

Molecular Motors, Actuators, and Mechanical Devices

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Atomically precise manufacturing systems, such as those described in *Nanosystems* [1], will utilize molecular motors and actuators¹ that drive components to perform useful work. The conversion of electrical and chemical energy into mechanical motion is facilitated by the use of gears, bearings, drive shafts, springs, and so forth, to direct the motion of components and minimize energy losses. Thus, research efforts dedicated to produce these sorts of components are considered to be both a direct pathway in our Roadmap and an enabler of other pathways that can take advantage of these molecular mechanical devices and the fabrication techniques developed to produce them. This section summarizes the state-of-the-art in the construction of these devices and describes their relevance to the Roadmap. Table 3 at the end of this section provides a summary of representative molecular motors, actuators, and mechanical devices.

Electric Nanomotors and Nanoactuators.

In 2003, the Zettl Group at Lawrence Berkeley Laboratories and UC Berkeley fabricated the smallest-known non-biological nanomotor [3]. The device employed a multi-walled carbon nanotube (MWNT), which served as both a bearing for the rotor and as an electrical conductor, and had the following characteristics:

- Doped silicon substrate covered with $1\mu\text{m}$ SiO₂.
- Rotor, anchor pads, and electrodes—constructed lithographically; 90 nm gold layer with 10 nm Cr adhesion layer
- Rotor length 100 – 300 nm
- Bearing—MWNT's, 10-40 nm diameter, 2 μm length between anchor pads
- Torsional spring constant of the outer nanotube, $10^{-15} - 10^{-12}$ N-m "as produced;" however the researchers broke the bonds with an electrical jolt (~80v d.c.) torquing the rotor and causing the tube to rotate freely
- Speed—operated at several Hz, but potentially could run at gigahertz frequencies
- Vacuum— $10^{-6} - 10^{-5}$ torr

¹ As Kay, Leigh, and Zerbetto point out in their excellent review article [2], molecular machines are a subset of molecular devices that provide mechanical movement toward a useful end. While molecular switches are molecular machines that perform useful work by changing state (in molecular computational systems, for instance) they are not treated in this section.

This breakthrough is highly relevant because motors based on this concept could be used to drive systems of molecular mechanical components. If the outer nanotube were fractured at the far ends rather than right next to the rotor, then this motor-driven outer shaft could be connected (e.g., by molecular gears) to other components. It's additionally significant because the operation of the motor is controlled with electrical circuitry, offering precise control from the desktop. Most importantly, the device is *individually addressable* from the desktop as opposed to broadcast architectures where light or chemical signals trigger operations on a large array of devices.

This research was additionally significant because in order to fabricate this device new technologies were developed:

- A method for peeling off successive layers of nanotubes [4]
- Precision cutting of, and selective damage to, nanotubes [5]
- A manipulator capable of pulling out the inner nanotube in a MWNT. [6] This spawned a commercial product [7].

In 2005, the Zettl group constructed a molecular actuator able to reversibly push apart two carbon nanotubes [8]. Mobile atoms of indium formed a nanocrystal ram between two nanotube electrodes under an applied voltage.

- Variable distance between nanotubes, 0-150 nm
- Cross sectional area of nanocrystal, 36 nm^2
- Force, 2.6 nN
- Extension velocity, $>1900 \text{ nm/s}$
- Power, 5 fW
- Power density, $20 \text{ MW/m}^3 - 8 \text{ GW/m}^3$

Using similar methods, the size of liquid droplets of indium on a nanotube surface could be controlled by varying the electrical current through the nanotube [9]. These droplets are capable of exerting pressure in an oscillating manner (peak power, $20 \mu\text{W}$, peak force 50 nN). Mechanical devices based on levers or plates attached to the droplets or nanocrystal ram could be used to convert electricity into repetitive linear motion. Again, these devices are individually addressable.

Photonic Nanomotors and Nanoactuators.

