Molecular Rotors and Motors: Recent Advances and Future Challenges

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ABSTRACT At the "Molecular Rotors and Motors" symposium of the Spring 2009 ACS National Meeting in Salt Lake City (March 22–26), a diverse mix of talks addressed many current issues in the field. Speakers described topics that varied from single-molecule rotors and nanomachines to exquisite synthetic approaches toward building functional materials and mathematical and computational methods aimed at uncovering design opportunities and highlighting the fundamental limitations of molecular motors. While the realization of building useful nanomachines remains far off, a general consensus abounded that investigating biological systems and understanding the implications of the laws of thermodynamics and quantum mechanics for the behavior of nanostructures will help drive important advances in the quest for molecular machinery. Molecular rotors were demonstrated to have practical applications as probes for microviscosity, and many speakers presented experimental studies that indicated that highly directed translation and rotation of individual molecules, as well as interacting dipolar arrays, are just around the corner. While this Nano Focus is not intended to be a comprehensive review of the subject, it will focus on several key advances that were presented at the ACS meeting and highlight future challenges for the field of molecular rotors and motors.

To view a select number of talks from the "Molecular Rotors and Motors" symposium, visit http://www.softconference.com/acschem/.

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Molecular motors are everywhere in nature; they exhibit functions as varied as organizing the cellular cytoplasm by vesicle transport to powering the motion of cells and even driving whole body locomotion *via* muscle contraction.[1] In stark contrast, current synthetic devices, with the exception of liquid crystals, make no use of nanoscale molecular motion. This is partly due to a gap in the understanding of how individual molecular components behave in the face of opposing forces such as friction, thermal fluctuations, and coupling to neighboring molecules. The "Molecular Rotors and Motors" symposium at the Spring 2009 ACS National Meeting in Salt Lake City brought together a wide range of experimentalists and theorists interested in aspects of molecular rotation. This article serves as a brief summary of the symposium with a focus on some of the most exciting advances in the area put in a broader context of the field of molecular rotors and motors.

Ensemble Measurements of Molecular Rotors and Motors in Solution. The vast majority of the current understanding of molecular rotors has been generated by synthesizing complex organic structures and studying their properties in solution.[2–5] In 1994, Kelly *et al.* designed and built a molecular "brake" using a molecule that would complex reversibly with Hg^{2+} ions and restrict the rotation about a single bond.[6] A few years later, the group created a solution-phase molecular version of Feynman's ratchet and pawl (Figure 1).[7] The molecules were designed to have an asymmetric torsional potential and exhibit directional motion; however, ^{1}H NMR experiments showed that they rotated in both directions as no external source of energy was supplied. Kelly then achieved 120° unidirectional motion using a similar ratchet structure coupled with a chemical reaction to supply energy, in order to obey the second law of thermodynamics.[8,9]

The Feringa group is another key player in the field.[13] Speaker Gregory Carroll, a postdoctoral researcher in the group, described the group's achievements over the last 10 years while focusing on the most recent results and future goals. In 1997, the Feringa group designed a molecular brake similar to the Kelly system in which the rate of rotation could be varied by altering the position of a nearby group *via* a *cis–trans* isomerization.[14] In 1999, Feringa and co-workers reported a light-driven unidirectional molecular motor that utilized chiral helicity of the molecule and produced 360° unidirectional motion around a double bond upon irradiation with light, coupled with thermally activated relaxation steps.[15] The group then designed a second-generation motor in which all thermal steps were at the same temperature and the molecule could be bound to surfaces *via* a thioether linker.[16,17] While the initial system proved to be very slow, by tuning the exact structure of the molecular motors, a maximum rotation rate of 3 MHz at room temperature was recently demonstrated
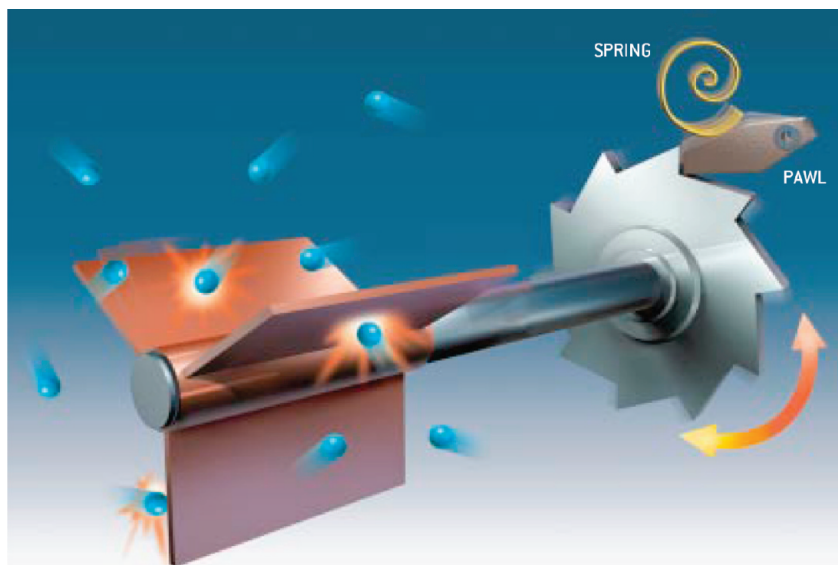
Figure 1. Artistic rendering of a ratchet mechanism originally studied by physicist Richard Feynman, synthesized by T. Ross Kelly *et al.*[7] and discussed theoretically during the "Molecular Rotors and Motors" symposium by speaker Dean Astumian.[10−12] Published from ref 10. Copyright 2001 Scientific American, Inc.

