Towards the directional transport of molecules on surfaces

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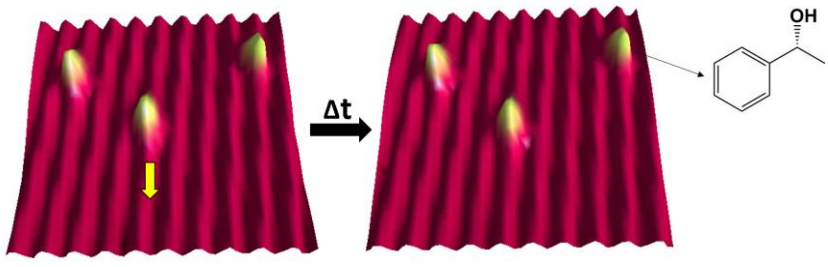
Abstract:

Control of the translational motion of individual molecules on surfaces is necessary for the development of novel methods for mass transport, separations, enantiopurifications and reactions, as well as in new applications including pumps, sensors, and assembly. Herein we discuss a concept whereby a flashing temperature ratchet-like mechanism comprised of asymmetric potential energy landscapes of individual molecules on surfaces coupled with excitation by electrons may enable directed molecular transport in a wide variety of nanoscale systems. Towards this goal we have studied the inelastic electron tunneling induced diffusion of molecules on surfaces with defined potential energy landscapes including surface step edges and low symmetry (110) facetted surfaces. Our results indicate that, with careful selection of components, 1D motion can be induced but that unidirectionality is still elusive.

Keywords:

Nanoscience; Diffusion; Directed Motion; Scanning Tunneling Microscopy; Surface Science

TOC Figure:



1. Introduction

The majority of progress of molecular machines has been generated by synthesizing complex organic structures and studying their properties.[1–9] Many of these studies were performed on molecules in solution; however, in nature most molecular machines operate at interfaces like those at membrane surfaces or on microtubules. Therefore, mastering the properties of surface-bound systems is essential for harnessing their utility. Studying the motion of molecules bound to surfaces also offers the advantage that a single layer can be assembled and monitored using the tools of surface science.[10–19] This was the approach taken in a seminal work where Feringa and co-workers reported a light-driven unidirectional molecular motor that utilized the chiral helicity of a molecule that produced 360° unidirectional motion.[4] Liquid-crystal films doped with 1% of their light-driven unidirectional molecular motor have been shown to be capable of rotating objects with near-macroscopic dimensions.[15] This experiment was the first demonstration of collective rotations of molecules driving macroscopic motion and illustrates the great potential for incorporation of molecular machines into useful devices.[20–25] Translational molecular motion on surfaces has also been investigated by several groups.[26–30] The general approach has been to design molecules with functionality that leads to symmetry breaking in their adsorbed state. Thermal or STM tip induced motion along specific substrate directions has been demonstrated.[19,31–33] For example, a variety of nano vehicles have been synthesized and tested by the Tour/Kelly groups and some show anisotropic 1D diffusion.[34,35] Another impressive example of 1D diffusion has been demonstrated experimentally by Bartels and co-workers.[36] Anthracene and anthraquinone based molecules were shown to "walk" along a 6 fold symmetric surface in just two directions by virtue of a near epitaxial fit of the molecule to the surface lattice.[37] Chemical modification of the number of linkers allowed investigation of the "walking" mechanism.[38] These molecules were also able to transport CO_2 molecules as "cargo."[39] Feringa and Ernst synthesized and measured the electrically driven motion of a nanocar that could be moved unidirectionally via vibrational and electronic excitation by tunneling electrons.[40,41]

While state-of-the-art, all of these translation systems use very specific molecular designs to achieve 1D or directional motion on surfaces; changing the molecule even slightly would remove the bias towards directional diffusion. General approaches to the directional transport of molecules on surfaces, based on the mechanism discussed in the next section, are promising as they do not require the molecules to be a specific shape/functionality. A promising related effect was observed by Haq et al. where a bis(imidazolyl) molecule could move along a track on a Cu(110) surface.[19]

A necessary condition for unidirectional motion is that the system must be driven out of equilibrium; therefore, just having an asymmetric diffusion potential is not sufficient for a system to exhibit thermally driven unidirectional motion, which would violate the 2nd law of thermodynamics.[42,43] Due to the small mass of molecules inertial effects are negligible compared to frictional effects. Thus, a constant driving force is needed to keep a molecule going without its direction being damped or randomized by thermal effects. Ratchet mechanisms can induce directional motion via an energy input that pulses the ratchet potential or controlled thermal energy variations that drive directional transport of particles along the ratchet.[44] One of the most relevant ratchet mechanisms to our studies is the temperature ratchet shown in Fig. 1. The system begins with particles trapped by energy barriers greater than kT. The temperature is increased, so that kT is greater than the barrier, allowing for random motion of the particles for a short time (much shorter than the time required for global equilibrium). The temperature is then lowered and the particles relax back down on the asymmetric potential energy landscape. The asymmetry of the ratchet means that after every heating/cooling cycle, there is a greater probability of a particle being trapped in the potential minima left of its position. Continued fluctuation of the temperature yields net unidirectional particle transport.

