Moving Nanostructures: Pulse-Induced Positioning of Supramolecular Assemblies
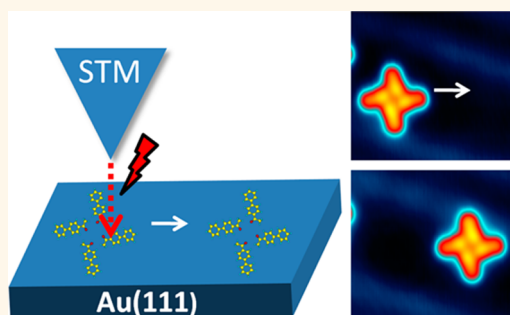
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ABSTRACT For the development of nanoscale devices, the manipulation of single atoms and molecules by scanning tunneling microscopy is a well-established experimental technique. However, for the construction of larger and higher order structures, it is important to move not only one adsorbate but also several at the same time. Additionally, a major issue in standard manipulation experiments is the strong mechanical interaction of the tip apex and the adsorbate, which can damage the system under investigation. Here, we present a purely electronic excitation method for the controlled movement of a weakly interacting assembly of a few molecules. By applying voltage pulses, this supramolecular nanostructure is moved in a controlled manner without losing its collective integrity. Depending on the polarity and location of the applied voltage, the movement can be driven in predefined directions. Our gentle purely electronic approach for the controlled manipulation of nanostructures opens new ways to construct molecular devices.

KEYWORDS: manipulation · supramolecular structures · voltage pulses · scanning tunneling microscopy · spectroscopy

The controlled manipulation of single atoms and molecules on surfaces by scanning probe techniques was developed during the last two decades.[1−3] In particular, the scanning tunneling microscope (STM) has proven to be a versatile tool for the atomic-scale manipulation and the construction of nanostructures.[1,4−9] Single atoms and molecules can be precisely positioned by lateral or vertical manipulation. The various existing manipulation modes depend critically on the type of the surface (*e.g.*, metal,[6] semiconductor,[10,11] or ultrathin insulators[12,13]). On metal surfaces, the standard method for lateral manipulation of single atoms,[6] single molecules,[7] or small groups of molecules[14] is to bring the tip of the STM close to the adsorbate, thereby increasing the tip–adsorbate interaction, and then move the tip to the desired final location on the surface.[5,6] This results typically in a pushing, sliding, or pulling of the adsorbate across the surface. The same procedure can be used to induce conformational changes in complex molecules.[7] Another method, known as vertical manipulation, relies on the transfer of the adsorbate to the tip, followed by a movement of the tip to the desired location and subsequent dropping of the adsorbate.[15−17] Other manipulation techniques employ electric fields,[18] inelastic tunneling electrons,[19−22] or, as was shown recently, trigger conformational changes[23] in a molecule such that it walks across the surface.[24] Voltage pulses were used to desorb[25] or dissociate[26] molecules, to induce conformational changes[27] or chemical reactions.[26]

STM lateral manipulation has so far mainly been developed for the displacement of single atoms and molecules and not for the controlled manipulation of weakly bonded supramolecular assemblies. Additionally, from a methodological point of view, a controlled manipulation procedure triggered just by electronic excitations is desirable in order to avoid any direct mechanical interactions of the STM tip apex with the adsorbate.
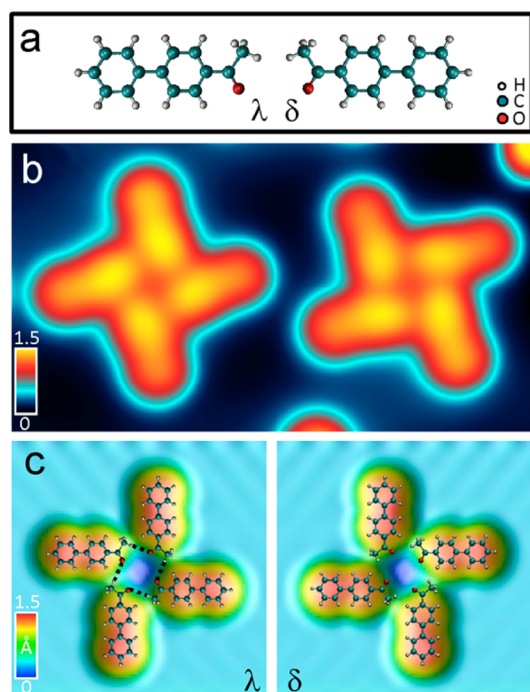
Figure 1. (a) Molecular structure of 4-acetylbiphenyl (ABP) (λ and δ chirality). (b) STM topography image of self-assembled tetramers of ABP on Au(111) (λ and δ chiral windmill motif). Image size: 38.4×69.3 Å^2, bias = -1 V, I = 2.9 nA. (c) Calculated STM image with the optimized geometry superimposed. The dashed lines symbolize the intermolecular hydrogen bonds.

