

## MOLECULAR MACHINES

# The molecular wagon that stays on track

Single molecules are sent and received accurately over long distances across a surface

By Friedrich Esch and Barbara A. J. Lechner

Ever since the 2016 Nobel Prize in Chemistry was awarded “for the design and synthesis of molecular machines,” growing attention has been aimed at connecting and embedding molecular machines into hierarchically more complex systems for sophisticated applications. Such connections would, for example, enable the targeted delivery of molecules over larger distances. An important question that arises in this context is what kind of transporter would do such a job, over what distances, and with what degree of precision. On page 957 of this issue, Civita *et al.* (1) found a distinct example of a bromine-terminated terfluorene molecule on a metal surface that can be sent and received deliberately across more than a hundred nanometers with atomic precision.

The bromine-terminated terfluorene molecules can be moved easily on a Ag(111) support by applying electric fields between the surface and a scanning tunneling microscopy (STM) tip. The close-packed rows of the metal support essentially act as railway tracks for the molecular wagons. To characterize this movement on the single-molecule level, the authors had to sense the molecule at specific start and end points. This required bringing the molecule on the desired track and locally inducing motion along that track. The beauty of the experiment by Civita *et al.* lies in the successful application of a two-probe STM setup: Each tip provides a separate probe and manipulation device at the start and end points of the movement. In addition, each tip can individually generate local fields. The experiment thus constitutes a near-ideal sender–receiver setup where atomic-scale cargo is transmitted.

Previous experiments have already demonstrated that molecules can be accelerated along a surface using an STM tip (2) and that preferential diffusion directions can be accessed by rotating the molecules (3, 4), but they have never reached this long-distance precision and high level of motion control. The interaction of the bromine-terminated terfluorene molecule

with the silver surface is unusually well suited for this application. The linear molecule consists of three stiff fluorene units linked by rotationally flexible junctions and is not bonded strongly to a particular adsorption site on the surface. The reason lies in lateral methyl distancers that lift the molecule, while guiding it with its long axis along the track of the close-packed rows. However, keeping the molecule safely on the track is only achieved by the additional terminal bromine substituents, which add a further interaction to the support atoms. Furthermore, the molecule–surface system has a permanent dipole moment pointing out of the surface that is the handle to induce lateral movement. The authors convincingly show that the electric fields

**“The experiment thus constitutes a near-ideal sender–receiver setup where atomic-scale cargo is transmitted.”**

can be used to induce the movement from afar (150 nm) by both repulsion and attraction. The fortunate combination of all these properties leads to the particular mobility observed here, constituting a seminal quality and thus opening up important questions with regard to the design of hierarchical nanomachineries.

An interesting part of the experiment is that all molecules initially adsorb in locked-in, static orientations, upon deposition at low temperatures. Only after rotation by STM manipulation do the molecules snap to the track and become mobile. They reach a state with low lateral diffusion barriers along their long axis, which might point to incommensurability. One could speculate that the difficulty of dissipating the excess adsorption energy in this orientation is what keeps the molecules from adsorbing in the highly mobile orientation in the first place. Additionally, this might be the reason for the concomitant facile diffusion. The role of rotational flexibility along the long axis and of internal vibrational modes for the molecules’ mobility will be interesting to assess.

From previous studies, we know that these aspects influence the long jumps in the diffusion path (5) and modulate the degree of incommensurability that can lead to particular diffusion behaviors, such as, for example, Lévy flights (6). In Civita *et al.*’s experimental setup, such an influence can be studied by systematic structural variation of the molecules. The two-tip setup, however, reaches its time resolution limit when it comes to understanding in more detail the acceleration and maximal velocities that the wagons can reach. For quantitative access to the thermally activated diffusion properties, helium spin-echo measurements would be the way forward (7). However, observations of this type require a considerable population of molecules moving along tracks in an equilibrium state, at temperatures where immobilization at steps and island edges can be overcome.

Civita *et al.* show that the possibility exists to reliably move molecules along tracks. Moving closer toward nanomachineries will require implementation into more-complex systems, opening up several challenges. Similar track–molecule systems have to be realized on functionalized supports. Also, reversible cargo attachment to the nanowagons and an adequate handover process need to be established. And easily addressable or alternative acceleration mechanisms that can be actioned by nanomachines have to be explored. Nanomachines might generate the required local fields or induce chemical reactions that steer the cargo transport by energy release into distinct degrees of freedom. One might even envisage the use of light to photostimulate reactions or to create optically rectified fields in plasmonic nanoreactors that control the reactant supply. The possibilities are boundless—exciting times lie ahead. ■

## REFERENCES AND NOTES

1. D. Civita *et al.*, *Science* **370**, 957 (2020).
2. S. W. Hla, K. F. Braun, B. Wassermann, K. H. Rieder, *Phys. Rev. Lett.* **93**, 208302 (2004).
3. R. Otero *et al.*, *Nat. Mater.* **3**, 779 (2004).
4. B. Vasić *et al.*, *Nanoscale* **10**, 18835 (2018).
5. K. D. Dobbs, D. J. Doren, *J. Chem. Phys.* **97**, 3722 (1992).
6. W. D. Luedtke, U. Landman, *Phys. Rev. Lett.* **82**, 3835 (1999).
7. A. P. Jardine, H. Hedgeland, G. Alexandrowicz, W. Allison, J. Ellis, *Prog. Surf. Sci.* **84**, 323 (2009). f

Department of Chemistry and Catalysis Research Center, Technical University of Munich, 85748 Garching, Germany. Email: bajlechner@tum.de

10.1126/science.abe5959