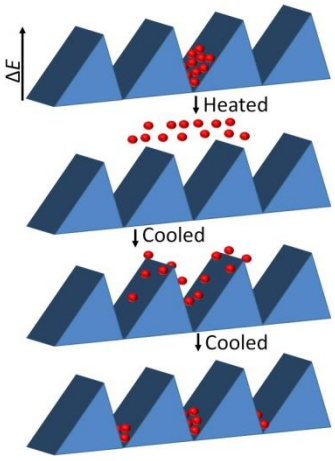


Fig. 1. Schematic of a temperature ratchet. Particles driven to the left.

Coupling asymmetric potential energy landscapes of individual molecules on surfaces with excitation by electrons in a temperature ratchet-like mechanism should enable directed molecular transport, separation, and enantiodifferentiation. This ratchet-like asymmetry in an adsorbed molecule's potential energy landscape can be induced by using stepped chiral surfaces or intrinsically chiral molecules on achiral surfaces. While current technological limitations mean that the electronic or vibrational states of a molecule is generally excited using electrons from a scanning tunneling microscope tip, this method allows for globally inducing directed motion of all the molecules on a surface is possible by coupling to the same modes either with a macroscopic electron or light source.

Towards this goal we report our attempts to produce unidirectional 1D molecular motion using surface features like step edges and lower symmetry facets. These systems have allowed us to confine the motion of several molecules to one dimension and to probe their motion as activated by tunneling electrons from a STM tip. We study the STM tip induced diffusion of various molecules at 5 K in order to trap individual molecules within the potential energy well by eliminating any random thermal motion.

2. Results and Discussion

2.1. Transport of achiral molecules on chiral surfaces

Our first experiments involved studying the motion of achiral molecules on the kinked step edges of chiral surfaces. The diffusion barriers around these chiral kinks have been shown to be asymmetric.[45,46] Chiral surfaces can be created by cutting single crystals to expose surfaces with

periodic arrays of steps, terraces, and kinks. Fig. 2b shows such a surface, the Cu(643)^{R} surface, which consists of small (111) terraces, step edges with a (100) orientation and (110) kinks.[47,48] As STM is a local measurement we initially use flat crystals for these experiments as they exhibit local steps running in all directions and a variety of naturally occurring chiral kinks.

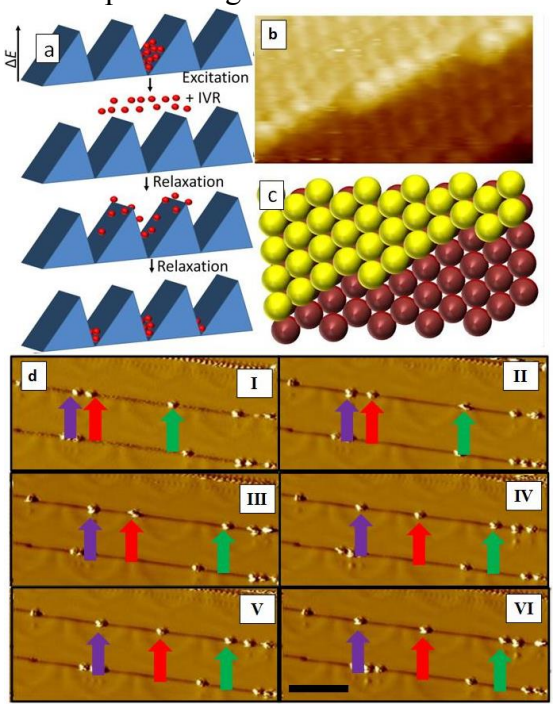


Fig. 2. (a) Temperature-like ratchet mechanism. (b) Atomically resolved STM image of a Cu(643)^{R} crystal step edge with two chiral kinks. (c). Schematic of same. Yellow atoms, top layer, red, second layer. (d) Select frames of a STM movie showing electrically induced diffusion of ethyl benzene molecules along steps on Au(111). Molecules, including those highlighted, exhibit preferential diffusion to the right. Scale bar = 10 nm

Fig. 2d shows 6-time lapse STM images of electrically excited ethylbenzene molecules bound to chiral step edges. At 5 K thermal diffusion does not occur and the system is electrically excited by rastering the STM tip over the surface at 400 mV. The molecules show a 70% preference for diffusion to the right of the image regardless of scanning direction.