Another class of nanomotors is that which can be controlled by photons (light and magnetic fields). There are a considerable number of examples of molecules that can be caused to rotate or change conformation with photons; see reference [2] for a comprehensive review and [10, 11] for noteworthy examples. In the pathway to APM, nanosystems made from these devices may be driven by arrays of motors performing operations in parallel. A broadcast of electromagnetic

radiation onto the motors would provide energy for the array, which could be controlled by modulating the frequency and amplitude of the radiation.

Nanocar. One of the most prominent examples of the application of this technology is the Rice U. Nanocar (and its evolving product line of wheelbarrows and trucks) [12]. What distinguishes this effort is that a Feringa motor, which powers the device, was successfully integrated with other molecular structures to create a molecular machine. The motor rotates and pushes a protruding molecular group against the substrate propelling the molecular car forward along an atomically flat surface under 365nm wavelength light. While the utility of this particular application may or may not lead to APM, it shows that a Feringa motor (which had also been used to rotate glass rods on the surface of a liquid crystal [13]) can be connected to a device in order to effect directed motion. One can envision alternative configurations such as Feringa motors pushing against gear teeth to rotate a shaft, or provide linear motion as in a rack and pinion.

Molecular valve. In another example, in 2005 researchers at the Biomade Technology Foundation and the University of Groningen developed a molecular valve controlled by light [14]. To do this, they modified a protein found in *e. coli* bacteria that in nature serves as a safety valve for excessive pressure in the cell. The modifications allow it to be opened by UV light (366 nm wavelength, applied for about 2 minutes) and closed by visible light (>460 nm, for about 2 seconds) by building up and releasing localized charge. The valve operates within a lipid bilayer, is about 10 nm in external diameter, 21 nm long [15], and has an internal pore size of 3 nm when open. When the valve is closed it resists being forced open under pressure to nearly the breaking point of the cell wall. Although the valve has been developed and tested in an open system—embedded in the lipid bilayer of a cell wall, or more accurately, a patch clamp to measure current within this environment—one can envision fluid channels (pipes) leading to and from the valve in order to have it regulate fluid or gas transport in a closed system.

Chemical Nanomotors and Nanoactuators.

A third class of devices are those that respond to chemical changes in their environment, or rely on chemical fuel. As with light-controlled devices, actuators that respond to changes in environmental chemistry have been demonstrated for a broadcast architecture where large numbers of devices are controlled simultaneously. While near-term applications of these chemical nanoactuators may provide some utility, it is unclear whether a system design that modulates a changing chemical environment would be competitive with electric and light-activated designs.

By contrast, biological molecular motors that rely on chemical fuel pose some interesting advantages for the development of APM:

- Biomotors derived from living systems are available now, and can be produced in quantity.

- Most have been proven to work outside the living cell, for example mounted on glass slides.
- They are potentially individually addressable, by direct channeling of fuel to the motor input region via molecular tubes.
- The average motor speed can be modulated by controlling the feed rate of fuel (or, in a broadcast system, by controlling the concentration of fuel in solution).
- Biomotors can be connected to other components to drive the motion of a nanosystem. In the case of the flagellar motor, flagellar hooks are natural points of attachment.

Data on the characteristics of various types of biomotors are compared in Table 1. The highest speeds and forces are provided by the flagellar motors.

Table 1. Electromechanical characteristics of biomotors. After Berry [16].

	Motor	Max Force	Max Speed	Max Power
R O T A R Y	Flagellar motor (8 units, E. coli)	2400 pN-nm 95 pN	300 Hz 35 $\mu\text{m/s}$	2000 pN-nm @ 150 Hz 1.9×10^6 pN-nm/s
	(Vibrio)		1700 Hz 220 $\mu\text{m/s}$	
	(single unit)	300 pN-nm 12 pN	300 Hz 35 $\mu\text{m/s}$	250 pN-nm @ 150 Hz 2.4×10^5 pN-nm/s
	F₁-ATPase	40 pN-nm 40 pN	150 Hz 0.9 $\mu\text{m/s}$	20 pN-nm @ 75 Hz 9×10^3 pN-nm/s
L I N E A R	Myosin (single molecule in muscle or <i>in vitro</i>)	6 pN	10 $\mu\text{m/s}$ (speed of array, each molecule mostly detached)	2 pN @ 10/s x 20 nm 400 pN-nm/s
	Kinesin	5 pN	1 $\mu\text{m/s}$	2.5 pN @ 0.5 $\mu\text{m/s}$ 1.25×10^3 pN-nm/s
	RNA polymerase	20 pN	0.01 $\mu\text{m/s}$	~ 200 pN-nm/s