> In nature, motors operate at interfaces and thus surface-mounted rotors offer the most potential for nanoscience.

(Figure 2).[18] The group has since focused on surface-mounted rotors with a view toward controlling macroscopic surface properties, as discussed in the next section.

Very recently, molecular rotors have been used to measure microviscosity in liquids and, perhaps, most importantly, in living cells, in which microviscosity has been linked to disease and malfunction.[19−22] It is straightforward to measure macroscopic viscosity; however, microviscosity is difficult to quantify. Knowing the viscosity of microscopic objects such as cells is vital to understanding the flow of chemicals and other biomolecular processes. Mark Haidekker described his collaboration with Emmanuel Theodorakis in which they used simple synthetic molecular rotors to monitor viscosity with preci-

sion that rivals (and in some cases surpasses) commercial viscosity sensors. The sensor operates by exciting a fluorescent rotor molecule, which then decays by either (1) emitting radiation or (2) coupling to intramolecular rotation in a ratio that depends on the free volume (microviscosity) of the local environment.[19,20] Figure 3 shows another interesting application for viscosity-sensing molecular rotors in which fluid flow can be probed noninvasively in real time.[19]

Ensemble Studies of Rotors and Motors on Surfaces. In nature, motors operate at interfaces and thus *surface*-mounted rotors offer the most potential for nanoscience.[3] Therefore, mastering the properties of surface-bound rotors is the next logical step toward harnessing their utility. Studying the rotation of

molecules bound to surfaces offers the advantage that a single layer can be assembled and monitored using the tools of surface science. This approach opens up the possibility to engineer artificial molecular machinery that can respond to electrical and optical stimuli and perform useful work such as driving fluid flow. It also allows for the study of coupling between dipolar molecules and the investigation of collective phenomena.

After describing earlier solution-phase work on molecular rotors, Gregory Carroll discussed the Feringa group's work on liquid-crystal (LC) films doped with 1% of their light-driven unidirectional molecular motor. Upon irradiation, a glass rod with near-macroscopic dimensions (28 μm long) supported on the LC film could be rotated unidirectionally for a short period of time before steady state was reached.[17,23] This experiment is the first demonstration of collective rotations of molecules driving macroscopic motion and illustrates the great potential for incorporation of molecular machines into useful devices.

