the viruses to find new entry points into this fast-moving field.

James C. Carrington is at the Institute of Biological Chemistry, Washington State University, Pullman, Washington 99164-6340, USA. 

e-mail: carrington@wsu.edu


Nanotechnology

In control of molecular motion

Ben L. Feringa

Nature leads the way when it comes to motors on a molecular scale. But chemists are in hot pursuit, designing controllable structures that can mimic muscles or rotary motors.

If you could build a motor one millionth of a millimetre across, you could fit a billion billion of them on a teaspoon. It seems incredible, but biological systems already use molecular motors on this scale. Linear motion is produced by skeletal muscle\(^1\), and rotary motion by the enzyme ATP synthase\(^2\). The underlying principle of these natural motors is the production of continuous motion while energy is being consumed. Can scientists engineer similar movements in a synthetic system?

Two recent findings suggest a way of using chemical synthesis to build molecular-scale components for artificial motors. In Angewandte Chemie International Edition, Sauvage and co-workers\(^3\) report a molecular assembly that can contract and stretch as desired under the influence of a chemical signal. It is the first synthetic molecule in which two filaments can glide along each other, as they do in real muscles. And in the Journal of the American Chemical Society, Aida and co-workers\(^4\) describe the acceleration or deceleration of motion in rotating disc-like structures in response to changes in their electronic state. By using a metal ion sandwiched between two porphyrin ligands, the rotary motion can be controlled by oxidation (removing electrons) or reduction (adding electrons) at the metal centre, producing a device reminiscent of transmission systems in much larger motors.

Most artificial systems that produce linear or rotary motion are more like molecular switches than motors. It is not enough to build a system that moves or rotates freely. To reproduce the actions of a motor it is essential to incorporate control into the system, so the motion can be started and stopped at will. There are many ways to do this. For example,
polyacrylamide gels and polypyrroles have been designed to mimic the behaviour of muscles by bending or contracting in response to electric current. Other approaches to linear motion rely on the use of rotaxanes - molecular rings threaded by strings - in which the position of the ring can be altered by electrochemical or photochemical means.

In their system, Sauvage and colleagues use a doubly threaded structure to mimic the stretching and contracting of a real muscle (Fig. 1). Their design is based on two molecular units, each consisting of a ring attached to a string, which can slide along each other. Each ring has a metal ion at its core, and there is a bulky stopper at the other end of the string to prevent the strings from coming apart. Each ring contains a bidentate ligand (so called because it has two points of attachment for a metal ion), whereas each string contains both a bidentate and a tridentate ligand (which has three points of attachment). The geometry of the structure changes, depending on which ligands bind to the metal ions.

In the presence of two copper ions, the most favourable geometry has two bidentate ligands binding to each ion. This is the ‘stretched’ geometry. Replacing the copper ions with zinc ions causes the strings to slide along each other so the zinc ions can adopt their preferred configuration, with each ion bound to one bidentate ligand and one tridentate ligand. This is the ‘contracted’ geometry. Replacing zinc with copper reverses the process, stretching the molecule. The length of the structure changes by roughly 27% - coincidentally, about the same as that seen in natural muscles.

How similar this is to the motion of muscle filaments is arguable. But this is the first demonstration of stretching and contracting motions induced by a chemical reaction in an artificial molecular assembly. The stage is set for the design of other ‘molecular muscles’ triggered by electrochemical or photochemical processes. For these artificial molecular muscles to perform useful mechanical work, they will ultimately have to be connected to macroscopic systems. The organization and concerted action of a large number of these...
molecular motors is one of the key issues to address next.

So much for linear motion, but how about rotary motion? Particularly promising are studies with interlocked rings (catenanes) in which circular motion can be induced.\(^1,2\)

Last year, two studies demonstrated the controlled conversion of energy into unidirectional rotation, a fundamental property of a rotary motor.\(^3,4\) The next challenge is to control the rate of rotation to produce a motor capable of more than one speed.

Aida and co-workers\(^5\) have found an elegant solution to this problem with a molecular system called a bisporphyrinate double-decker complex (Fig. 2). In these complexes a cerium or zirconium ion is sandwiched between two porphyrin ligands that rotate with respect to one another. The metal ion acts as a kind of ball-bearing between two rotating discs. The configuration of bulky side chains attached to the porphyrin ligands means that the metal complexes are chiral — that is, they can be mirror images of each other. This feature allows the authors to study the dynamics of the rotary motion by measuring their optical activity. (Mirror-image chiral molecules rotate polarized light in opposite directions.)

Aida and colleagues\(^6\) found that reducing the cerium complex led to the rotation of the porphyrin ligand being accelerated more than 300-fold. Oxidation of the zirconium complex, on the other hand, decelerated it by a factor of 21 or 99, depending on the oxidation state of the complex. The change in rotary motion is attributed to a change in distance between the two porphyrin ligands. In the cerium complex, reduction of the metal centre increases the ionic radius, so the interaction between the porphyrin ligands weakens, which leads to faster rotation. In the zirconium complex, oxidation reduces the distance between the porphyrin ligands, strengthening the interaction between the ligands and slowing down the rotary motion.

The chemical control of rotation is a powerful tool to be used in more advanced molecular motors. But there are many hurdles to overcome before the structures designed by these and other groups can lead to molecular machinery becoming a reality. To make their construction easier, self-assembly processes are needed. It is also not clear whether the motors described here will retain their properties when they are used as part of a more complex system. Nonetheless, we are adding important components to our toolkit for making nanomachines.

Ben L. Feringa is in the Department of Organic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

E-mail: feringa@chem.rug.nl