Given that the step edges in this data set do not have a high chiral kink density and yet the molecules show a high degree of net unidirectional motion, the mechanism may be surface strain induced.[49,50] It is known that local surface strain can alter the magnitude, shape and symmetry diffusion barriers for adatoms.[51,52] The Au(111) native 22 × √3 or "herringbone reconstruction" is an elastic deformation of the positions of the surface atoms, regions in the vicinity of a chiral kink may have their strain network modified in a way that extends much further than a few atoms as would be expected on an unreconstructed surface. This may be the origin of the directional motion seen in Fig. 2d. These effects must be further explored by correlating the step type, kink density and degree of directed motion as a function of distance from a chiral kink in order to parse out the effect of the chiral kink itself and the local strain in the surface.

2.2. DFT motivation for transport of chiral molecules on low-symmetry surfaces

At the molecular scale, the addition of chirality is a useful method for introducing ratchet-like potential energy landscapes.[53,54] Chirality can arise when achiral molecules are bound to surfaces or from intrinsically chiral molecules. As mentioned, surfaces can also be chiral when their parent crystals are cut along low-symmetry axes exposing step edges that are kinked (see Fig. 2b and c).[48,55] The temperature ratchet mechanism should enable a degree of net directional molecular transport to be achieved when the molecules are excited and relax back onto their asymmetric potential energy landscape.

To interrogate the effect of molecular chirality on the energy landscape for diffusion we used DFT to investigate the diffusion of a chiral molecule, 1-phenylethanol, on a stepped Cu(322) surface. The results are shown below in Fig. 3 and reveal that the barrier to diffusion has a slight

asymmetry to it which, as previously discussed is a requirement for a functioning flashing temperature ratchet mechanism.

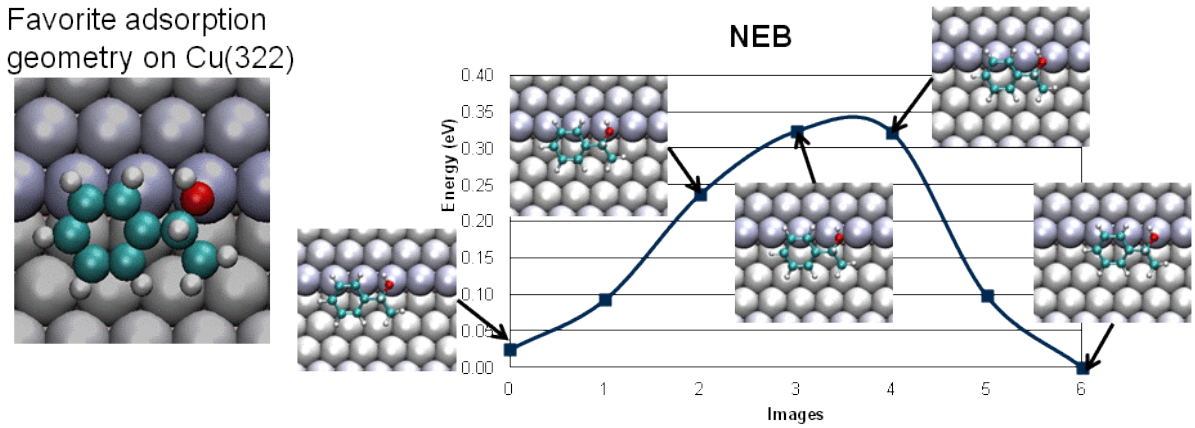


Fig. 3. Diffusion of 1-phenylethanol on Cu(322): The light blue color denote the step edge. The climbing image NEB assumed a translational diffusion along the step edge. There is an appreciable diffusion barrier that appears to be asymmetric.

2.3. Transport of chiral molecules on low-symmetry, achiral surfaces

Motivated by the DFT result and as a step towards inducing chiral separations, the electrically induced motion of intrinsically chiral molecules adsorbed on both flat and stepped surfaces have been studied. In order to first break the surface symmetry and restrict motion from 2D to 1D, stepped surfaces and (110) surfaces were used.