Biomotors connected to inorganic structures. In 2000, Soong, et al. in Montemagno's group reported the successful integration of a F₁-FTPase biomotor with a nickel substrate and a nickel propeller [17]. The motor, which measured ~ 8 nm in diameter x 14 nm in length, was able to move the propellers (150 nm diameter x 750-1400 nm long) at a mean velocity of 4.8 rps. The calculated torque was about 20 pN-nm, and the energy usage was 119-125 pN-nm/revolution

with an estimated efficiency of ~80%. In this study, the yield of working propellers was low—five out of 400 propellers in the array were able to turn when the ATP fuel was introduced into the surrounding environment. The pathway significance of this work was the demonstration that a biomotor could be used to move a structural component in a molecular mechanical system.

Bacteria flagella are powered by a motor that is driven by the flow of ions (protons or Na⁺) across a membrane. These biomotors have been the subject of much study [18], although the exact mechanism of the conversion of ion flow into mechanical motion is still not fully understood. The flagellar motor measures about 45 nm in diameter, can rotate up to 20,000 rpm, and has the additional characteristics shown in Table 2 [19].

Table 2. Electromechanical characteristics of flagellar motors. After Berry [16].

Driving Force	Proton or sodium electrochemical gradient
Number of Protons per revolution (energy per proton)	~ 1000 ~ 2.5×10^{-20} J (6kT)
Maximum rotation rate	300 Hz (protons), 1700 Hz (sodium)
Torque at stall	~ 4×10^{-18} Nm
Maximum power output	~ 10^{-15} W
Efficiency	50-100% (stall) ~ 5% (swimming cell)
Number of steps per revolution	~ 50 per torque generator

Flagellar motor torque is dependent on both speed and temperature, as shown in Figure 1.

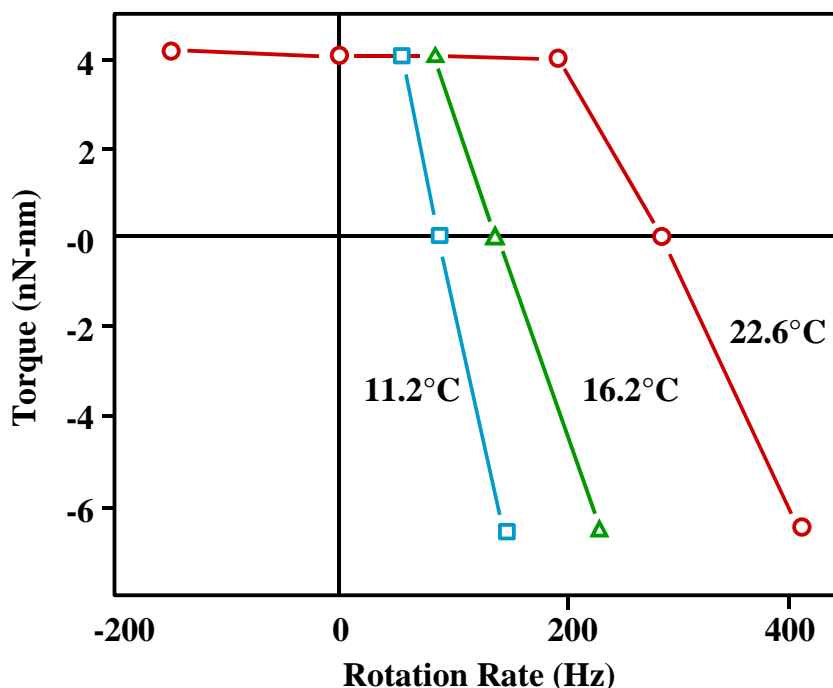


Figure 1. Torque vs. Rotation Rate curves for the bacterial flagellar motor. After Berry [19]

In order to study the mechanics of flagellar motors, researchers have attached small beads to truncated flagella and measured speeds and torques under various operating conditions [19, 20]. While this has proven to be an excellent tool for the intended research, from our perspective it proves that nanostructures can be attached to and driven by flagellar motors. Furthermore, research has proven that speed can be modulated, and even reversed, although methods to improve the precision of this control may be an area for development.