In this article, we show for the first time the controlled manipulation of a supramolecular structure induced by voltage pulses. By applying voltage pulses on one selected molecule of the structure, we can move a supramolecular assembly to a chosen position on the surface without destroying it.

RESULTS AND DISCUSSION

Characterization of Supramolecular Structures. Figure 1a shows the 4-Acetylbiphenyl (ABP) molecule used in this study. It is composed of two phenyl rings and an acetyl group. On Au(111), the ABP molecules self-assemble into small weakly bonded supramolecular structures. Single molecules adsorb at defects and step edges and cannot be moved away by manipulation.

In Figure 1b, a STM topography image of a supramolecular ABP tetramer (ABP$_4$) is shown. The ABP molecules are here organized in a windmill nanostructure. These windmills are present on the surface in two mirror symmetric forms as a consequence of the prochiral nature of the single molecules. A calculated constant current image of the windmill is presented in Figure 1c. The calculated geometry confirms the hydrogen-bond-like stabilization of the windmill nanostructure[28,29] and shows a bond length of 3.1 Å. The hydrogen bonds are indicated by dashed lines in the image. The proposed structure agrees well with the distances in the windmill structure determined experimentally from the STM images.

Nanoscale Manipulation. Attempts to move the windmills using the conventional lateral manipulation technique[5,6] resulted in a destruction of the supramolecular nanostructure and the separation of its ABP components. In order to move the individual windmills, we applied voltage pulses on top of or close to one of the ABP molecules of the nanostructure as it has been done so far on single molecules.[13,22] These resulted in a controlled collective movement of all ABP molecules of the chosen windmill at the same time. In Figure 2, topography images taken before (top row) and after (bottom row) the voltage pulse are shown. By changing the applied voltage, we observe different types of motions. For negative voltages (Figure 2a), we predominantly find a collective translational movement of all molecules of a windmill in the direction away from the position of the tip. For positive voltages, we find two possible movement types. Most frequently, translational movements (Figure 2b) are induced. In the other cases, we observe a rotation of the windmill (Figure 2c). For sufficiently high positive voltages, a total reorganization of the windmill nanostructure occurs (Figure 2d). It is important to note that for positive voltages the direction of the translation is opposite to that for negative voltages; that is, the center of the supramolecular structure moves toward the position of the tip. For translational movements, we typically observe lateral jumps of the windmill of 3 Å, corresponding to the surface lattice constant of Au(111). Rotational movements are mainly observed at positive voltage pulses (in more than 40% of the cases in contrast to less than 5% at negative voltages) with rotational angles of 15° (33%) or 30° (66%) in the clockwise or counterclockwise direction. Before manipulation, the windmills are adsorbed with different angles on the Au(111) surface, showing that energetically equivalent adsorption sites exist apart from symmetry considerations. Note that the rotation is possible on the open surface even without any geometrical constraints such as a surrounding cavity.