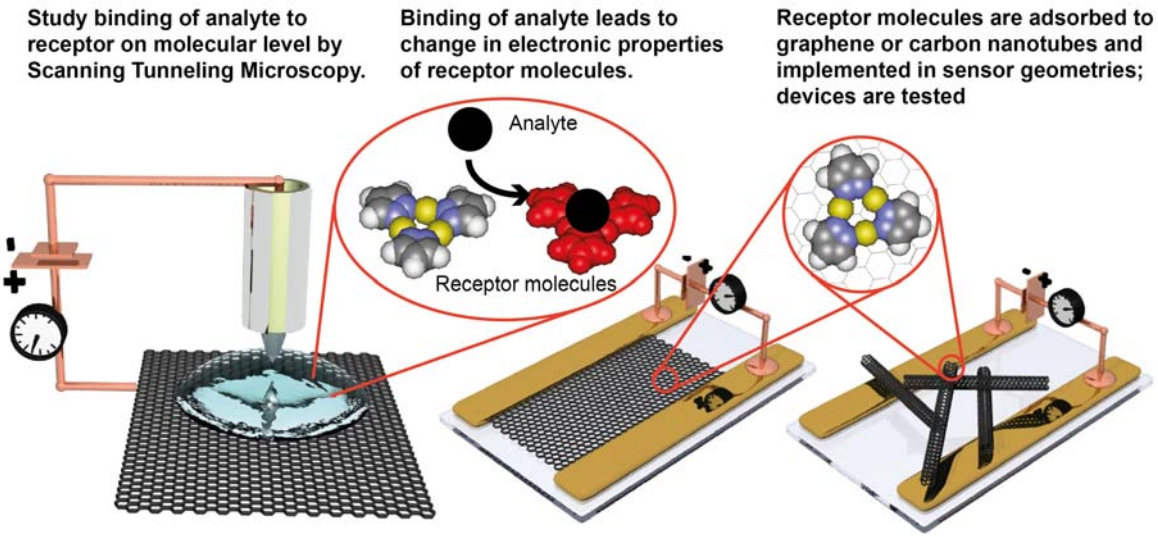
Publishable summary

Description of project objectives

The goal of the project is to **image supramolecular binding processes on the molecular level** with the purpose to **gain fundamental understanding of how a sensor operates**. This understanding will subsequently be applied as a basis for new sensor design.



Work progress and achievements

Gold(I) Pyrazolates (published in: *The Journal of Physical Chemistry C* **117**, 8290**)**

The electronic, optical, and chemical properties of trimeric gold complexes suggest utility as electronic materials and chemical sensors. Carbon nanotube (CNT) and graphene based devices have the potential to lead to very sensitive chemical sensors. To improve selectivity, they generally require functional molecules adsorbed to their surface. For the operation of these devices, it is crucial to obtain detailed information of these molecular layers. Therefore, time-dependent Scanning Tunneling Microscopy was used to study such layers on the single molecule level. These detailed studies provided information on several distinct morphologies, layer evolution, cooperative dynamics, conformation of alkyl chains, chirality and subtle effects in the topographical contrasts.

Templating fullerenes (published in: *Langmuir* **30**, 762**)**

The controlled self-assembly of functional molecules on surfaces at the single molecule level is crucial for emerging nanoscience and nanotechnology (e.g., electronics, catalysis, photonics and medicine). A powerful approach is the use of a templating molecular command layer to control the location of functional guest molecules, for example within the pores of a 2-dimensional (2D) nanoporous network. These well-defined pores in the network can immobilize functional molecules and produce periodic patterns, for applications such as molecular memory devices.

A new templating strategy was developed, employing domain boundaries in molecular nanoporous networks. This strategy can be used to obtain non-periodic patterns, which are better suited for complex applications like solar cells or transistors. Furthermore, the strategy allows for the templating of guests with various sizes without the need of tailoring the network for each specific guest.

Graphene Oxide (published in: *Chemistry of Materials* **26**, 4849**)**

Detailed characterization of graphene oxide (GO) and its reduced forms continues to be a challenge. We have employed scanning tunneling microscopy (STM) to examine GO samples with

varying degrees of deoxygenation via controlled chemical reduction. Analysis of the STM topography measurements revealed a correlation between increasing deoxygenation and decreasing apparent roughness. This analysis can therefore be a useful supplement to the techniques currently available for the study of GO and related materials.
The presence of a high electric field underneath the STM tip can locally induce a reaction on the GO basal plane that leads to local deoxygenation and the restoration of the sp2 hybridization of the carbons promote increased planarity. We show the first example of employing an STM tip to locally reduce GO to reduced GO (rGO) and partially reduced GO (prGO). Such local manipulation on the nanoscale has utility for graphene nano-electronics.

Selective epitaxial graphene sensor (manuscript in preparation)

Recently, a highly sensitive and selective gas sensor, based on quasi freestanding epitaxial graphene on SiC was developed in the research group in Eindhoven. These sensors had a very high sensitivity for NO_2 of 1 ppb and were insensitive to N_2, NH_3 and CO. As a continuation, we have explored the possibility to adapt this selectivity through chemical functionalization. Therefore cobalt-porphyrins were deposited on the graphene surface. Such porphyrins are known to bind CO and NH_3. Recent calculations indicate a dipole-like charge separation upon binding of an NH_3 to the cobalt centre of the porphyrin. Such a dipole is expected to result in a shift of the Fermi-level and can be detected by Van der Pauw and Hall transport measurements. With this functionalization, we were so far able to reach a sensitivity for NH_3 of 0.5 ppm, whereas there was no response at all in the case of unfunctionalised graphene.