

# A standing molecule as a coherent single-electron field emitter

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**Abstract—** The assembly of single-molecule devices with the help of the manipulation capability of scanning probe microscopes offers many opportunities for quantum- and nanotechnology. A key challenge is fabricating device structures that can overcome their attraction to the underlying surface and thus protrude from the two-dimensional flatlands of the surface. In my talk, I will report the fabrication of such a structure: we use the tip of a scanning probe microscope to lift a large planar aromatic molecule into an upright, standing geometry on a pedestal of two metal adatoms. This atypical upright orientation of the single molecule, whose stability can be understood as the result of a fine balance between chemical and dispersion forces, enables the system to function as a quantum dot and an on-demand coherent single-electron field emitter. If attached to the tip of the microscope, the standing molecule can also be applied as a sensitive quantum dot sensor. We anticipate that other metastable adsorbate configurations might also be accessible, thereby opening up the third dimension for the design of functional nanostructures on surfaces. Finally, we have made first steps into the direction of an autonomous robotic nanofabrication of single-molecule devices.

## I. INTRODUCTION

During the last 200 years, starting with Michel Chevreul in 1816 and Friedrich Wöhler in 1826, chemists have learned to synthesize almost any conceivable molecule. And there are many: It has been estimated that there are  $10^{60}$  possible organic compounds with up to 30 carbon, nitrogen, oxygen or sulfur atoms [1]. To put this in perspective: There are  $10^{78}$  to  $10^{82}$  atoms in the known, observable universe [2]. So, if we wanted to synthesize even a small macroscopic quantity of each of these

$10^{60}$  molecules (on the order of one mol each), not even thinking about larger molecules, we would quickly run out of atoms in the universe!

Nature knows how to build with molecules. Biological organisms are a living testimony to this. While nature uses self-assembly to make functional structures from molecules, human construction in the macroscopic world is largely based on the manufacturing paradigm. Therefore, the question arises whether building with molecules “brick-by-brick”, following the manufacturing paradigm, is at all possible. The benefit would be tremendous: Getting a grip on molecules, we could fully exploit the potential of the most versatile collection of functional components in the universe for a range of human technologies.

The scanning probe microscope (SPM) has brought the vision of molecular-scale fabrication closer to reality, since it offers the capability to rearrange atoms and molecules on surfaces, thereby allowing the creation of metastable structures which do not form spontaneously. The standing molecule [3,4] is an instructive example.

## II. RESULTS

### A. The fabrication of the standing molecule

A single 3,4,9,10 perylene-tetracarboxylic dianhydride (PTCDA) molecule can be brought into a standing configuration on the Ag(111) surface, if a pedestal of two Ag adatoms is first created [3,4]: Once the adatoms have been

attached to one side of the flat-lying molecule by atomic manipulation, the SPM tip is moved into contact with a carboxylic oxygen atom at the opposite side. Next, the tip lifts PTCDA on a curved trajectory into the vertical. When the molecule stands upright, the tip is moved straight up, whence its bond to the molecule breaks and the molecule remains standing.

### B. Structure and stability of the standing molecule

The standing molecule adsorbs with the silver atoms of its pedestal in hollow sites of the Ag(111) surface. Two types of standing molecules exist: adatoms in identical hollow sites (fcc-fcc or hcp-hcp), adatoms in non-identical hollow sites (fcc-hcp). They can be distinguished by their azimuthal orientation and their thermal stability. The latter also reveals the potential energy barrier that stabilizes the molecule in its standing configuration. Density functional theory (DFT) calculations show that this barrier results from a fine balance between covalent and van der Waals (vdW) interactions. Because the experimentally measured barriers are in the range of only 30 meV, standing PTCDA serves as a highly sensitive benchmarking system for state-of-the-art ab initio theory. For example, we find that many-body screening effects are an essential element of the standing molecule's stability.

### C. Field emission from the standing molecule

The standing molecule functions as a quantum dot [5], accepting electrons one-by-one. Because the quantum dot is very small, it does not fulfil the constant interaction approximation [6]. Furthermore, under a large negative bias the additional electron is field-emitted towards the tip of the SPM [3]. Scanning the tip in the  $xy$  plane over standing molecule, one observes an interference pattern that can be modelled by combining coherent emission from the lobes of the relevant molecular orbital ("double-slit" experiment, Fig. 1) and field-emission resonances of the trapezoidal barrier (Gundlach oscillations). The standing molecule withstands extreme current densities of  $10^8 \text{ A m}^{-2}$ .

### D. The standing molecules as sensor

If the standing molecule is fabricated on the SPM tip, its quantum dot functionality and the joint electrostatic screening by tip and surface enable quantitative surface potential imaging across all relevant length scales down to single atoms (SQDM-Scanning Quantum Dot Microscopy)[5,7-9].

### E. Prospects of autonomous fabrication

In a proof-of-concept study, we have demonstrated that autonomous robotic nanofabrication with single molecules is in principle possible, using the approach of reinforcement learning [10]. We anticipate that this work opens the way toward autonomous agents for the robotic construction of functional supramolecular structures with speed, precision, and perseverance beyond our current capabilities.

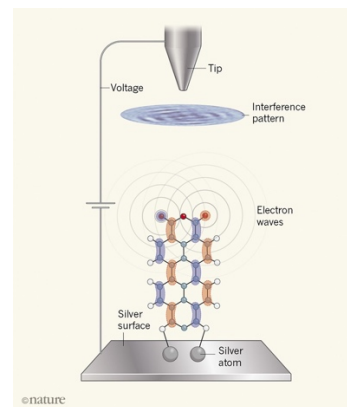


Fig. 1 A tiny „double-slit“ experiment based on a standing PTCDA molecule, which serves as a coherent single-electron field emitter (From ref. [4]).

## III. CONCLUSIONS

Metastable structures, apart from being more abundant than stable ones, tend to offer attractive functionalities, because their constituent building blocks can be arranged more freely and in particular in desired functional relationships. The metastable standing molecule exemplifies that the swift development of quantum- and nanotechnologies could be further advanced if we learned to freely design quantum matter by placing atoms and molecules in precisely the right places, not being constrained by availability and stability of exotic (quantum) materials.

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