles (e.g. electron microscopy) we have studied its structure and chemical configuration. (Surface-enhanced) Raman spectroscopy allows us to study molecular vibrations in these networks. We find that the ligands and the gold nanoparticles are connected via Au-S bonds. In addition we have determined that increasing the temperature in these ligand-gold nanoparticle ensembles causes a

significant change in the conformation and orientation of the ligands on the gold nanoparticles. These effects in the junctions of a ligand-gold nanoparticle ensemble appear to be related to another effect encountered during temperature-dependent conductance measurements of a ligand-gold nanoparticle network. Here, the conduction continues to increase when increasing the temperature beyond room temperature. Such an effect is not found in C8-gold nanoparticle networks. The surprising conductive properties of a ligand-gold nanoparticle network could be caused by the increased interactions and fluctuations in gold nanoparticle-ligands-gold nanoparticle junctions when increasing the temperature.

Finally Chapter 6 presents my research on the properties of gold nanoparticle ensembles containing spin crossover molecules. These spin crossover molecules are an exceptional type of complex compounds that can reversibly change spin state via temperature and other stimuli. This phenomenon is called spin transition and it mostly occurs in Fe^{2+}-ion-based complex compounds. Complex compounds originate from coordination chemistry where (transition) metal ion(s) can interact with the functional groups of ligands. During spin transition, two electrons in the d orbitals of the metal ion are transferred from a lower energy state toward a higher energy state or vice versa. Simultaneously, the dimensions of a spin crossover molecule will change a little. For this research we have used a spin crossover molecule that consists of one Fe^{2+} ion and two ligand molecules, similar to the ligands used in Chapter 5. These spin crossover molecules are inserted in C8-gold nanoparticle ensembles via a modified molecular exchange process.

Surface-enhanced Raman spectroscopy is used to determine if at room temperature the spin crossover molecules functionalize the gold nanoparticles via Au-S bonds. Interestingly, temperature-dependent Raman spectroscopy on the arrays shows that significant changes occur in the molecular vibrations of the spin crossover molecules. Analyzing these data, we derive that the majority of the spin crossover molecules in the arrays change from a low-spin state ($S = 0$) to a high-spin state ($S = 2$) when increasing the temperature from low to high. The spin transition phenomenon takes place reversibly, close to room temperature. Also magnetization measurements on these spin crossover molecule-gold nanoparticle ensembles have been performed. These results give indications of a (incomplete) spin transition, as a transition takes place from diamagnetic behaviour to paramagnetic behaviour (and vice versa) around temperatures consistent with the Raman measurements.

At last we have studied the conductance properties of spin crossover molecule-gold nanoparticle networks as a function of the temperature. In reference types of networks (see Chapters 4 and 5), the electrical resistance decreases monotonically with increasing temperature. The spin crossover molecule-gold nanoparticle network, however, shows a clear minimum in the resistance versus temperature curves. This minimum appears to be related to the spin transition, also because theoretical calculations show that the resistance of the spin crossover molecule in the high-spin state should be higher than in the low-spin state. The minimum in the temperature-dependent resistance curves can hence be explained via a simple model based on percolation theory. Percolation theory describes the formation of conduction pathways in a network in which more and more points (here: nanoparticles) are connected (here:

conducting molecules). In a way, this theory can be compared with how water tries to find the easiest way to flow through a medium, for example through coffee in an espresso machine (sometimes called a percolator).
To summarize, this thesis has led to two important new insights. First, the properties of a switchable molecular device can be strongly enhanced artificially by making use of a charge transport mechanism called multiple inelastic cotunneling (see Chapter 4). Second, we show that the spin transition phenomenon can take place in a molecular-nanoparticle ensemble (see Chapter 6).