Josef Michl's interests[3,24,25] are in high-frequency (>GHz) motion of surface-mounted molecular rotors with possible ultimate applications in nanoelectronics and nanofluidics. He summarized prior work, which involved both molecular dynamics computations[26] and experiments, and reported progress toward the fabrication of regular arrays of dipolar rotors that are described briefly below. The molecular dynamics simulations examined driving mo-
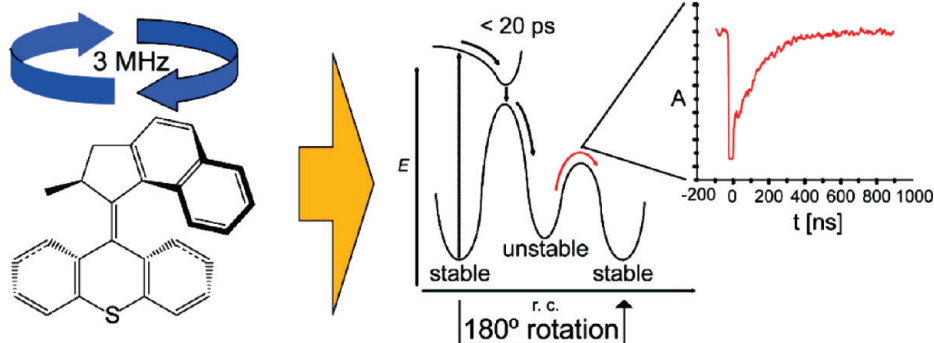

Figure 2. Molecular motor capable of photodriven unidirectional rotation at 3 MHz.[18] Republished from ref 18. Copyright 2008 American Chemical Society.
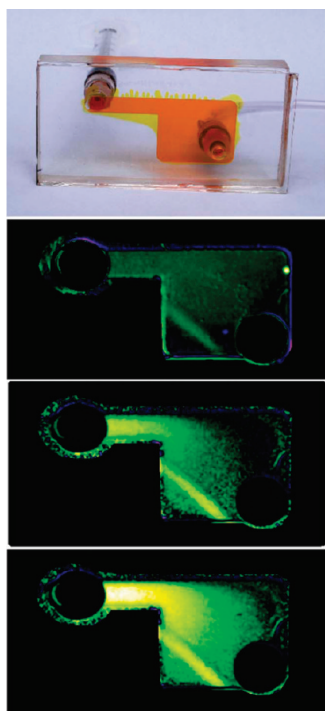
Figure 3. Fluorescence patterns in a flow chamber where fluid flow enters a wide basin from a narrow channel. The photographs show the fluorescence emanating from molecular rotors seeded in the liquid. The relationship between fluid velocity and fluorescence intensity can be observed directly.[19] Published with permission from ref 19. Copyright 2007 The Royal Society of Chemistry.

lecular rotors by directed fluid flow,[27] by electric field,[28−30] and by light.[26] Particular emphasis was placed on exploring the effects of thermal motion and mechanical friction, including electronic friction, which is crucial when a dipolar rotor is mounted on a metal.[29] These molecular dynamics simulations illustrated the difference between the Brownian and directed regimes of unidirectional molecular rotation induced by electric fields. As shown in Figure 4a, gradual increase in rotor temperature from very low to room temperature im-
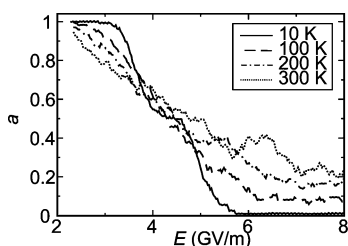

Figure 4. The average lag $a(E)$ of a molecular rotor at a driving frequency of 90 GHz as a function of field strength.[29] Published with permission from ref 29. Copyright 2005 National Academy of Sciences.

proves the performance of a rotor operating in the Brownian regime (in a relatively weak oscillating electric field) but hinders the performance of a rotor operating in the driven regime (in a strong electric field). The experimental work presented by Michl ranged from an initial examination of essentially noninteracting rotors randomly deposited on a quartz surface[31] to the study of one individual molecular rotor at a time.[32,33]

In another surface science talk, Laura Clarke described how dielectric spectroscopy can also be used to quantify and to understand the molecular motions of siloxane-based self-assembled monolayers as a function of both their chemistry and packing density and hinted that this method may be useful for uncovering complex phenomena that occur in both two- and three-dimensional polymers.[34]

Single-Molecule Studies of Rotors on Surfaces. Just over 10 years ago, Gimzewski and co-workers performed the first study of the rotation of a single molecule. They found that individual porphyrins embedded in a network could be manipulated into vacancies where they spun fast at room temperature (>30 kHz) and then reversibly locked back into position in the network.[35] Apart from porphyrins, there is only a small amount of data on the rotation of surface-bound molecules.[36−41] Ludwig Bartels described his group's study of halogenated thiophenol molecules on a Cu{111} surface, which function as single-molecule rotors.[42,43] They found that the molecules rotate freely at temperatures as low as 15 K until the S−H bond is cleaved by tunneling electrons and rotation ceases. Bartels explained that, by altering the chemical functionality of the rotor, the rate of electron-induced S−H cleavage could be altered. The group found that the relationship between different substituents on the phenyl group of the rotor and the ease with which the S−H bond could be cleaved could be simply explained using the Hammett equation.[43]