2.3.1. S-1-Phenylethanol on Cu(111) steps

S-1-phenylethanol was deposited on a Cu(111) surface with naturally occurring steps. Cu(111) exhibits two types of straight step facets: {111} and {100}. An STM image with adsorbed S-1-phenyethanol molecules (white protrusions) along {100} steps is shown in Fig. 4a. These steps do exhibit a few kinks where a majority of molecules adsorb and show no lateral movement along the step. The only molecule within the scan area that moves along an unkinked region of the step edge, as defined by the red lines, is highlighted with the black arrow in Fig. 4a. Translation of the molecule was tracked by taking a STM movie (400 frames) with select frames shown in the panels of Fig. 4b. We find that, during the course of the movie, the molecule took 59 downward steps versus 45 upward steps, potentially indicating a slight preference in directional motion. The distance of the 'hops' the molecule made between frames varied between 0.60 nm and 1.35 nm. More data and statistics are needed to fully determine whether direction preference exists in this system and are currently underway.

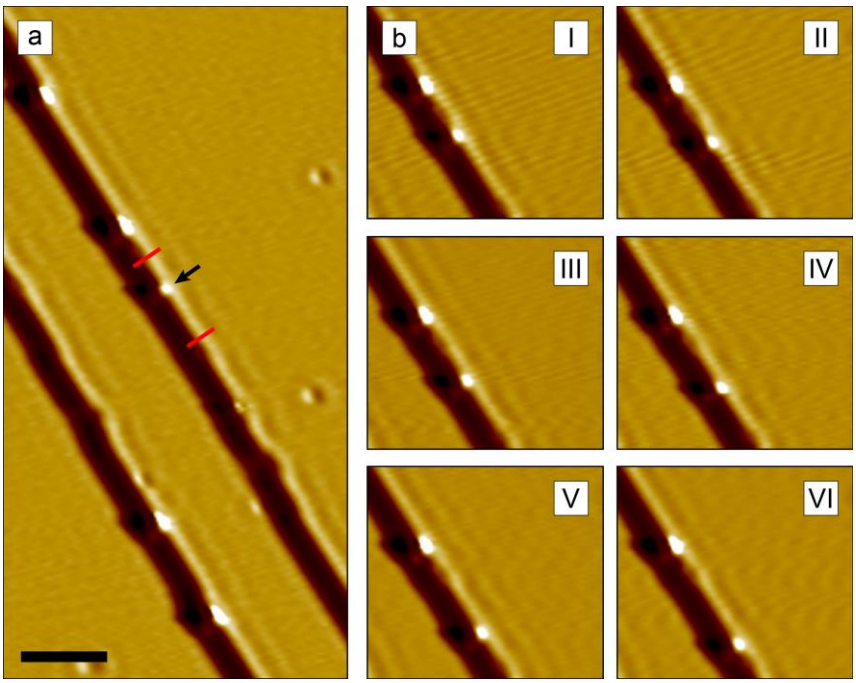


Fig. 4. (a) Derivative images of S-1-phenylethanol molecules adsorbed along Cu(111) steps. The red lines indicate the unkinked region of the step the molecule moves along and protrusions on terraces are adsorbed CO molecules. Scan condition: 300 mV and 1 nA. (b) Select frames of a STM movie showing diffusion of S-1-phenylethanol moving downward along a Cu(111) step. Scale bar = 5 nm.

2.3.2. R-1-Phenylethanol on Cu(111) steps

Au(110) single crystals, as shown in Fig. 5a, exhibit a (2×1) "missing row" reconstruction, exposing the 111 faceted rows along the $[1\bar{1}0]$ direction thereby breaking the surface symmetry and restricting molecular motion in 1D.[56,57] Very low concentrations (~0.02 L) of R-1-phenylethanol, a chiral alcohol, were deposited onto a Au(110) single crystal and probed with 5 K STM, shown in Fig. 5b. In order to probe directional motion, the C-H vibrational mode of the molecule was excited by the STM tip to activate translational motion via inelastic electron tunneling excitation of C-H stretching vibrations which can be excited with electrons of ~360 meV of energy.[58] Movies recorded and analyzed below 360 mV did not show evidence translational motion. Thus, STM movies up to 13 hours ~250 frames were recorded and analyzed at 380 mV, just above the C-H stretching frequency to study the onset of diffusion.

