

MOLECULAR MACHINES

Nanoscale gadgets

Meeting their biological counterparts halfway, artificial molecular machines embedded in liquid crystals, crystalline solids and mesoporous materials are poised to meet the demands of the next generation of functional materials.

Miguel A. Garcia-Garibay

is in the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569, USA.

e-mail: mgg@chem.ucla.edu

Few areas of science attract as broad a spectrum of disciplines as the field of molecular motors, molecular machines and functional nanostructures. This could be easily appreciated at a symposium on this topic held during the 2008 Materials Research Society Spring meeting in San Francisco, which brought together physicists, chemists, biologists, materials scientists and engineers.

In general, there are two approaches to molecular machines: One is based on the analysis of biological systems, which have been perfected over billions of years, and the other on the synthesis of artificial molecular machines, the entire history of which is about fifty years old¹. Although the complexity of artificial molecular machines remains behind that of its biological counterparts, the gap is closing.

For biological systems, experiments usually take advantage of reconstituted biological components in artificial environments. In a step further, Taro Uyeda (National Institute of Advanced Industrial Science Technology, Japan) illustrated the harnessing of the motility of living cells to drive artificial micromechanical assemblies². Using biotin-avidin linkages, Uyeda described the attachment of silicon dioxide microrotors, fabricated by conventional photolithography, to bacterial cells moving within circular tracks (13 μm in diameter). This first bacteria-driven microrotary motor was shown to rotate with a frequency of 2 r.p.m.

For the study of artificial molecular machines, synthetic strategies are used that allow the design and preparation of functional molecules and aggregates. Chemists have learned how to control degrees of freedom based on covalent, non-covalent and mechanical bonds, and used stimuli to explore changes in equilibrium, thermal fluctuations and

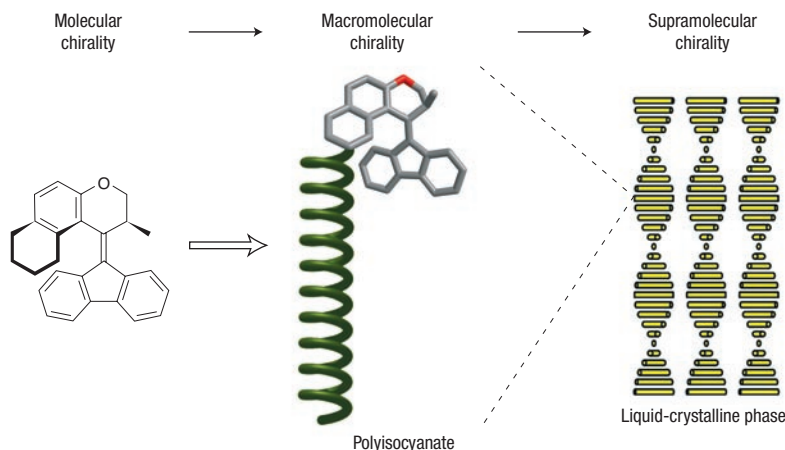


Figure 1 The induction of supramolecular chirality in a liquid-crystalline phase. Information is transferred from a chiral molecular motor, to the helical sense of a polyisocyanate, and finally, to the macroscopic chirality of the liquid-crystalline phase. Reprinted with permission from ref. 3.

dissipative processes. One of the highlights of the symposium were demonstrations of how the mechanical functions of small molecules have been successfully interfaced with their supporting media, to control the molecular and macroscopic properties of the corresponding assemblies. Examples of this interaction include unidirectional molecular motors in cholesteric liquid crystals³, the design of crystalline solids capable of supporting ultrafast internal motions⁴, and the design of controlled delivery systems with mechanochemically activated nanovalves⁵.

Ben Feringa (University of Groningen) described how the supramolecular chirality of liquid crystals could be determined by the chirality of a synthetic molecular motor. By adding a small amount of a homochiral molecular motor to a unidirectionally aligned cholesteric liquid crystal, the helical organization of the sample is determined. When exposed to ultraviolet light, unidirectional rotation and a change in the helical chirality of the molecular motor cause the macroscopic fingerprint texture of the sample (visible

as a pattern of closely spaced lines across the surface of the sample) to rotate in a direction that depends on the configuration of the motor and the wavelength of light. Feringa illustrated this process with helical polyisocyanide-molecular motor conjugates³ (Fig. 1). Not only is the handedness of the polymer helix determined by the configuration of the molecular motor, but the helical sense of the polymer can be switched by irradiation with light of an appropriate wavelength. The molecular-level information in the structure of the motor is efficiently transferred to the macroscopic texture of the liquid-crystalline phase.

Although molecules in liquid crystals retain rotational and translational degrees of freedom in a relatively viscous environment, their average orientational order results in useful optical properties. The control of analogous processes in crystalline solids represents an additional challenge, but it offers a number of interesting possibilities from a materials perspective. With this in mind, molecules with the appropriate structural design, for