[30] Given that the windmill nanostructures are chiral, we investigated if there is a rotational preference. However, out of the 200 measured rotational events, no significant preference for one or the other rotation direction was observed. If there is a preferential rotation direction due to the chirality of the molecules, as suggested by a recent work on a single chiral molecular rotor,[31] it will be rather small. From our measurements, we can give an upper limit for rotation directionality of about 5%. This confirms that molecule—surface chirality is only a necessary condition for unidirectional rotation of an adsorbate. One also needs to filter the random time-dependent fluctuations of the tunneling current and synchronize with intramolecular time-dependent processes necessary for the rotation to occur in a specific direction.[32]
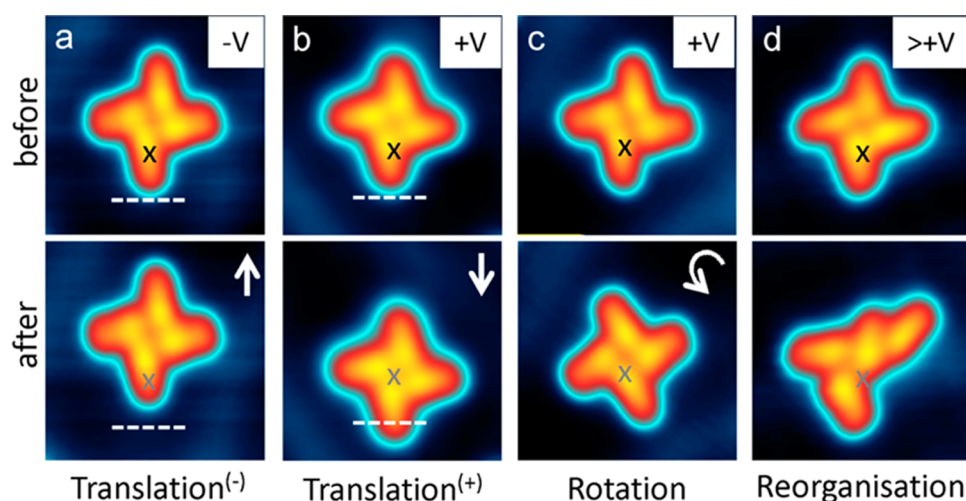
Figure 2. STM topography images of self-assembled ABP on Au(111) taken before (top row) and after (bottom row) applying a voltage pulse at the position indicated by the black cross. A negative voltage pulse leads in the majority of cases to translation (a), whereas a positive voltage pulse leads either to translation (b) or rotation (c) or, for sufficiently high voltages, reorganization of the supramolecular structure (d). Note that the direction of translation is opposite for negative and positive voltages. The white dashed lines are a guide for the eyes, and the gray crosses indicate the position of the tip where the voltage pulse was applied. Image parameters: (a) bias = −0.1 V; (b−d) +0.1 V, I = 50 pA; size 50 × 50 Å^2. The color scale is the same as in Figure 1b. Manipulation parameters: (a) bias = −2.3 V, I = 1.7 nA, t = 20 s; (b) 2.1 V, 3 nA, 10 s; (c) 2.5 V, 0.5 nA, 10 s; (d) 2.7 V, 0.25 nA, 10 s.
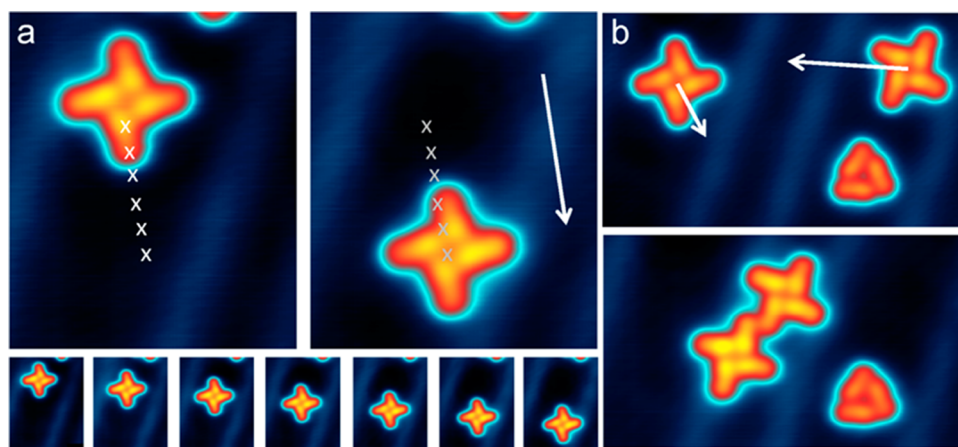

Figure 3. Controlled lateral manipulation using consecutive voltage pulses. (a) Total traveling length after six pulses is 36 Å. The brighter appearance of the right molecule of the windmill in the final position is due to the influence of the reconstruction lines of the Au(111) surface. At the bottom, the intermediate positions of the windmill after each pulse are shown. (b) Construction of a novel nanostructure by bringing two windmills together. The molecular aggregate on the bottom serves as reference for the movement of the two windmills. The herringbone reconstruction of the Au(111) surface does not limit the motion. Manipulation parameters: 2.3 V, 1.7 nA, 10 s. Image sizes: (a) 68 × 80 Å^2, (b) 125 × 73 Å^2. The color scale is the same as in Figure 1b.