Chemical actuator example. In 2005, Stoddart's group developed a molecular seal based on a pseudo-rotaxane molecule [21]. The molecular device effectively sealed nanopores measuring 1.5-2.0 nm diameter on silica spheres, trapping guest molecules Ir(ppy)₃ and Rhodamine B (which measure about 1nm in diameter) in the pores with variable efficiency. Adding an iron salt via solution in the environment moved the QBPQT⁴⁺ ring component of the rotaxane (the stopper) down to the surface, closing the pores and preventing the guest molecules from leaving. Adding ascorbic acid moved the rings away from the pores, opening the pores and releasing the guest molecules to the environment or allowing them back in. There was no estimate of the effective force keeping the pores closed; containment efficiency was related to the depth of attachment of the DNP unit of the molecule within the nanopores. In their second paper [22], the group reported pH-driven control of the seals, and their most recent paper updating this work is [23]. Although the authors refer to their device as a nanovalve, a "molecular seal" is a more accurate label, since a valve "is a device that regulates the flow of substances. . . by opening, closing, or partially obstructing various passageways" [24]. In this case, the action is more akin to corking and uncorking a bottle.

Molecular Mechanical Devices.

In 1981 Drexler observed [25] that biological molecular machines and devices were functionally equivalent to macroscopic parts such as motors, bearings, pipes, drive shafts, and so forth. It is beyond the scope of this section to provide a listing of existing biological nanomechanical devices, so here we focus on the synthetic work that is being performed to create and integrate these devices—with particular regard to efforts that are most relevant to the molecular machine pathway in our Roadmap.

Molecular bearings. Nested carbon nanotubes are a natural choice for a sleeve bearing, because they can rotate freely against each other. Measurements of the intershell friction show that the static (0.2-0.85 MPa) and dynamic (0.43 MPa) friction are very low [26-28]. The utility of a nested carbon nanotube bearing was proven in a working device—the molecular motor cited earlier [3]. While there have been proposals to use nested carbon nanotubes as molecular oscillators and telescoping arms [29-31], to date there have not been any experimental realizations of a method to drive the motion of the inner or outer tubes.

Nanosprings. As Cumings and Zettl showed [26], there is a restorative force between shells in carbon nanotubes due to Van der Waals forces. In the case of one nanotube on which they performed experiments, the force was calculated to be 9 nN when they used a manipulator to pull an inner nanotube out of its nested environment. Thus, a nested carbon nanotube can provide a spring-like force, but unlike a traditional Hookean spring, the nanotube force is constant (except for at the rest position) and does not increase with the length of extension.

Williams, et al. showed that multi-wall carbon nanotubes can act as torsional springs, as well [32]. They used lithographic methods to fabricate paddles, or torsional levers, onto nanotubes suspended at each end. From AFM measurements, for a 7.8 nm, 10 wall nanotube, they

determined that the torsional spring constant was 1.5×10^{-13} N-m. The shear modulus, G , was estimated to be 600 GPa—close to the theoretical value of 541 GPa. Subsequently, they used an applied voltage to impart an oscillating motion to $\sim 600 \times 500$ nm paddles [33]. The paddles were oscillated at various frequencies up to about 9 MHz. Intershell coupling varied considerably between the nanotubes, resulting in torsional spring constants ranging from 0.37×10^{-14} to 7.4×10^{-14} N-m.

Table 3. Representative Molecular Motors, Actuators, and Mechanical Devices.