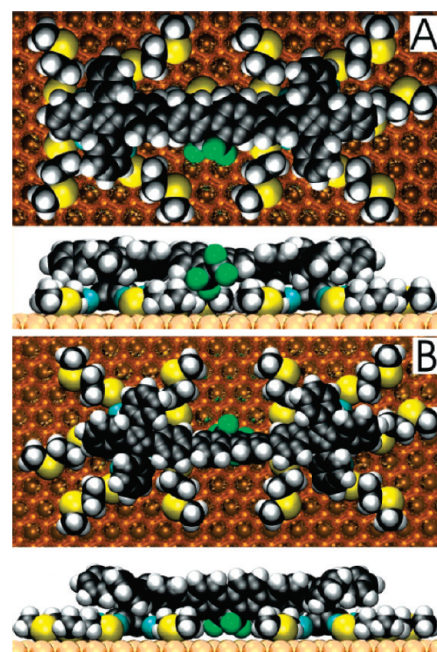Complex molecules that resemble macroscopic objects like cars and

Figure 5. Optimized representative eclipsed (A) and staggered (B) conformations of Michl's dipolar molecular rotor on Au(111).[33] Reproduced with permission from ref 33. Copyright 2004 American Chemical Society.

wheelbarrows have also been synthesized and studied on surfaces with the significant result that controlled, directional manipulation by a scanning tunneling microscope (STM) tip is possible.[44−51] Kevin Kelly described experiments in which the directional motion of "nanocars", comprising C_{60} "wheels" and a conjugated hydrocarbon "chassis", could be actuated thermally or by dragging the molecule with the STM tip. Anatoly Kolomeisky followed the presentation with his molecular dynamics work that explains the motion of nanocars in terms of thermally decoupling the C_{60} wheels from the surface so that they could rotate freely.[52,53] In another presentation, Dean Astumian showed mathematically that, while conventional engines do not operate at maximum power and efficiency, nanoscale devices should be able to do just that; yet he cautioned that just because certain molecules look like their macroscale counterparts does not mean that they necessarily behave the same.

Another molecular rotor that has been examined as a single molecule is the altitudinal structure shown in Figure 5, which has been synthesized and characterized experimentally and by com-

puter simulation in the Michl group.[33] The molecule consists of two metal sandwich posts attached to tentacles having an affinity to metal surfaces and holding an axle that carries a dipolar or a nonpolar rotator. Several techniques including IR spectroscopy,[54] ellipsometry, X-ray photoelectron spectroscopy, and STM[55] were used to ascertain that in a submonolayer the molecules are attached to the gold surface with sulfur and mercury atoms in the 10 tentacles contacting the surface. Interestingly, even after the sulfur-based tentacles are removed by oxidation, the rotor adheres well to the gold surface through its 10 mercury atoms alone. Differential barrier height imaging revealed that the rotators in about one-third of the adsorbed molecules are free to rotate around the altitudinal axle (Figure 5A), whereas in the rest the rotators are blocked, presumably as depicted in Figure 5B.[33]

