



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) faceted surfaces. Our results indicate that, with careful selection of components, 1D motion can be induced but that unidirectionality is still elusive.

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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} Along these lines, seminal work of 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 were then shown to be capable of rotating objects with near-macroscopic dimensions.¹⁵ These experiments were 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 CO₂ 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 example of using simple molecular design was reported by Haq et al. where a bis(imidazolyl) molecule could move along a

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track on a Cu(110) surface.¹⁹ Though this specific molecule did not perform unidirectionally, the authors state that unidirectional motion may be possible by slightly modifying walker mobility.

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} This is due to microscopic reversibility which dictates that despite the barrier being asymmetric, the barrier height is the same regardless of which direction it is crossed, therefore, at thermal equilibrium, particle transport occurs at the same rate in both directions. Furthermore, due to the small mass of molecules, inertial effects are negligible compared to damping effects like electronic and phononic friction. 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 Brownian motion of the particles from their initial position above the potential energy well for a short time (much shorter than the time required for global equilibrium). The temperature is then lowered and the particles relax back down into the potential wells. Due to the asymmetry of the potential energy landscape, there is a greater probability for the particles to relax into the potential well to the left of their original position. Therefore, continued fluctuation of the temperature yields net unidirectional particle transport.^{43,45}

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 enantio-differentiation. This ratchet-like asymmetry in an adsorbed molecule's potential energy landscape

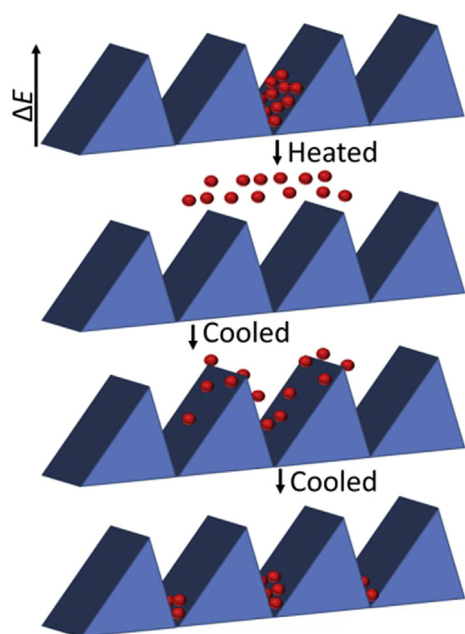


Fig. 1. Schematic of a temperature ratchet. Due to the asymmetry of the barriers, particles are driven to the left.

can be induced by using stepped chiral surfaces or intrinsically chiral molecules on achiral surfaces. These chiral adsorption configurations can result in asymmetric barriers to diffusion. While current technological limitations mean that the electronic or vibrational states of a molecule are generally excited using electrons from a scanning tunneling microscope tip, this approach could be harnessed to induce directed motion of all the molecules on a surface by coupling their same modes to either 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 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

As STM is a local measurement, we initially use flat crystals for these experiments as they exhibit local steps running in all directions and naturally occurring chiral kinks. Fig. 2 shows six time-lapse STM images of electrically excited ethylbenzene molecules bound to chiral step edges on Au(111). 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 to inelastically excite C–H modes in the molecule. 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.^{46,47} It is known that local surface strain can alter the magnitude, shape and symmetry diffusion barriers for adatoms.^{48,49} The Au(111) native $22 \times \sqrt{3}$ 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. 2. 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.^{50,51} 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, R-1-phenylethanol, on a stepped Cu(322) surface which provides (111) terraces and (100) microfacets like some steps on the Cu(111) 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. We note that the S enantiomer would produce mirror image diffusion barriers to the R enantiomer.

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