Molecular Device	Function	Representative Reference
Nanotube Nanomotor	Motor with MWNT serving as a bearing for the rotor and as an electrical conductor	A. M. Fennimore, T. D. Yuzvinsky, Wei-Qiang Han, M. S. Fuhrer, J. Cumings, and A. Zettl, "Rotational actuators based on carbon nanotubes," <i>Nature</i> 424 (July 24, 2003): 408-410
Molecular Actuator	Molecular actuator able to reversibly push apart two carbon nanotubes	B.C. Regan, S. Aloni, K. Jensen, R.O. Ritchie and A. Zettl, "Nanocrystal-Powered Nanomotor," <i>Nano Letters</i> 5 (2005): 1730-1733.
Molecular Seal	Nanoseal that can be opened and closed at will to trap and release molecules – can be triggered and reversed by redox chemistry or changes in pH	Nguyen TD, Liu Y, Saha S, Leung KC, Stoddart JF, Zink JI., "Design and optimization of molecular nanovalves based on redox-switchable bistable rotaxanes" <i>J Am Chem Soc.</i> 2007 Jan 24;129(3):626-34
Molecular Bearings	Nearly frictionless bearing made from two co-rotating nested nanotubes	Cumings, J.; Zettl, A. " Low-Friction Nanoscale Linear Bearing Realized from Multiwall Carbon Nanotubes," <i>Science</i> 289 (2000): 602-604.
Nanosprings	Lithographic methods were used to fabricate paddles or levers, onto multi-wall carbon nanotubes acting as torsional springs	P. A. Williams, S. J. Papadakis, A. M. Patel, M. R. Falvo, S. Washburn, and R. Superfine, "Fabrication of nanometer-scale mechanical devices incorporating individual multiwalled carbon nanotubes as torsional springs," <i>Applied Physics Letters</i> , v. 82 , no. 5 (3 Feb 2003): 805-807.
Telescoping Arms	Manipulator capable of extending the inner nanotube in a MWNT	Cummings and Zettl, "Low-Friction Nanoscale Linear Bearing Realized from Multiwall Carbon Nanotubes". <i>Science</i> 289 , 602-604 (2000)
Biomotors [see also Table 1]	Molecular motors evolved by nature that perform a variety of mechanical tasks	Montemagno, C. D., and Bachand, G. D., "Constructing nanomechanical devices powered by biomolecular motors." <i>Nanotechnology</i> 10 (1999): 225-331
Radio frequency controlled biomolecules	Nanocrystals attached to biomolecules cause DNA to unzip and rejoin under RF control	K. Hamad-Schifferli, J.J. Schwartz, A.T. Santos, S. Zhang and J.M. Jacobson, <i>Nature</i> 415 , 152 (2002); http://www.nature.com/nlink/v415/n6868/abs/415152a_fs.html
"Nanocar"	Molecular Feringa motor rotates	Shirai Y, Morin JF, Sasaki T, Guerrero JM,

