

Summer Scholar Report

Observing and Controlling Molecular Rotors and Motors at the Atomic Scale

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Introduction. Sources of microscopic biological motion include flagellar motors and kinesin and myosin on actin filaments which are driven by chemical phenomena such as proton and sodium gradients, or conformational changes due to ATP binding.¹ Lately, some studies have elucidated the mechanisms for such motion in biological systems.² In a very different approach simple synthetic systems have been devised in order to study chemical and photon-driven molecular motion in an understandable manner. In recent work, using scanning tunneling microscopy (STM), we demonstrated a synthetic, electrically driven single-molecule motor with up to 5% directionality.³ This was accomplished by using butyl methyl sulfide (BMS) on Cu(111) and a chiral tungsten STM electrode. The BMS molecule adsorbs to the surface via one of two lone pairs of the central sulfur atom and rotates about this sulfur-copper bond, which we observe using ultra high vacuum low-temperature STM (UHV LT-STM). Because the speed of rotation (on the order of 50 Hz) is faster than the imaging capabilities of the instrument (~ 0.01 Hz),⁴ the molecule appears as six lobes as dictated by the meta-stable residence of the molecule in six equivalent energetic minima on the Cu(111) surface. Additionally, although the molecule is achiral in the gas phase, adsorption to the surface generates chirality in the system, causing the molecule's lobes to image asymmetrically, like a so-called "pinwheel." We have posited that this chirality imparts a bias critical to a driving mechanism informed by the model of a flashing temperature ratchet and vibrational excitation dynamics.³

To extend this proof of principle study, we are exploring rotor ligands with more complex functionality or geometry than those of linear aliphatic ligands—a process of so-called "chemical tuning." If manufactured, a precise arrangement of motors on a metal surface, such that the rotation of one molecule can propagate throughout the array, will lead to pathways for unobtrusive sensing, fluid pumps and other novel molecular electronics.⁵⁻⁷ The most obvious place to begin seeking this sort of intermolecular cooperation is in dipole-dipole interactions. Three functionally distinct systems are herein described on single-crystal metal surfaces. In the first, the presence of a phenyl group lends both dipolar character and opportunity for π - π interactions. In the second, a hydroxide group has potential to retard rotation due to oxygen lone-pairs interacting with the metal surface and yield stronger rotor-rotor interactions. Finally, in the third system, chiral branched functionality could, by the current mechanism, lead to heightened anisotropic directionality and potentially the formation of enantiopure molecular motor arrays.

Experimental. All data have been acquired with an Omicron UHV LT-STM at a temperature of either 5 or 80 K. Pre-deposition, high-energy Ar ion sputtering and annealing

cycles were performed to ensure the cleanliness of the Cu and Au single crystals. All chemicals were purchased from Sigma-Aldrich, Inc. at $\geq 98\%$ purity and further purified *in situ* by freeze-pump-thaw cycles. In all cases, an etched W metal electrode ("tip") was used to probe the system.

Results and Discussion. The first molecule studied, phenyl methyl sulfide (thioanisole), has a dipole moment of 1.38 D (Debye).⁸ Deposited on both Cu(111) and Au(111) at low coverage (~ 0.17 mono layer), the molecule is expected to exhibit a six-lobed pinwheel-like configuration; however, the imaged molecules do not display any obvious asymmetry and rarely the expected six lobes—more regularly, four lobes resolve (Figure 1). The effect could be attributed to the fact that a transition from the molecule's naturally planar structure⁹ to a parallel ring-to-metal structure requires surmounting an energy barrier greater than the energy gained by electron donation from π molecular orbitals to the surface. Note that the molecule in such a perpendicular orientation interacts less strongly with the metal surface through radial phenyl hydrogen atoms than it does through the hybridized carbon atoms. Additionally, the steric strain generated by a thioanisole ring oriented perpendicular to the metal surface is highly unfavorable. This hypothesis is further substantiated at increased surface coverage where, despite displaying the expected intermolecular ordering, rows terminate in an unconventionally smooth, rounded pattern. This directly suggests that the phenyl rings stack roughly perpendicular to the surface, in order to maximize π - π interactions. Conversely, this structure is not found in small thioethers with aliphatic ligands, which instead terminate abruptly.¹⁰ Although high-coverage ordering of the thioanisole system is intriguing, the absence of obvious 2D chirality renders the system untenable in the short term for quantifying rotor dynamics in search of anisotropic directionality. Future work is needed to ascertain the binding site of thioanisole and, in doing so, give reason for the rare manifestation of chirality.