Ashleigh Baber and Heather Tierney from the Sykes group described recent progress in their study of thioether molecular rotors.[56−58] The unique properties of the low-temperature STM enables monitoring the rotation of individual molecules as a function of temperature, applied electric field, tunneling electron energy, and the proximity of neighboring molecules. By making careful temperature-dependent measurements, Baber and Tierney demonstrated how the rotational energetic barriers and pre-exponential factors of a set of thioethers could be quantified. The direction in which individual molecules rotated could be determined, as shown in Figure 6. They also demonstrated the ability to switch the rota-
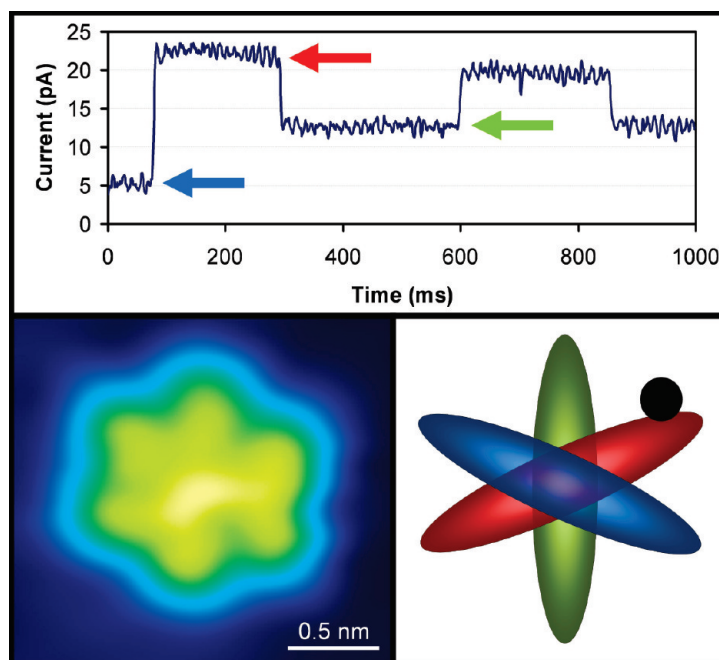

Figure 6. Plots of the tunneling current (*I*) *vs* time (*t*) reveal that individual molecular rotors reside in three distinct molecular orientations (shown schematically as green, red, and blue) with respect to the STM tip position (black dot). Changes in the position of the thioether rotor's alkyl tail result in three distinct levels of tunneling current from which both the rotation rate of the molecule and the direction of rotation can be measured.[56] Republished from ref 56. Copyright 2008 American Chemical Society.

tion on and off reversibly by altering either the proximity of the tip or by moving the molecules toward or away from one another in controlled STM experiments. Molecular dynamics calculations performed by Kolomeisky and his group revealed that the complex dependence of the torsional barrier on rotor length stems from both rotor−surface interactions and branching within the rotor tail itself.[58]

Regular Three-Dimensional Rotor Arrays. The ultimate goal in three-dimensional (3D) rotor array synthesis is the fabrication of an array of dipolar rotors with a ferroelectric ground state and a Curie temperature above 300 K. Such a ma-

terial would have many novel optical and electronic properties and would be of great technological importance for energy modulation and signaling applications. Toward this end, both the Garcia-Garibay[59] and the Michl[60] groups have synthesized metallo-organic framework structures carrying rotators in a cubic grid as seen in Figure 7.

Miguel Garcia-Garibay described his work constructing 3D crystals in which custom syntheses enable solids to be built with control over rotor spacing, dipole moment, and rotational barrier.[59,61−64] Such solid-state engineering is aimed at making molecules whose
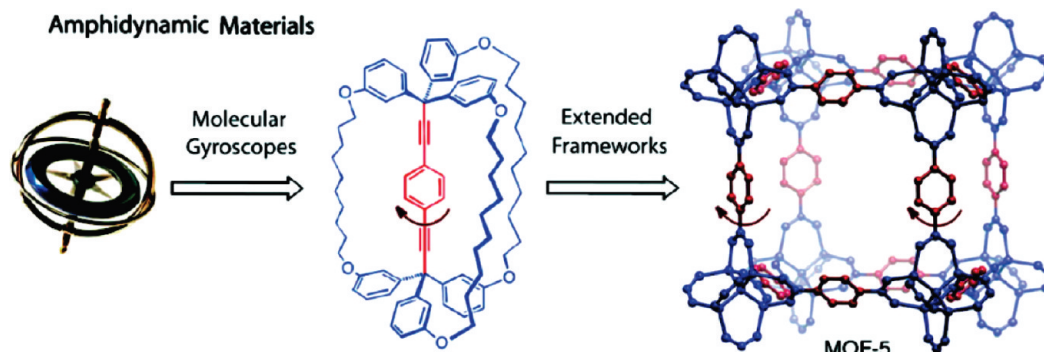

