Regular Scanning Tunneling Microscope Tips can be Intrinsically Chiral

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We report our discovery that regular scanning tunneling microscope tips can themselves be chiral. This chirality leads to differences in electron tunneling efficiencies through left- and right-handed molecules, and, when using the tip to electrically excite molecular rotation, large differences in rotation rate were observed which correlated with molecular chirality. As scanning tunneling microscopy is a widely used technique, this result may have unforeseen consequences for the measurement of asymmetric surface phenomena in a variety of important fields.

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The study of chirality is ubiquitous in science, from the question of the origin of homochiral life to enantioselective drug production. Over the last decade, pioneering scanning probe studies have revealed that chiral recognition, separation, amplification, and transfer into supramolecular structures can all be tracked and understood at the single-molecule level [1–15]. Furthermore, theory has been used to predict many novel interactions between chiral molecules and electrons [16,17]. Herein we report the discovery that regular scanning tunneling microscope tips can themselves be chiral. This chirality leads to different electron tunneling efficiencies through left-handed and right-handed molecules. The effect manifests itself as small topographic height differences between the two chiralities. When using the tip to electrically excite molecular rotation, large differences in the rate of molecular rotation were observed that correlated with each individual molecule's chirality. While this work has major consequences for the study of two-dimensional chiral systems [1–5,7,9,11,14,18,19], more importantly it offers a new method for interrogating the effect of chirality on electron transport in a controlled manner, on a molecule-by-molecule basis.

Butyl methyl sulfide (BuSMe) is one of a family of thioether (RSR′) molecular rotors [20–22]. When adsorbed on the terrace of a (111) facet of a metal surface, thioethers rotate around the central sulfur-metal bond on a time scale much faster than that of STM imaging and appear hexagonal in shape due to the threefold symmetry of the underlying Cu(111) surface [Fig. 1(a)] [20–22]. BuSMe is achiral in the gas phase but, due to its asymmetry, has two prochiral lone pairs on the central *S* atom that give rise to chirality in the surface-bound molecules [see Fig. 1(b) for a schematic] [22–24]. Previous DFT studies have shown that binding occurs to a Au surface through one of the lone pairs on the sulfur atom and that the alkyl tails lie almost parallel to the surface [22]. The unbonded lone pair remains unperturbed and the geometry around the *S* atom is essentially tetrahedral; hence, left- and right-handed versions (enantiomers) of the prochiral molecule are formed with an inversion barrier between enantiomers that is calculated to be 0.24 eV. The rapidly rotating molecules can be clearly distinguished upon atomic-scale imaging by their mirror image pinwheel appearance on Cu(111) [25] (as seen in Fig. 1(a)] which arises from an off-center precession of the central *S* atom around the top of a surface atom with a precession diameter of 0.1 nm [22]. The left-handed and right-handed enantiomers are identified in this work using the Cahn-Ingold-Prelog priority rules commonly used for the assignment of the absolute configuration of groups around the stereocenter of a chiral molecule (*R* and *S* labels).

Just as one's right and left hands should have the same dimensions, one would expect the *R* and *S* enantiomers of surface-bound BuSMe to have the same widths and heights. Interestingly, careful measurements of the topographic heights of *R* and *S* molecules from STM images

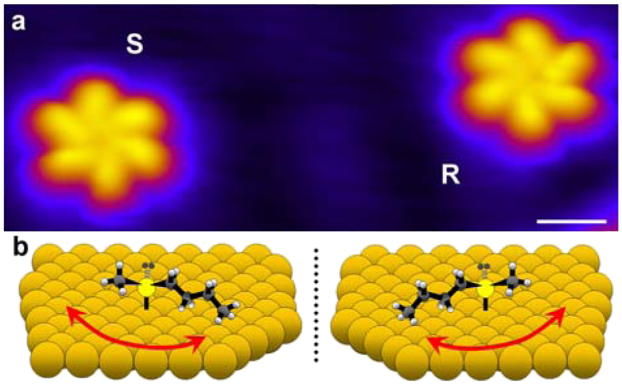

FIG. 1 (color online). Single-molecule chiral identification. (a) STM image of the two enantiomeric, mirror image forms (*R* and *S*) of BuSMe adsorbed on Cu(111). The pinwheel appearance of the molecule arises from the fast rotation of the alkyl groups around the central *S* atom. (b) Schematic showing that while BuSMe is achiral in the gas phase, adsorption on a surface results in two enantiomers depending on which of the prochiral lone pairs bonds to the surface [22]. (Imaging conditions: $I = 300$ pA, $V = 100$ mV, $T = 7$ K. Scale bar = 1 nm).