In an attempt to elucidate the utility of a strong dipole moment in coupling rotors, 3-(methylthio)propanol was studied. This is a lesser studied molecule but fits in the character of molecules to be studied for motor-like properties as it has limited functionality and dipolar character. A thorough search of the literature did not yield a value for the dipole moment for 3-(methylthio)propanol, yet it is similar, with respect to the quantity in question, to 1-propanol. The assumption of similar dipole moments can be justified by the negligible difference in electronegativity between sulfur and carbon, such that this substitution should not engender a difference in electron density distribution across the molecule. Therefore, as a reference point, 1-propanol has a gas phase dipole moment of 1.65 D.¹¹

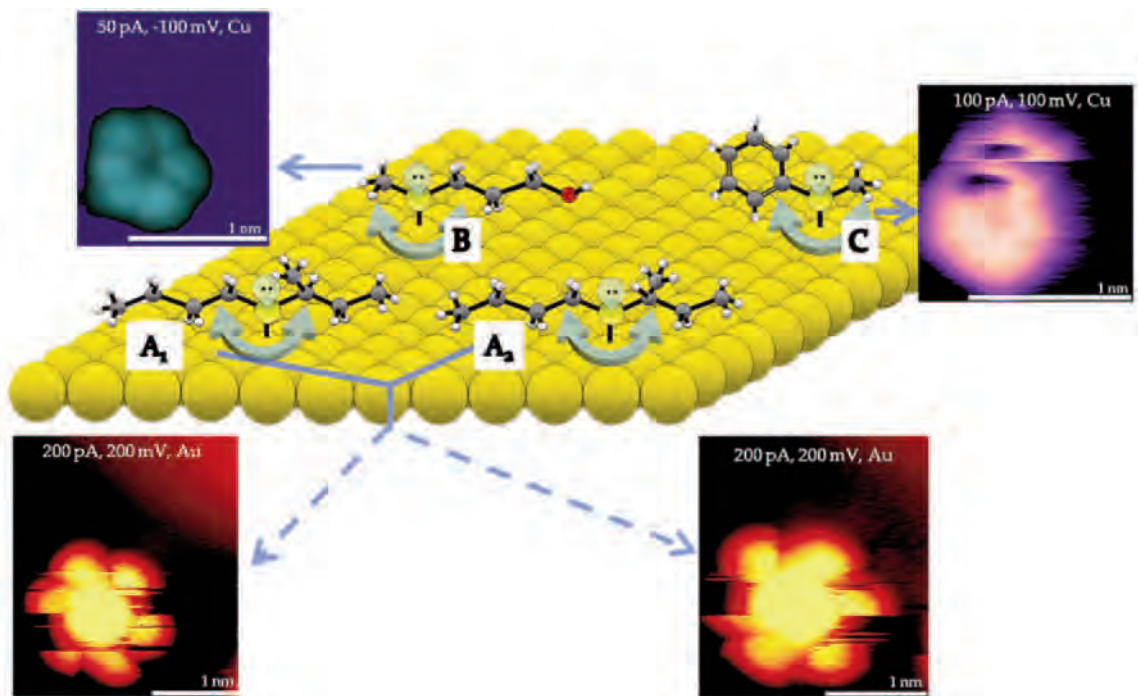


Figure 1. Schematic representation of the interrogated molecules adsorbed on an ambiguous (111) surface. A1 and A2 are butyl sec-butyl sulfide molecules of different handedness at the sec-butyl α -carbon. B is 3-(methylthio)propanol and C is thioanisole. Arrows indicate axes of rotation.

Exposure of the Cu(111) and Au(111) crystals to 10^{-9} mbar of 3-(methylthio)propanol for 30 seconds gives a partial monolayer (0.09 ML). At such a coverage, 3-(methylthio)propanol images as a six-lobed rotor species on both Cu and Au (Figure 1). Although some asymmetry in the lobes is often evident, it is inconsistent and does not resemble a pinwheel structure; therefore, chirality has not been assigned. Thus, again, the lack of obvious 2D chirality hindered the use of a molecule for rotational dynamics studies. The molecular coverage was increased to 0.18 ML and the sample was annealed to roughly 34 K, causing the mole-

cules to aggregate into small H-bonded motifs composed of 4, 5 and 6 molecules (Figure 2). Further investigation of 3-(methylthio)propanol at high coverage would reveal whether these networks truly form a 2D inverse micelle with hydrophilic hydroxide groups that drive nucleation and radial non-polar tails. Such a structure would be of use in nanoscale surface functionalization.