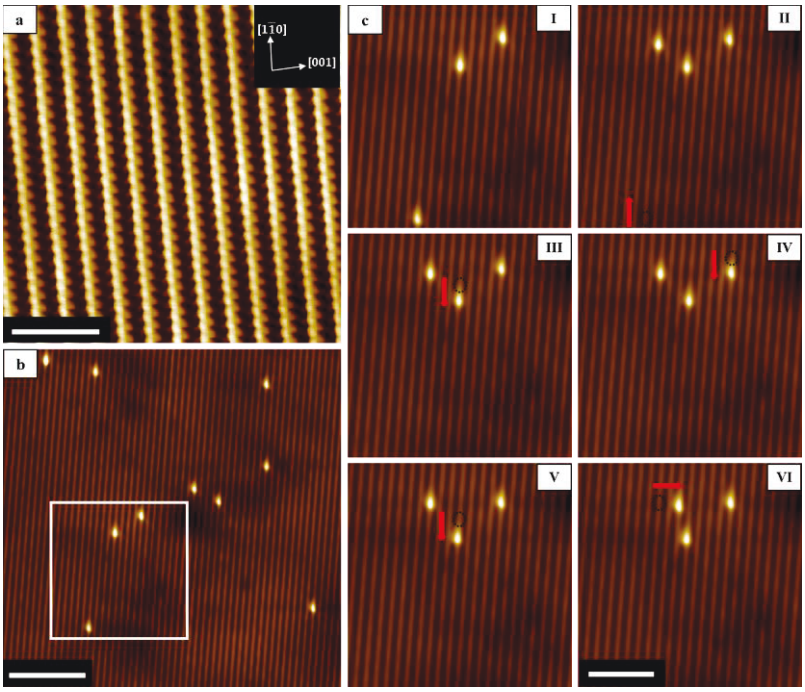


Fig. 5. (a) Atomically resolved STM image of Au(110) surface which exhibits the (2×1) reconstruction. Scale bar = 1 nm. (b) STM image of R-1-phenylethanol on Au(110). Scale bar = 10 nm. (c) Select frames of a STM movie showing electrically induced diffusion of three R-1-phenylethanol molecules on Au(110) terrace. The red arrow indicates the direction of diffusion. Scale bar = 5 nm.

Fig. 5c shows 6-time lapse STM images of electrically excited R-1-phenylethanol molecules on a Au(110) terrace. The scan direction is parallel to the [1$\bar{1}$0] direction of the surface. In this movie, three molecules show evidence of preferential diffusion along the [1$\bar{1}$0] direction. From frames I to II, the distance of the upward "hop" is 12.38 nm. The distance of downward "hops" varied between 0.84 nm and 1.01 nm in frames III-V. As shown in frame VI, the molecule also diffused along the [001] direction. Upon analysis of seven similar STM movies with 250–500 frames, there is strong evidence of electrically induced molecular motion on the surface, preferentially along the [1$\bar{1}$0] direction. The phenyl ring in the cyclic molecule may have several adsorption configurations on the surface, which may possibly alter the asymmetric potential resulting in random diffusion across the surface.

3. Conclusions

Control of the translational motion of individual molecules on surfaces is necessary for the development of novel methods for mass transport, separations, enantiopurifications and reactions, as well as in new applications including pumps, sensors, optoelectronics, and assembly. Therefore, fundamental new knowledge of the microscopic mechanisms underpinning the control of directional transport, separation and shuttling of molecules across surfaces will yield valuable design principles for the broader field of molecular machines and devices. Long term, understanding new mechanisms for the directional transport of molecules across surfaces but provide a completely novel means to separate different (even very subtly different) species in

a manner somewhat analogous to GC or HPLC. For example, once we understand the separate effects of molecular and surface chirality on directional transport, both can be combined. The motion of chiral molecules along a chirally kinked step edge is somewhat analogous to a HPLC chiral column, with diastereometric interactions between the molecules and chiral kinks. Thermally driven diffusion of chiral molecules on homochiral kinked step edges will yield different diffusion rates but importantly no net directionality as dictated by the 2nd law of thermodynamics. However, given the asymmetry of the energy landscapes and the different absolute binding strengths of R and S molecules to, for example, R kinks[59,60] there will be a possibility to experimentally address some very important questions about enantioselective molecular interactions with chiral surfaces, which underpin technologies like chiral separations and heterogeneous enantioselective catalysis.[59,61] This paper presents our initial attempts to confine molecular motion to 1D and introduce asymmetric potential energy landscapes via both surface and molecular chirality. While we have not observed any definitive examples of directed motion it appears that both surface step edges and lower symmetry surface facets are promising systems for confining molecular motion in 1D. Our DFT work reveals that chiral molecules at straight step edges have asymmetric potential energy landscapes for diffusion that may enable directed motion via a temperature ratchet-like mechanism.