Figure 7. Schematic showing synthesis of 3D rotor arrays known as *molecular gyroscopes*.[59] Republished with permission from ref 59. Copyright 2008 American Chemical Society.
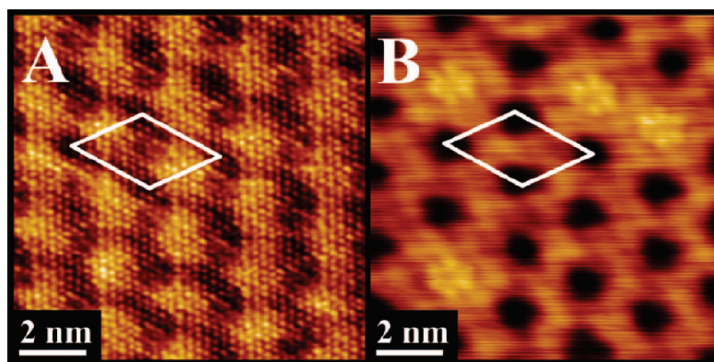
Figure 8. STM images of a Ag/Cu bimetallic surface that self-assembles into a regular hexagonal array of disslocations that can be used to control the ordering of single molcule rotors.[57] Reproduced with permission from ref 57. Copyright 2009 American Chemical Society.

crystal structures support and incorporate functional moving units that could exhibit useful collective effects and properties in the crystal such as dichrosim and birefringence. Garcia-Garibay refers to these systems as "molecular gyroscopes" because they resemble macroscopic machines. The molecular gyroscope possesses a phenylene rotor that can reorient about its 1,4 axis, which is fixed to the framework supplied by the bulky end groups (Figure 7).

Regular Two-Dimensional Rotor Arrays. Similar to the 3D systems, forming two-dimensional (2D) ordered arrays of dipolar rotors is a key step toward uncovering many interesting physical phenomena.[65] Rotor arrays may propagate waves of rotary motion at speeds much lower than typical phonon velocities.[66] This property may find use in radio frequency filters similar to those that currently employ surface acoustic waves. Collections of dipolar rotors also represent an artificial dielectric built from individual molecules and therefore may be useful as tunable dielectrics.[31,67,68] In his presentation, Michl described an approach his group is taking toward the preparation of such arrays, using a naturally occurring surface containing a triangularly disposed set of channels into which molecular rotors can be inserted (unpublished results).

Heather Tierney of the Sykes group described an alternative approach in which they have engineered a bimetallic surface system with a regular array of dislocations and studied the adsorption of a molecular rotor, dibutyl sulfide (Figure 8).[57] Due to size differences between the atoms, a single layer of Ag deposited onto Cu{111} reconstructs the Cu surface into a regular array of hexagonally close-packed domains with an average spacing of 2.6 ± 0.1 nm surrounded by face-centered cubic close-packed areas. STM imaging revealed that the affinity of adsorbates for these different domains can be used to control single-molecule adsorption spatially; individual dibutyl sulfide rotors have been arranged in a hexagonal pattern *via* their binding preference for hcp sites, in a manner analogous to placing cogs on a pegboard.[57] These results open up the possibility to study 2D arrays of either sterically or electrostatically interacting rotors with atomic-scale detail.

Regular One-Dimensional Rotor Arrays. A simple dipole chain is the main building block of many physical models in solid-state physics.[66,69−71] Several speakers alluded to the fact that

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dipole−dipole interactions in one-dimensional (1D) arrays may provide entirely new approaches to signal processing and may behave as nanoscale delay lines that function based on rotational motion of individual molecules.[65,66] While theory has been used to predict many interesting properties of 1D dipole chains, their experimental realization has not yet been reported.[66,69−71]

OUTLOOK

The two-day "Molecular Rotors and Motors" symposium witnessed quite a number of impressive advances in rotation science; however, many speakers discussed their recent work as an update on their progress toward several long-term goals. In particular, the Feringa group's work has opened the door to functional surfaces that may soon perform useful macroscopic work such as driving fluid flow in microfluidic channels. Efforts toward designing surface ferroelectricity were also discussed in terms of coupling surface molecular motion to photo- and electrical excitation and the design of new devices such as miniature delay lines and other novel nanoscale devices for signal processing. Several speakers reported efforts to control the rate and direction of individual molecular motion with a view toward building and driving single-molecule motors and "cars". These goals of directed and unidirectional motion appear realistic given that calculations predict that molecules can exhibit highly directional motion.[26] Overall,

this is a very exciting time for the young field of molecular rotors and motors.

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