We subsequently proceeded to tune the rotors in yet another way by studying the branched aliphatic butyl sec-butyl sulfide (BsBS). A structural isomer of dibutyl sulfide and a chiral molecule in the gas phase, BsBS has a geometric profile yet uninvestigated under our dynamics framework. At sub-monolayer coverage on Au, 2D chirality manifests itself as the pinwheel shape (Figure 1). Two ambiguities present themselves in these images: first is the bright center of the rotors. It is reasonable to posit that this corresponds with the methyl group of the sec-butyl chain projecting towards the sulfur atom and, being closer to the STM tip, generating a brighter image. The second ambiguity lies in the absolute chirality of these rotors. As the molecule is chiral in the gas phase and, upon adsorption through a dative bond, the sulfur atom takes on chirality, theory predicts the presence of two BsBS enantiomers and two BsBS diastereomers. Because the dosed gas is a racemate, it is impossible to determine the absolute chirality of the observed molecules without further control of the system. To this end, we have requested the synthesis of the enantiopure BsBS by the Kumar group of Tufts University.

Although the absolute conformation of the imaged

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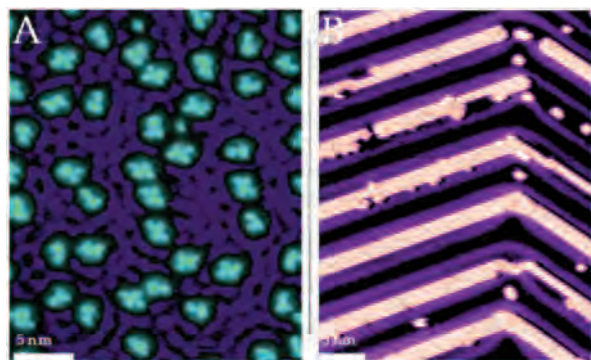


Figure 2. (A) 3-(methylthio)propanol at $\sim 17.5\%$ coverage on Cu(111) after anneal to 120 K. Scanning conditions: $T = 5$ K, $I_t = 40$ pA, $V_s = 100$ mV. (B) Thioanisole at $\sim 26.9\%$ coverage on reconstructed Au(111). Preferred binding occurs on fcc domains. Scanning conditions: $T = 80$ K, $I_t = 15$ pA, $V_s = 500$ mV.

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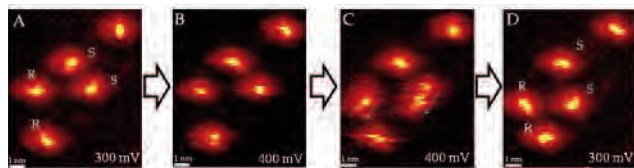


Figure 3. Sequential STM images taken on Cu(111) depicting the onset of rotation (indicated by streaky imaging) in chiral BsBS adsorbates with increase of bias voltage above the C-H resonant, rotation-inducing energy of 360 meV. (A) displays four single molecules of identifiable chirality. After rotation (B,C) and migration (C), the rotors cease to rotate with sub-resonance voltage and chirality is again identifiable. Imaging conditions: $T = 5$ K, $I_t = 200$ pA.

adsorbates has yet to be elucidated, previous work suggests some paradigms and relative assignments are still valid (Figure 3). It is clear, after all, that some part of the conformation is of opposite stereochemistry. A critical quantification in investigating the dynamics of chiral single-molecule rotors is how resiliently they maintain a given chirality. There is some probability in all such thioether systems that chirality could invert, involving a full dissociation of the sulfur-metal bond and subsequent bonding through the alternate lone-pair. While BsBS is relatively static at non-perturbative scanning conditions, the molecules experience ~ 375 meV when electronic coupling to a C-H stretch induces rotation—energy which could redistribute into chiral inversion.^{4,12} Figure 3 displays an experiment wherein a group of BsBS molecules were distributed across the Cu surface and, over the course of four consecutive images (~ 120 seconds/image), the scanning voltage was ramped from 300 mV in 3A to 400 mV in 3B and 3C, and back to non-perturbative 300 mV scanning conditions in 3D. The rotors here do not display lobes when rotating, but the streakiness of the images indicates that the rotational speed is faster than the timescale of imaging (i.e. this is an alternative version of the pinwheel motif). It is important to note that although the vibrationally excited molecules rotate and migrate across the Cu surface in C, when scanned in D, they maintain their chirality. The experiment described above suggests that the energetic barrier to chirality inversion is greater than that to rotation or migration (or that the probability of coupling to chirality inversion is very small)—either way a positive result when interrogating the molecules for motor applications. This, as well as preferential binding between diastereomers, could be further substantiated by density functional theory (DFT) calculations; however, the lengths of the butyl and *sec*-butyl ligands demand a slab of enough Cu atoms that the calculations would be impractically time-consuming. Therefore, we have requested that the Sholl group at Georgia Institute of Technology explore a smaller analogue, methyl *sec*-butyl sulfide.