4. Experimental

STM experiments were performed in an Omicron Nanotechnology GmbH low-temperature scanning tunneling microscope with a base pressure of $<1 \times 10^{-11}$ mbar. Au(111) and Cu(111) single crystals (MaTecK GmbH) were cleaned by cycles of Ar^+ bombardment and annealing to 1000 K. A Au(110) single crystal was cleaned in the same manner but was annealed up to 700 K. Cleanliness of the crystals was determined by STM prior to molecular deposition. All molecules investigated (ethylbenzene, S-1-phenylethanol, and R-1-phenylethanol) were purchased from Sigma-Aldrich and underwent several freeze-pump-thaw cycles prior to use. Each molecular species was introduced into the scanning chamber via a precision leak valve and vapor deposited (<1% ML) onto the crystal held at 5 K in the STM stage.

Periodic DFT calculations were performed with the Vienna *ab initio* simulation package.[62–66] Core-electron interactions were described with the projector augmented-wave (PAW) potential.[67,68] The electron-election exchange and correlation interactions were described with the PW91-GGA functional.[69] Calculations used a plane wave expansion cutoff of 500 eV. Structural optimization was performed by a conjugate gradient algorithm with a force stopping criterion of 0.03 eV/Å. Calculations employed $2 \times 2 \times 1$ *k*-points. The resolution in *k*-points was chosen to ensure adequate convergence while minimizing computational cost.

The stepped Cu(322) surface was modeled with $p(2 \times 6)$ surface unit cells. The model utilized a 7 Å slab with the bottommost 3 Å immobilized, and molecules were only adsorbed on the top side of the slab. Adjacent slabs were separated by vacuum spacing of 10 Å. Initial pathways with a set of five intermediate geometries were first optimized using the linear and mixed Cartesian approach in the Opt'nPath suite.[70] The optimized geometries obtained by Opt'nPath suite were then used as the initial geometries for nudged elastic band (NEB) calculation in VASP.[71]

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References and notes

1. Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chemi. Int. Ed.* **2007**, *46*, 72–191.
2. Kottas, G. S.; Clarke, L. I.; Horinek, D.; Michl, J. *Chem. Rev.* **2005**, *105*, 1281–1376.
3. Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174–179.
4. Koumura, N.; Zijlstra, R. W. J.; van Delden, R. A.; Harada, N.; Feringa, B. L. *Nature* **1999**, *401*, 152–155.
5. Fletcher, S. P.; Dumur, F.; Pollard, M. M.; Feringa, B. L. *Science* **2005**, *310*, 80–82.
6. Hernandez, J. V; Kay, E. R.; Leigh, D. A. *Science* **2004**, *306*, 1532–1537.
7. Hawthorne, M. F.; Zink, J. I.; Skelton, J. M.; Bayer, M. J.; Liu, C.; Livshits, E.; Baer, R.; Neuhauser, D. *Science* **2004**, *303*, 1849–1851.
8. Collier, C. P.; Wong, E. W.; Belohradsky, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, *285*, 391–394.
9. von Delius, M.; Geertsema, E. M.; Leigh, D. A. *Nat. Chem.* **2010**, *2*, 96–101.
10. Mo, Y. W. *Science* **1993**, *261*, 886–888.
11. Gimzewski, J. K.; Joachim, C.; Schlittler, R. R.; Langlais, V.; Tang, H.; Johannsen, I. *Science* **1998**, *281*, 531–533.
12. Stipe, B. C. *Science* **1998**, *279*, 1907–1909.
13. Rao, B. V; Kwon, K. Y.; Liu, A. W.; Bartels, L. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 17920–17923.
14. van Delden, R. A.; ter Wiel, M. K. J.; Pollard, M. M.; Vicario, J.; Koumura, N.; Feringa, B. L. *Nature* **2005**, *437*, 1337–1340.
15. Eelkema, R.; Pollard, M. M.; Vicario, J.; Katsonis, N.; Ramon, B. S.; Bastiaansen, C. W. M.; Broer, D. J.; Feringa, B. L. *Nature* **2006**, *440*, 163.
16. Chiaravalloti, F.; Gross, L.; Rieder, K.-H.; Stojkovic, S. M.; Gourdon, A.; Joachim, C.; Moresco, F. *Nat Mater* **2007**, *6*, 30–33.
17. Manzano, C.; Soe, W.-H.; Wong, H. S.; Ample, F.; Gourdon, A.; Chandrasekhar, N.; Joachim, C. *Nat Mater* **2009**, *8*, 576–579.
18. Perera, U. G. E.; Ample, F.; Kersell, H.; Zhang, Y.; Vives, G.; Echeverria, J.; Grisolia, M.; Rapenne, G.; Joachim, C.; Hla, S.-W. *Nat Nano* **2013**, *8*, 46–51.
19. Haq, S.; Wit, B.; Sang, H.; Floris, A.; Wang, Y.; Wang, J.; Perez-Garcia, L.; Kantorovitch, L.; Amabilino, D. B.; Raval, R. *Angew. Chemie - Int. Ed.* **2015**, *54*, 7101–7105.
20. Berna, J.; Leigh, D. A.; Lubomska, M.; Mendoza, S. M.; Perez, E. M.; Rudolf, P.; Teobaldi, G.; Zerbetto, F. *Nat. Mater.* **2005**, *4*, 704–710.
21. Chatterjee, M. N.; Kay, E. R.; Leigh, D. A. *J. Am. Chem. Soc.* **2006**, *128*, 4058–4073.
22. Khuong, T.-A. V; Nuñez, J. E.; Godinez, C. E.; Garcia-Garibay, M. *Acc. Chem. Res.*

