## **Controlling the Motion of Molecules; Prototypes for Molecular Machines**

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The idea of constructing molecular-level machines was first seriously considered by Nobel Laureate in physics, Richard Feynman. In his famous address, "There's plenty of room at the bottom" in 1959,<sup>1,2</sup> he suggested the possibility of such machines and uses for them. More recently, microfabrication using photolithography and etching techniques has led to micromachines such as gears, bearings and even motors smaller than a human hair.<sup>3,4</sup>

This miniaturization of components for the construction of micromachines, which is an essential feature of modem technology, is usually pursued by a "top-down" approach.<sup>5.6</sup> The main idea of this approach is to make large things smaller. However, this approach, which requires physicists and engineers to manipulate progressively small pieces of matter, has some limitations.<sup>7</sup> For example, the bulk properties of materials change as the size shrinks to dimensions equivalent to just a few atoms. In addition, we simply cannot expect that the current miniaturization trend can be maintained forever.<sup>5</sup>

An alternative strategy is offered by a "bottom-up" approach.<sup>8</sup> This approach is receiving attention because it holds the potential to overcome the limitations of typical top-down approach. The central idea of this approach is that functional devices can be synthesized through the rational assembly of atoms or molecules, which are the smallest possible building blocks.

To design molecular machines, a common approach is to restrict the degree of freedom of submolecular components so that they can move with respect to each other through discrete, large amplitude internal motions under external stimuli.<sup>9</sup> Rotaxanes and catenanes are archetypal example of such molecules.<sup>10,11</sup> Rotaxanes are a molecules composed of a macrocycle ring and a dumb bell-shaped component. The macrocycle ring encircles the linear rodlike portion of the dumbbell-shaped component and is trapped mechanically around it by two bulky stoppers.<sup>6,10</sup> Thus, the two components cannot dissociate from one another, even though they are not linked covalently. The first rotaxane was made in 1967 by Harrison by using a inefficient statistical approach.<sup>12</sup> Template-directed approaches make it possible to synthesize rotaxanes in higher yields.<sup>5,6</sup> Catenanes are molecules composed of two or more interlocked macrocylic components. Just as for the catenanes, the two or more macrocycles are not linked by covalent bonds but instead are held together mechanically. <sup>6,10</sup> The first catanane was made in 1960 by Wasserman by using cyclization reactions and taking advantage of the random occurrence of linear molecules that self fold around themselves.<sup>13</sup>

In order to control the motion of these that molecular machines, three types of stimuli are most often used;<sup>6</sup> chemical control, photochemical control and electrochemical control. One example of electrochemically-controlled motion is exhibited by a solid based reconfigurable switch(Fig. 1).<sup>14</sup> The system is fabricated from

a single monolayer of a bistable [2]catenane that is anchored with amphiphilic phospholipid counterions and sandwiched between a polycrystalline Si electrode and a Al/Ti top electrode(Fig. 2). The switch is open (i.e., no current flows) at an applied voltage of +2 V, and closed at -2 V, and can be used for several months without loss of response.

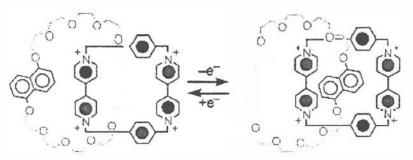


Fig 1.15 Molecular structure of the bistable [2]catenane

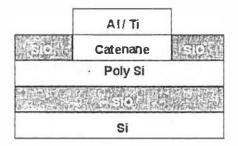


Fig. 2.<sup>15</sup> Molecular-based device

These molecular machines also suffer from limitations;<sup>5</sup> among these are that it has not yet proven possible to construct rotors that move unidirectionally, to design systems that exhibit continuous motion, or to make devices with long life times. One of most serious problems is to create organized arrays of molecular machines. To solve this problem, several attempts have been to attach the machines to a support or a surface.

## References

- 1. Trimmer, W. S. *Micromechanics and MEMS*, IEEE press 1997
- 2. Online web site http://www.zyvex.com/nanotech/feynman.html
- 3. Wise, K. D.; Najafi, K. "Microfabrication Techniques for Integrated Sensors and Microsystems," *Science* 1991, 254, 1335-1341
- 4. Gimzewski, J. K.; Joachim, C.; Schlittler, R. R.; Langlais, V.; Tang, H.;

Johannsen, I. "Rotation of a Single Molecule Within a Supramolecular Bearing," *Science* **1998**, 281, 531-533

- 3. Sauvage, J.-P. Molecular Machines and Motors, Springer, New York 2001
- 4. Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. "Artificial Molecular Machines," Angew. Chem. Int. Ed. 2001, 39, 3348-3391
- 5. Jortner, J.; Ratner, M. *Molecular Electronics*, Blackwell Science, Malden 1997
- 6. Ungaro, R.; Dalcanale, E. Supramolecular Science: Where It Is and Where It Is Going, Kluwer Academic Publishers, Norwell 1999
- Brouwer, A. M.; Frochot, C.; Fatti, F. G.; Leigh, D. A.; Mottier, L.; Paolucci, F.; Roffia, S.; Wurpel, G. W. H. "Photoinduction of Fast, Reversible Translational Motion in a Hydrogen-Bonded Molecular Shuttle," *Science* 2001, 291, 2124-2128
- 8. Schill, G. Catenanes, Rotaxanes and Knots, Academic Press, New York, 1971
- 9. Sauvage, J.-P; Dietrich-Buchecker, C. Eds., Molecular Catenanes, Rotaxanes and Knots, Wiley-VCH, Weiheim, Germany 1999
- 10. Harrison, I. T.; Harrison, S. "The Synthesis of a Stable Complex of a Macrocycle and a Threaded Chain," J. Am. Chem. Soc. 1967, 89, 5723-5724
- 11. Wasserman, E. "The Preparation of Interlocking Rings: A Catenane," J. Am. Chem. Soc. 1960, 82, 4433-4434
- 12. Collier, C. P.; Mattersteig, G.; Wong, E. W.; Luo, Y.; Berverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. "A [2]Catenane-Based Solid State Electronically Reconfigurable Switch," *Science* 2000, 289, 1172-1175
- Pease, A. R.; Jeppesen, J. O.; Stoddart, J. F.; Luo, Y.; Collier C. P.; Heath, J. R.
  "Switching Devices Based on Interlocked Molecules," Acc. Chem. Res. 2001, 34-433-444

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