During the course of experiments with BsBS, perturbative currents of 20 nA ($\sim 100\times$ normal scanning current for

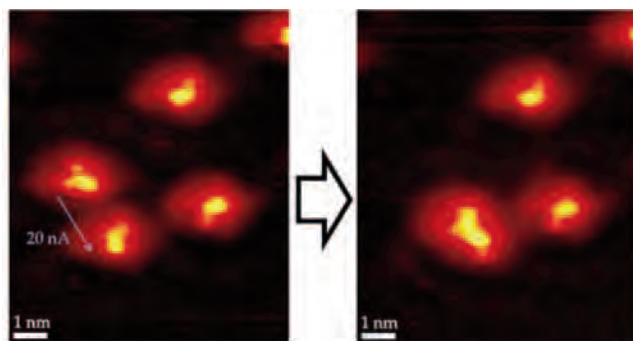


Figure 4. Using perturbative current (20 nA), one BsBS molecule is dragged with the W STM tip towards another, inducing the dimer seen at right. Imaging conditions: $T = 5$ K, $I_t = 400$ pA, $V_s = 300$ mV.

this system) were used to drag individual molecules across the crystal surfaces to either form or disrupt molecular assemblies (Figure 4). Beyond the intrigue of manipulating single molecules, the practice of doing so indicates a labile sulfur-metal bond, amenable to chemical modification.

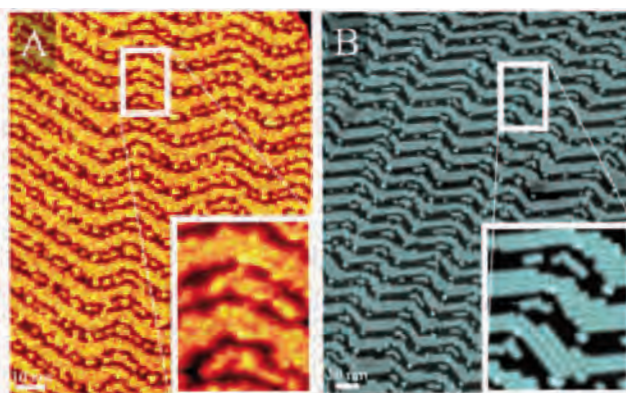


Figure 5. At left, BsBS and at right, dibutyl sulfide at high coverage ~ 0.7 ML on Au(111). Imaging conditions— $T = 80$ K; BsBS: $I_t = 50$ pA, $V_s = 500$ mV; DBS: $I_t = 30$ pA, $V_s = -30$ mV.

High-coverage data was also taken for BsBS (Figure 5A) wherein the intermolecular disorder shown for the BsBS system contrasts sharply with the order of its linear structural isomer, dibutyl sulfide (Figure 5B). The disorder could be due to branching in the *sec*-butyl chain or due to the presence of multiple conformers on the surface. The strongest step towards elucidating this difference will be experimenting with enantiopure BsBS.

Conclusions. The results discussed suggest that studying the rotational dynamics of more functionally complex thioether molecules (in comparison with butyl methyl sulfide) introduces new intricacies in the overall system, such that certain molecules do not fit into the current framework which correlates chirality to directed motion. Due to our confidence in the versatility of our framework, we proceed

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with chemical tuning until appropriate molecules are found. BsBS is one such molecule and will garner further study upon the generation of the enantiopure compound and DFT results for its analogue. Experiments using the enantiopure molecule will yield current vs. time curves correlated to absolute chirality—a correlation necessary to generate precise rotational dynamics conclusions that will augment the current body of knowledge concerning single- molecule motors. Evidence of only two of four possible conformers indicates that there may be a preferential binding conformation due to chirality at the *sec*-butyl α -carbon, which would lend itself to studies as a vector for enantioselective synthesis and surface patterning. These studies will proceed as soon as the necessary chemical and theoretical resources are made available.

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