2006, *39*, 413–422.
23. Juluri, B. K.; Kumar, A. S.; Liu, Y.; Ye, T.; Yang, Y.-W.; Flood, A. H.; Fang, L.; Stoddart, J. F.; Weiss, P. S.; Huang, T. J. *ACS Nano* **2009**, *3*, 291–300.
24. Coskun, A.; Banaszak, M.; Astumian, R. D.; Stoddart, J. F.; Grzybowski, B. A. *Chem. Soc. Rev.* **2012**, *41*, 19–30.
25. Lewandowski, B.; De Bo, G.; Ward, J. W. W.; Papmeyer, M.; Kuschel, S.; Aldegunde, M. J. J.; Gramlich, P. M. E. M. E.; Heckmann, D.; Goldup, S. M. M.; D'Souza, D. M.; Fernandes, A. E. E.; Leigh, D. A. A.; D'Souza, D. M.; Fernandes, A. E. E.; Leigh, D. A. A. *Science* **2013**, *339*, 189 LP-193.
26. Ohara, M.; Kim, Y.; Kawai, M. *Phys. Rev. B* **2008**, *78*, 201405.
27. Komeda, T.; Kim, Y.; Kawai, M.; Persson, B. N. J.; Ueba, H. *Science* **2002**, *295*, 2055–2058.
28. Backus, E. H. G.; Eichler, A.; Kleyn, A. W.; Bonn, M. *Science* **2005**, *310*, 1790–1793.
29. Paterson, S.; Allison, W.; Hedgeland, H.; Ellis, J.; Jardine, A. P. *Phys. Rev. Lett.* **2011**, *106*, 256101.
30. Rapenne, G. G. *Org. Biomol. Chem.* **2005**, *3*, 1165–1169.
31. Linderoth, T. R.; Horch, S.; Petersen, L.; Helveg, S.; Lægsgaard, E.; Stensgaard, I.; Besenbacher, F. *Phys. Rev. Lett.* **1999**, *82*, 1494–1497.
32. Schunack, M.; Linderoth, T. R.; Rosei, F.; Laegsgaard, E.; Stensgaard, I.; Besenbacher, F. *Phys. Rev. Lett.* **2002**, *88*,
33. Komeda, T.; Kim, Y.; Kawai, M. *Surf. Sci.* **2002**, *502–503*, 12–17.
34. Shirai, Y.; Osgood, A. J.; Zhao, Y.; Kelly, K. F.; Tour, J. M. *Nano Lett.* **2005**, *5*, 2330–2334.
35. Shirai, Y.; Osgood, A. J.; Zhao, Y.; Yao, Y.; Saudan, L.; Yang, H.; Yu-Hung, C.; Alemany, L. B.; Sasaki, T.; Morin, J.-F.; Guerrero, J. M.; Kelly, K. F.; Tour, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 4854–4864.
36. Kwon, K.-Y.; Wong, K. L.; Pawin, G.; Bartels, L.; Stolbov, S.; Rahman, T. S. *Phys. Rev. Lett.* **2005**, *95*, 166101.
37. Pawin, G.; Wong, K. L.; Kwon, K.-Y.; Frisbee, R. J.; Rahman, T. S.; Bartels, L. *J. Am. Chem. Soc.* **2008**, *130*, 15244–15245.
38. Cheng, Z.; Chu, E. S.; Sun, D.; Kim, D.; Zhu, Y.; Luo, M.; Pawin, G.; Wong, K. L.; Kwon, K.-Y.; Carp, R.; Marsella, M.; Bartels, L. *J. Am. Chem. Soc.* **2010**, *132*, 13578–13581.
39. Wong, K. L.; Pawin, G.; Kwon, K.-Y.; Lin, X.; Jiao, T.; Solanki, U.; Fawcett, R. H. J.; Bartels, L.; Stolbov, S.; Rahman, T. S. *Science* **2007**, *315*, 1391–1393.
40. Sykes, E. C. H. *Angew. Chemie Int. Ed.* **2012**, *51*, 4277–4278.
41. Kudernac, T.; Ruangsupapichat, N.; Parschau, M.; Macia, B.; Katsonis, N.; Harutyunyan, S. R.; Ernst, K.-H.; Feringa, B. L. *Nature* **2011**, *479*, 208–211.
42. Reimann, P.; Bartussek, R.; Haussler, R.; Hänggi, P.; Hanggi, P. *Phys. Lett. A* **1996**, *215*, 26–31.
43. Astumian, R. D. D. *Science* **1997**, *276*, 917–922.
44. Craig, E. M.; Zuckermann, M. J.; Linke, H. *Phys. Rev. E* **2006**, *73*,
45. Cox, E.; Li, M.; Chung, P.-W.; Ghosh, C.; Rahman, T. S.; Jenks, C. J.; Evans, J. W.; Thiel, P. A. *Phys. Rev. B* **2005**, *71*, 115414.
46. Maca, F.; Kotrla, M.; Trushin, O. *Surf. Sci.* **2000**, *456*, 579–583.
47. Gellman, A. J.; Horvath, J. D.; Buelow, M. T. *J. Mol. Catal. A Chem.* **2001**, *167*, 3–11.