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revealed that, in any given experiment, either the *R* or *S* enantiomers would appear topographically higher. While any particular STM tip yielded reproducible height differences between the enantiomers, alteration of the tip state led to a different height difference. Changes in the tip state were produced in the form of minor alterations via voltage pulses (4–10 V) or surface indentations (~ 0.1–1 nm), or as major changes such as substitution of an entirely new tip. Figure 2(a) shows height difference data from ten representative STM tips revealing that, even with the relativity large error bars associated with such small height differences, either of the two enantiomers can appear higher with a given tip state and that some tips yield no discernable height difference. As the topographic heights of two enantiomers (*R* and *S*) measured with an achiral probe on an achiral surface must be the same, the only explanation for these results is that regular STM tips themselves can be chiral. Figure 2(b) shows a schematic in which the three atoms of the STM tip closest to the surface are colored, and a proposed tip trajectory for a chiral tip. Providing the last three or more atoms are at different heights above the surface, the three-point contact model predicts that a diastereomeric relationship exists between a surface-bound enantiomer and the tip. This diastereomeric interaction can lead to different electron tunneling efficiencies, and therefore topographic height differences. Just as bare metal surfaces can possess chirality due to the arrangement of atoms at kink sites [26,27] and metal nanoparticles can adopt chiral structures [28], we propose that bare metal STM tips can be chiral based on the arrangement of the atoms at the end of the tip.

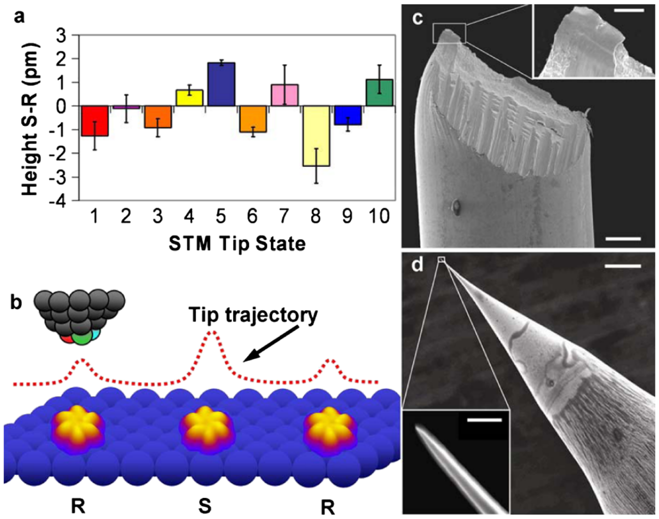

FIG. 2 (color online). (a) Graph of height difference between the *R* and *S* enantiomers of BuSMe on Cu(111) measured with ten different STM tip states revealing that regular STM tips can be intrinsically chiral. Height measurements for each tip state are taken for populations of >50 molecules. Error bars are reported to 1 standard deviation. (b) Schematic showing that if the last three or more atoms on the STM tip are different heights above the surface, then the three-point contact model leads to a diastereomeric relationship, different tunneling efficiencies, and the ability to differentiate between enantiomers based on their topographic height. (c) SEM images of a cut Pt/Ir STM tip. Scale bar $= 50\ \mu$m, inset $= 10\ \mu$m. (d) SEM images of an etched *W* STM tip. Scale bar $= 50\ \mu$m, inset $= 0.5\ \mu$m.

All the data in this Letter were taken with mechanically cut Pt/Ir tips of $Pt_{85}Ir_{15}$ composition, but we have obtained the same results with etched *W* tips (see supplementary information [29]). Importantly, these are the two most common types of STM tip used in research. Figs. 2(c) and 2(d) show scanning electron microscope (SEM) images of regular Pt/Ir and *W* STM tips. From these images it is apparent, especially for the cut Pt/Ir tip, that even at the microscopic level ($> 1000\times$ larger than the atoms through which tunneling occurs) the tip is an asymmetric entity. While atomic resolution is beyond the limit of SEMs, it is not unreasonable to expect that if more than one atom from the tip contributes to the tunneling current, as long as these atoms are not in a completely symmetrical geometric arrangement, the tunneling portion of the STM tip will be chiral.