We have also explored how our manipulation method can be used to reproducibly move a windmill nanostructure over large distances. To do so, voltage pulses were applied consecutively to the windmill along a predetermined line on the surface. In Figure 3a, such a manipulation procedure is shown. The left image shows the initial and the right image the final position of the windmill after applying a regular series of voltage pulses. The windmill follows the position of the tip stepwise along the predetermined line. At the bottom, the intermediate positions after each pulse are presented. Importantly, by selecting the molecule to which the voltage pulse is applied, the direction of the

manipulation can be chosen. Intact windmills can be controllably moved to defined positions on the surface. This can be seen in Figure 3b. By moving two windmills to a desired position, a new nanostructure is built. Moreover, this example shows that the Au(111) surface reconstruction does not affect the windmill motion. Notice that such highly controlled surface positioning does not require the complex intramolecular mechanical mechanisms described for single-molecule machines.[24]

Statistical Analysis. In order to understand the described manipulation events, we have systematically analyzed the tip height traces taken during the time interval of the voltage pulses in constant current mode.
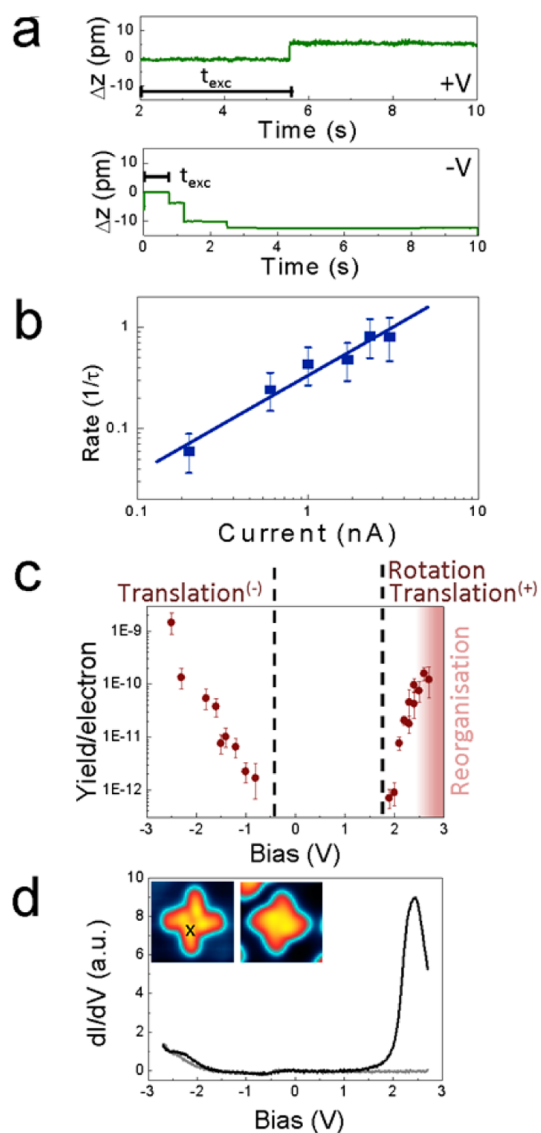
Figure 4. Statistical analysis of the voltage pulses: (a) tip height measured as a function of time during a positive and negative voltage pulse on a supramolecular structure. (Top) Bias = +2.6 V, I = 0.25 nA. (Bottom) Bias = −2.3 V, I = 3 nA; t_{exc} is the time needed to excite an event. (b) Inverse of the lifetime (*i.e.*, rate) as a function of current plotted in double logarithmic scale. Bias voltage: −1.8 V. Measurements at other voltages show the same dependence. (c) Quantum yield as a function of bias voltage. (d) dI/dV spectra taken on top of the supramolecular structure (black) and an off spectrum taken on the bare Au(111) surface (gray). The inset shows STM images taken at 0.1 V (left) and 2.2 V (right) (the black cross indicates the position of the tip during the spectrum).