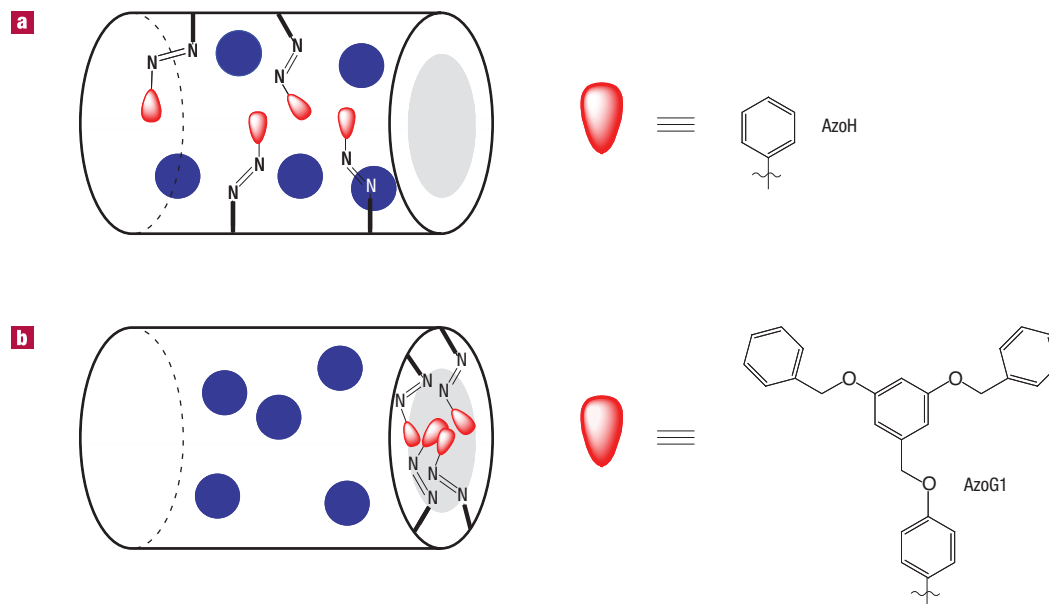


Figure 2 Stimuli-responsive nanocontainers. **a**, Azobenzene molecules (AzoH; red) attached to the walls of silica nanopores act as nanoimpellers that help control the transport of dye molecules (blue) through and out of pores. This is achieved by the photoinduced *cis*-*trans* isomerization of azobenzene molecules. **b**, Large azobenzene derivatives (AzoG1; red) can be localized near the entrance of the pore openings and act as gatekeepers. Reprinted with permission from ref. 6.

example that of a compass and a gyroscope, are capable of retaining rotational degrees of freedom in the crystalline state with frequencies that range from a few hertz to the gigahertz regime at ambient temperature⁴. These early designs of crystalline molecular machinery are based on molecular units that create internal cavities around their moving parts, so that motion can occur even after crystallization.

Artificial molecular machinery in liquid crystals and crystalline solids suggests applications that exploit macroscopic order, but porous materials with nanoscale order and compartmentalization offer a host of interesting possibilities⁵. One of these is the development of nanocontainers with molecular cargo that can be released in response to ultraviolet light or chemical processes. Functionality can be introduced to porous systems by attaching molecular machines capable of opening and closing the gates to the pores to control molecular traffic. Jeffrey Zink (UCLA) reported an example of this in the form of a photo-driven nanoimpeller^{6,7}. The device incorporates azobenzene molecules attached either at the entrance or along the length of the nanopores (Fig. 2). The pores' gates can be opened and closed by the photoinduced *trans*-to-*cis*

isomerization of azobenzene molecules near the channel entrance. Alternatively, sustained irradiation of molecules inside the channel causes continuous *trans*-to-*cis* isomerization, helping to push guest molecules along the channel length. The devices have the potential of precisely controlling the time and rate of release of molecules contained in their pores.

In addition to these advances in the synthesis of artificial systems, convergence of artificial and biomolecular molecular machinery also comes from the biological community. Jonathan Bath (Oxford University) and Niles Pierce (Caltech) independently reported, from a biological perspective, on their studies involving the use of DNA as a building block for nanomachines. Inspired by protein motors, Bath uses the complementarity of DNA strands, along with the changes in binding energy that occur on addition of sequence-specific signals and key enzymatic reactions, to create autonomous DNA motors⁸. The energy released by hydrolysis of the DNA backbone, or hybridization of two strands, allows DNA to be used as both a construction material and fuel. Pierce explained processes underlying the replication and regulation of biological systems by using a reaction

graph abstraction to program various self-assembly and disassembly pathways to control the complementarity between modular domains of a DNA hairpin⁹. Given the degree of structural control available with DNA, devices capable of responding to external triggers and for a wide range of applications should be within reach.

In conclusion, although strong motivations to create new nanomachines come from the promise of materials with properties and functions controlled by mechanical phenomena of molecules, it is clear that the lure of fundamental science, increasingly powerful analytical methods and novel engineering paradigms cannot be ignored.

References

1. Feynman, R. P. *Eng. Sci.* **23**, 22–36 (1960).
2. Hiratsuka, Y., Miyata, M., Tada, T. & Uyeda, T. Q. P. *Proc. Natl Acad. Sci. USA*, **103**, 13618–13623 (2006).
3. Pijper, D., Jongejan, M. G. M., Meetsma, A. & Feringa, B. L. *J. Am. Chem. Soc.* **130**, 4541–4552 (2008).
4. Khuong, T. V., Nuñez, J. E., Godínez, C. E. & García-Garibay, M. A. *Acc. Chem. Res.* **39**, 413–422 (2006).
5. Saha, S., Leung, K. C.-F., Nguyen, T. D., Stoddart, J. F. & Zink, J. I. *Adv. Funct. Mater.* **17**, 685–693 (2007).
6. Angelos, S., Liang, M., Choi, E. & Zink, J. I. *Chem. Eng. J.* **137**, 4–13 (2008).
7. Lu, J., Liang, M., Zink, J. I. & Tammanoi, F. *Small* **3**, 1341–1346 (2007).
8. Bath, J. N. & Turberfield, A. J. *Nature Nanotech.* **2**, 275–284 (2007).
9. Yin, P., Choi, H. M. T., Calvert, C. R. & Pierce, N. A. *Nature* **451**, 318–322 (2008).