When molecules leave tire tracks: A new approach to optimizing molecular self-organization

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Certain types of molecules form patterns when deposited onto substrates. Photovoltaic and sensor devices from organic compounds depend on this phenomenon of self-organization. Physicists of Ludwig-Maximilians-Universitaet in Munich, Germany, have now developed a model that predicts these patterns and thus allows optimization of the molecular synthesis in the future.

Some classes of molecules are capable of arranging themselves in specific patterns on surfaces. This ability to self-organize is crucial for many technological applications, which are dependend on the assembly of ordered structures on surfaces. However, it has so far been virtually impossible to predict or control the result of such processes.

Now a group of researchers led by Dr. Bianca Hermann, a physicist from the Center for Nanoscience (CeNS) at LMU Munich, reports a significant breakthrough: By combining statistical physics and detailed simulations with images obtained by scanning tunnelling microscopy (STM), the team has been able to formulate a simple model that can predict the patterns observed. "With the help of the model, we can generate a wide variety of patterns that reproduce surprisingly well the arrangements observed experimentally", says Hermann. "We want to extend this approach to other surface symmetries. Already now the areas of molecular electronics, sensor applications, surface catalysis and organic photovoltaics can profit from our model. Its ability to predict

structures formed by self-organization allows optimization of molecular building blocks prior to synthesis." (*Nano Letters* online, 16 February 2010)

When "mother nature" does the engineering, molecules can self-organize into complex structures - a first step in the formation of membranes, cells and other molecular systems. The principle of self-organization, which allows very economical use of resources, is also exploited in the production of functionalized surfaces required in molecular electronics, sensor applications, catalysis and photovoltaic components. The idea of the manufacturing process is that molecular components are brought into contact with a substrate material, and then "magically" find their preferred positions in the desired molecular network. The starting components are selected to display specific structural and chemical features intended for the envisaged application. However, the optimization of the molecular adlayers depends largely on a trial-and-error approach, and is therefore complicated and time-consuming.

To develop the new molecular-interaction site model, Dr. Herrmann's group collaborated with Priv. Doz. Dr. Thomas Franosch und Professor Erwin Frey within the Cluster of Excellence "Nanosystems Initiative Munich" (NIM). The problem was tackled using an approach from statistical physics known as Monte Carlo method, which allows one to conduct a detailed computer simulation on the statistics of molecular interactions. The structural motifs so generated were compared with experimental high-resolution images of molecular patterns obtained by STM. Marta Balbás Gambra, a doctoral student, began each simulation with a mathematical representation of a collection of hundreds of randomly oriented particles of defined conformation. These schematic molecules were then perturbed by - computationally - adding energy, causing the population to adopt a new configuration.

Using this simulation strategy, one can generate a greater variety of

patterns than are found naturally, and many of these corresponded closely to the real molecular patterns revealed by STM. "In one case we actually predicted a pattern that was only later verified with STM", reports doctoral student Carsten Rohr. According to the laws of thermodynamics, physical systems tend to adopt the state with the most favourable (i.e. lowest) energy. Experimental tests showed that different molecular configurations interconvert until an arrangement predominates that is reminiscent of tyre tracks. And indeed, the Monte Carlo approach had predicted that this arrangement corresponds to the state with the lowest energy.

"In the end, we were able to show that the molecular geometry and a few salient features encode the structural motifs observed", explains theorist Franosch. "We plan to extend the approach to other types of surface symmetries, but the model already provides an important theoretical tool, because it helps us to forecast the type of surface pattern that a given functional molecule will form. This means that the design of molecules can be optimized during the synthetic phase, so as to obtain surfaces with the desired characteristics", says Hermann. The physicists in the group, who come from different scientific backgrounds and were able to pool their expertise for this project, envisage multiple potential applications for their model in molecular electronics, sensor technology, catalysis and photovoltaics. Further possibilities include its use for predicting the results of other types of molecular interactions also on partially patterned substrates.

More information: "Molecular Jigsaw: Pattern Diversity Encoded by Elementary Geometrical Features", C. Rohr, M. Balbás Gambra, K. Gruber, E. C. Constable, E. Frey, T. Franosch, and B. A. Hermann, *Nano Letters* online, 16 February 2009. DOI: 10.1021/nl903225j