Figure 5. Choosing the direction of motion by positioning the tip at a specific molecule of the supramolecular structure. The position of the tip during the voltage pulse is indicated by the colored crosses. The different directions are visualized by the corresponding colored arrows. To follow the motion of the structure, its center is represented by a white circle. The colored circles denote the previous position of the structure in this sequence of images. Manipulation parameters: 2.6 V, 0.25 nA, 10 s. Image sizes: 98.2 × 56.1 Å^2. The color scale is the same as in Figure 1b.

Two representative examples of such traces, one for the positive voltage and one for the negative voltage, are shown in Figure 4a. A jump in the trace indicates a sudden change in the conductance at the position of the tip. For positive voltages, we usually see an increase in tip height (*i.e.*, increase in conductance), whereas for negative voltages, a decrease in tip height (*i.e.*, decrease in the conductance) for the first jump is obser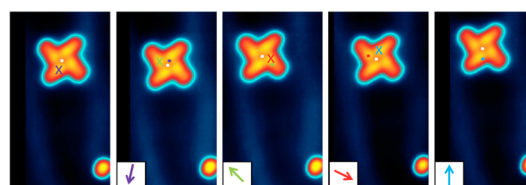ved. This agrees with the observation that for positive voltages the structure moves toward the tip, whereas for negative voltages, the windmill center moves away from the tip. After the first jump, more jumps can occur. From the time it takes for the first jump to occur, we deduced the rate as well as the quantum yield of the event, that is, the probability by which a movement is triggered. Plotting the rate, which is the inverse of the average time it takes until the first jump, as a function of current, we find a linear dependence indicating a one-electron inelastic process (Figure 4b).

The quantum yield, calculated *via* $e/I\tau$, where e is the elementary charge, I the current, and τ the average time of excitation, is shown in Figure 4c as a function of the applied bias voltage. It is evident that the behavior for positive and negative voltages differs. The threshold voltage to excite an event is much lower for negative than for positive voltages, where values above 2 V need to be applied to trigger an event. For positive voltage pulses, the quantum yield shows a maximum value at about 2.5 V, whereas for larger voltages, a reorganization of the windmill structure takes place (Figure 2d).

Electronic Structure. To measure the electronic structure, we have recorded the STM tunnel junction dI/dV spectrum over an ABP$_4$ windmill at the same position where the voltage pulse has been applied for manipulation. For positive voltages, a well-resolved resonance at about 2.5 V is observed (see Figure 4d) which can be assigned to the lowest electronic excited state of the ABP adsorbate.[33] For negative voltages, the spectrum appears relatively flat. Nevertheless, a broad and weak resonance at about −2.2 V can be distinguished in the spectrum. For positive voltages, the energy onset position of the observed resonance exactly corresponds to the measured quantum yield (see Figure 4c), indicating the presence of an inelastic input channel on the windmill. For negative voltages, the energy onset begins already at 0.8 V, and because of the broadness of the resonance, also in this case, the increase of the quantum yield can be explained by the electronic resonance. Such localized inelastic excitations on just one ABP molecule of the windmill are

enough for the complete supramolecular windmill nanostructure to translate or to rotate without any internal apparent structural change.

Once a threshold voltage has been reached, where tunneling in molecular resonances is possible, the supramolecular structure can be moved. For voltages exceeding 2.5 V, the windmill nanostructure is getting destroyed. In this case, some hydrogen bonds are broken and a new noncovalently bonded network is formed (see Figure 2d), which differs from the self-assembled arrangement. Occasionally, we observe that this reorganization can be reversed by additional voltage pulses, recovering the original windmill configuration. Notably, the structural chiral fingerprint remains in the new structures. For voltages between 2.5 V and the lowest measured negative value of -3.0 V, the strength of the hydrogen bonds between the ABP molecules in a windmill is large enough to keep the nanostructure intact during its excitation and its concerted motion (translation, rotation). From the statistical analysis of the time series of the voltage pulses, we conclude that the process is driven by the inelastic tunneling of a single electron. The quantum yield is in good agreement with the electronic structure, confirming an inelastic input channel.