48. Baber, A. E.; Gellman, A. J.; Sholl, D. S.; Sykes, E. C. H. *J. Phys. Chem. C* **2008**, *112*, 11086–11089.
49. Brune, H.; Bromann, K.; Röder, H.; Kern, K.; Jacobsen, J.; Stoltze, P.; Jacobsen, K.; Norskov, J. *Phys. Rev. B* **1995**, *52*, R14380–R14383.
50. Liu, Y. B.; Sun, D. Y.; Gong, X. G. *Surf. Sci.* **2002**, *498*, 337–342.
51. Schroeder, M.; Wolf, D. E. *Surf. Sci.* **1997**, *375*, 129–140.
52. Larsson, M. I.; Sabiryanov, R. F.; Cho, K.; Clemens, B. M. *Surf. Sci.* **2003**, *536*, L389–L395.
53. Pawin, G.; Wong, K. L.; Kwon, K.-Y.; Frisbee, R. J.; Rahman, T. S.; Bartels, L. *J. Am. Chem. Soc.* **2008**, *130*, 15244–15245.
54. Sonnleitner, T.; Swart, I.; Pavliček, N.; Pöllmann, A.; Repp, J. *Phys. Rev. Lett.* **2011**, *107*, 186103.
55. Gellman, A. J. *ACS Nano* **2010**, *4*, 5–10.
56. Binnig, G.; Rohrer, H.; Gerber, C.; Weibel, E. *Surf. Sci. Lett.* **1983**, *131*, L379–L384.
57. Linderoth, T. R. R.; Horch, S.; Lægsgaard, E.; Stensgaard, I.; Besenbacher, F.; Laegsgaard, E.; Stensgaard, I.; Besenbacher, F. *Phys. Rev. Lett.* **1997**, *78*, 4978–4981.
58. Gregory, S. *Phys. Rev. Lett.* **1990**, *64*, 689–692.
59. Horvath, J. D.; Koritnik, A.; Kamakoti, P.; Sholl, D. S.; Gellman, A. J. *J. Am. Chem. Soc.* **2004**, *126*, 14988–14994.
60. Horvath, J. D.; Gellman, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 2384–2392.
61. Baddeley, C. J. J. *Top. Catal.* **2003**, *25*, 17–28.
62. Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558–561.
63. Kresse, G.; Hafner, J. *Phys. Rev. B* **1994**, *49*, 14251–14269.
64. Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15–50.
65. Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186.
66. Sholl, D. S.; Steckel, J. (John Wiley & Sons, 2009).
67. Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953–17979.
68. Kresse, G. *Phys. Rev. B* **1999**, *59*, 1758–1775.
69. Perdew, J.; Chevary, J.; Vosko, S.; Jackson, K.; Pederson, M.; Singh, D.; Fiolhais, C. *Phys. Rev. B* **1993**, *48*, 4978–4978.
70. E, W.; Ren, W.; Vanden-Eijnden, E. *Phys. Rev. B* **2002**, *66*, 52301.
71. Mills, G.; Jonsson, H. *Surf. Sci.* **1995**, *324*, 42.