	and pushes a protruding molecular group against a substrate, propelling a molecular chassis forward along an atomically flat surface, powered by 365nm wavelength light	Tour JM, "Recent progress on nanovehicles". Chem Soc Rev. 2006 Nov;35(11):1043-55
Microgenerator	Prototype nanotube-based (micron-scale) generator that produces continuous direct-current electricity by harvesting mechanical energy from ultrasonic acoustic waves	X. Wang, J. Song, J. Liu, Z.L. Wang, "Direct-current nanogenerator driven by ultrasonic waves," Science 316(6 April 2007):102-105
DNA-based robotic arm	DNA-based robot arm inserted into a 2D array substrate and verified by atomic force microscopy to be a functional nanomechanical device with a fixed frame of reference	Ding B, Seeman NC., "Operation of a DNA robot arm inserted into a 2D DNA crystalline substrate." Science. 2006 Dec 8;314(5805):1583-5
Molecular carrier	A molecule called 9,10-dithioanthracene (DTA) with two "feet" configured in such a way that only one foot at a time can rest on the substrate. Activated by heat or mechanical force, DTA will pull up one foot, put down the other, and walk in a line across a flat surface w/o tracks. Can carry molecular payloads of Co ₂ .	Wong KL, Pawin G, Kwon KY, Lin X, Jiao T, Solanki U, Fawcett RH, Bartels L, Stolbov S, Rahman TS., "A molecule carrier" Science. 2007 Mar 9;315(5817):1391-3.
Light-driven rotaxane-based motor	Motor resembles a dumbbell roughly 6 nanometers long that threads a ring about 1.3 nanometers wide. The ring can move up and down the rod of the dumbbell but cannot go past the stoppers at its ends. There are two sites on the dumbbell's rod that the ring encircles. When one of the dumbbell's stoppers absorbs sunlight, it transfers an electron to one of these sites, driving the ring to shuffle to the other site. The ring returns to the old site after the electron transfers back to the stopper, allowing the cycle to repeat	Balzani V, Clemente-León M, Credi A, Ferrer B, Venturi M, Flood AH, Stoddart JF., "Autonomous artificial nanomotor powered by sunlight". Proc Natl Acad Sci U S A. 2006 Jan 31;103(5):1178-83
Molecular rack and	A STM tip drives a single	Franco Chiaravalloti, Leo Gross, Karl-Heinz

pinion	1.8-nm-diameter pinion molecule functioning as a six-toothed wheel interlocked at the edge of a self-assembled molecular island acting as a rack. The rotation of the pinion molecule is monitored by a chemical tag on one cog.	Rieder, Sladjana M. Stojkovic, André Gourdon, Christian Joachim, Francesca Moresco, "A rack-and-pinion device at the molecular scale," Nature Materials 6, 30–33 (2007); http://www.nature.com/nmat/journal/v6/n1/abs/nmat1802.html
Chemically powered nanodimer	A nanodimer comprises two linked spheres, one of which has equal interactions with A and B solvent species but catalyzes the reaction $A \rightarrow B$. The other sphere is not chemically active but interacts differently with the two species. The nonequilibrium concentration gradient generated at the catalytic end, in conjunction with the force difference at the noncatalytic end, leads to directed motion.	Rückner G, Kapral R., Chemically powered nanodimers. Phys Rev Lett. 2007 Apr 13;98(15):150603.

Conclusions.

We have seen from the range of examples above that some types of components that would be useful in an advanced nanosystem have already been either fabricated or isolated from biological systems. This is significant with respect to the often contentious issues of both feasibility and timeline: **groups are building molecular machines now.**

The motors are powerful enough, and the machine components are efficient enough, to drive complex systems of molecular mechanical devices and perform useful operations at the nanoscale.² Carbon nanotubes have proven to be quite versatile as both structural and multi-functional materials, however, variability in nanotube properties can cause large variations in the performance of nanotube devices. While there has been considerable progress in the fabrication and study of individual components, significantly more progress toward the integration of various types of components into more complex systems is needed. For example, a useful advance would be the introduction of gears to convert rotary motion into linear motion.

² We have in mind mechanical operations of the types illustrated on the NanoRex website, <http://nanoengineer-1.com/content/>

More advanced manipulation and construction tools are required to achieve this level of sophistication: the increased complexity means moving from a two-dimensional to a three-dimensional architecture. (For example, a simple rack and pinion operates on two separate planes.) We can envision that multiple manipulators, or some form of three-dimensional scaffolding, will likely be required to hold components in place on these multiple planes during the construction process.

Therefore, high priority targets for new and ongoing research initiatives are:

- Device uniformity and standardization. Methods to reduce defects in carbon nanotubes would enable devices with more consistent performance. In addition, the development of standard devices and interfaces would enable experimentation with systems of devices.
- Component integration. Ongoing research to improve actuators and motors should be coupled with research to integrate these devices with other components to perform more complex nanomechanical operations.
- Three-dimensional fabrication. Instrumentation to manipulate and fabricate devices in three dimensions is critical to this pathway. New methods to section and join nanomaterials in 3D structures are needed, and 3D scaffolding (to support nanotubes, in particular) would be an important advance.

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