Directionality. Now we turn to the observed directionality of the movement which varies with the polarity and the location of the tip on the structure. As already discussed, the movement direction depends first of all on the polarity of the voltage pulse. If the voltage pulse is positive, the center of the windmill will move under the tip while the center of the supramolecular structure will move away from the tip at negative voltage pulses. This attractive or repulsive interaction can be used to move the whole structure in a chosen direction by carefully choosing the position of the tip on the structure. Let us consider for simplicity the case of a positive voltage pulse. If we place the tip over the center of the structure and apply a voltage pulse, there will be no translational movement. If we apply the same voltage pulse by positioning the tip over one molecule in an off-center position, it results in an asymmetric geometry. The center of the assembly will be attracted by the tip and will move parallel to the chosen molecule in the direction of the tip. This means that, by choosing the molecule of the structure on which we apply the pulse, we can choose the direction of the movement of the whole structure. An example of directed manipulation is shown in Figure 5. The directions

of motion are chosen by positioning the tip at specific molecules of the supramolecular structure.

The observed dependence of the movement on the polarity is not explained straightforwardly. Recent studies on single molecules suggest an electrostatic effect between tip and molecule, which acts additionally to the hopping excitation.[22] When comparing refs 22 and 13, it is, however, evident that for positive voltages single molecules can hop either away or toward the tip. The latter was observed on an ultrathin insulating layer and agrees with our measured polarity dependence. For a complete rationale, many factors may need to be considered, such as the type of surface, quantum mechanical effects, or the local charge distribution.

In general, the ability to collectively move the ABP_4 molecules on a metal surface purely electronically with voltage pulses is possible due to a weak molecule–substrate coupling. Our calculations show that the molecule is indeed physisorbed. In the case of a strong interaction, internal modifications are more likely to occur or no movements at all would be expected. We performed further voltage pulse manipulation experiments on Au(111) with other molecular nanostructures (*i.e.*, trimers of ABP molecules or 1,4-bis(phenylethynyl)-2,5-bis(ethoxy)benzene molecules). These show similar results, confirming that our manipulation method can be generally applied to noncovalently bonded assemblies of molecules weakly adsorbed on surfaces. Since we can control the direction of the movement, our studies go beyond electrically or thermally excited diffusion phenomena.[34]

CONCLUSIONS

Our experiments demonstrate a method to controllably move supramolecular structures on a metal surface with a scanning tunneling microscope. As a model structure, we used ABP molecules, which self-assemble on the surface into windmill structures composed of four noncovalently bonded molecules. By applying voltage pulses on top of one molecule, the whole structure can be manipulated in a controlled way, preserving its native structure.

We believe that our findings help in understanding the movements of weakly bound molecules on metal surfaces. They provide a novel procedure to gently and purely electronically manipulate individual nanostructures to desired positions on the surface without the need for complex intramolecular mechanical mechanisms, opening a new route for the construction of artificial molecular devices.

METHODS

4-Acetylbiphenyl (ABP) molecules were studied on the Au-(111) surface with a custom-built low-temperature STM (5 K) under ultrahigh vacuum conditions ($<10^{-10}$ mbar). The gold single-crystal surface was cleaned by repeated cycles of Ne ion

sputtering and subsequent annealing at 720 K. The molecules were deposited from a Knudsen cell at 320 K onto the Au(111) substrate kept at room temperature. After the deposition, the sample was cooled to cryogenic temperatures and transferred to the STM. For topographic imaging, either low voltages (0.1 V)

or low currents (25 pA) were used to ensure that no manipulation happens during scanning.

For manipulation, the STM tip is precisely positioned on a windmill and a voltage pulse between tip and sample is applied. During the pulse, the feedback loop is kept closed and the tip height is recorded. A jump in the tip height indicates a manipulation event.

Differential conductance spectra were measured using lock-in detection with a modulation frequency of 833 Hz and a modulation amplitude of 20 mV. This is a common value for tunneling spectroscopy measurements on molecules, where resonances are normally weak in intensity due to the low current used and relatively broad in energy. To ensure the recording of a stable spectrum, the measurements have been done under closed feedback-loop conditions with a low set-point current (25 pA).

The exact adsorption conformation of a windmill structure was obtained by calculating the STM image of an ABP_4 supramolecule on the Au(111) surface after its optimization using the ASED+ semiempirical molecular mechanics technique, which is well adapted for such large supramolecular adsorbates.[35] Constant current images of the optimized geometry were calculated using ESQC (electron-scattering quantum chemistry).[36]

Conflict of Interest: The authors declare no competing financial interest.

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