This result is initially surprising given that the STM tip is normally considered to be a point source of electrons. However, well-known image artifacts arising from what are commonly referred to as ‘‘double’’ or ‘‘triple tips’’ are direct evidence for tunneling through more than one point (see supplementary information [29]). Our discovery indicates that a much more subtle version of this effect is also at play and only manifests itself when studying chiral molecules with very high spatial resolution.

As further evidence for this phenomenon a second set of experiments was conducted in which the rate of electrically driven rotation of *R* and *S* enantiomers was measured with the same STM tip. If the STM tip was achiral one would expect identical rates of rotation of *R* and *S* rotors for the same excitation conditions. The rotation of the molecules was both driven and measured by the electron tunneling current using a method described previously [21]. Briefly, by hovering the STM tip to side of a molecule with the feedback loop switched off, rotational events could be monitored as changes in the tunneling current. For each STM tip between 10^3 and 10^5 molecular rotational events were recorded and quantified, and a rotation rate was calculated. Our previous work has shown that this electrically-excited rotation is driven by electrons of energy >0.37 eV via excitation of a C-H vibration that in turn couples selectively to the rotation of the molecule [21].

Table I shows rotational rates for the *R* and *S* rotor enantiomers acquired using four different tip states. Extreme care was taken to ensure that the tip state remained unchanged for the duration of each experiment. Any STM tip changes during the measurement were readily observed as changes in the baseline tunneling current

TABLE I. Rotational rate (Hz) for each enantiomer as a function of STM tip state. All rate data are taken at identical tunneling conditions: 380 mV, 5 pA. Error bars are reported to 1 standard deviation.

Tip State	A	B	C	D
R enantiomer	30 ± 10	50 ± 20	30 ± 10	63 ± 9
S enantiomer	70 ± 20	82 ± 9	25 ± 7	40 ± 10

during electrical excitation. Immediately apparent from Table I is that the rotational rate is highly tip state dependent. All of these rate measurements were made using the same tunneling current and voltage; therefore, the overall rotational rate differences from tip state to tip state must be due differences in the inelastic electron tunneling efficiency of the tips. This effect of variations in coupling efficiencies for different STM tips has been observed previously when exciting vibrational or rotational motions [30]. Next, and most importantly, it is apparent that for a given tip state one of the enantiomers spins more quickly than the other. While the stochastic nature of single-molecule experiments leads to wide distributions in rotation rates that translate into large error bars, histograms of the same data (see supplementary information [29]) reveal that the average rate for a given tip state is markedly different for the *R* and *S* enantiomers. Just as with the height difference data, the only way to explain how identical electrical excitation of two surface-bound enantiomers can lead to different physical rates is via a diastereomeric interaction with a chiral entity, i.e., the STM tip.

It is initially somewhat surprising that in the ~30 years since STM was invented it has never been reported that regular STM tips can be intrinsically chiral. However, this quandary can be rationalized by the fact that the magnitude of the effect in a normal topographic imaging mode (1–2 pm) is below the detection limit of most instruments (typically >5 pm). These results have great significance for all surface studies of chirality given that the role of the scanning probe tip is often considered as merely a spectator. The fact that single enantiomers can be distinguished based solely on height measurements from a topographic image without functionalizing the tip yields a new method for chirality to be identified for a set of surface-bound enantiomers in a single-molecule version of Pasteur's famous experiment [31]. As the BuSMe molecule's chirality can be gleaned from its pinwheel appearance, it may be a useful "chirality standard" by which a STM tip's chirality can be assessed via height measurements. Of equal or potentially more importance is the result that this subtle tip chirality, not measurable by most STM instruments, can have a large effect on the dynamics of a probed chiral molecule. We have demonstrated that the diasteromerism arising from the interaction of a chiral tip and a molecule can lead to large differences in inelastic electron-induced dynamics of the enantiomers. This is another important consideration in the study of chiral surface systems and potentially offers a novel way to study enantiospecific interactions and the effect of chirality on electron transport at the single-molecule level.

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