

## synthesize a light-driven single-molecular motor in the near future.

THERE has been considerable interest in the design and fabrication of molecular devices<sup>1-16</sup>. Of particular interest are molecular motors in which the components are forced to move past each other by external stimuli<sup>1-11</sup>. Recent insights into the working of biological motors<sup>10,17,18</sup> have stimulated a surge of papers on such artificial molecular motors. Rotaxanes are the most widely studied as they offer the possibility of long range translational motion of a threaded 'shuttle' along a molecular wire or 'rail track'. The shuttle can be driven chemically, electrochemically or photochemically.

Natural molecular motors are usually driven by chemical energy and are believed to have high efficiency, often close to unity. One of the most efficient natural motors, the ATP synthase, rotates 15–20 times per second. Though chemically driven motors are plentiful in biology, their components are rather largish molecules and it does not look as if an artificial molecular motor of comparable efficiency satisfying the three desirable features will be made in the near future. Any synthetic molecular motor should have the following desirable characteristics: (a) It should draw energy from a source and produce mechanical work, with high efficiency, hopefully comparable to those of natural molecular motors. (b) The motion produced should be on a time scale, faster or at least comparable to those of natural molecular motors. (c) Its operation should not, if possible, lead to the formation of waste products.

In an interesting paper, unidirectional rotational motion in a mechanically interlocked catenane molecule has been reported<sup>8</sup>. The authors have studied a 'three-station' [2]catenane and a 'four-station' [3]catenane. 'Stations' are the binding sites in the macrocyclic ring of the catenane assembly. In these systems, there is a large macrocycle with the binding sites and smaller macrocycles which are bound to these sites. It was found that in response to external stimuli, the small ring in the three-station [2]catenane moves sequentially between the binding sites. In the four-station [3]catenane there are two smaller macrocycles and one of them blocks the backward Brownian movement of the other macrocycle, effectively making the rotation unidirectional.

The chemically driven motors that have been synthesized recently<sup>1-8</sup> are of great interest, though they have rather low efficiency and rotate by 360 degrees on a rather long time scale (for example, one day). They are in no way near the goals that one would like to achieve. The existing attempts based on rotaxanes have not put the ideas from Brownian motors to maximum use to get an efficient molecular motor.

Here, we suggest a design that we believe will lead to machines that satisfy all the three requirements above. It is to be stressed that the ideas that we use are well known

## Theoretical design for a light-driven molecular motor based on rotaxanes

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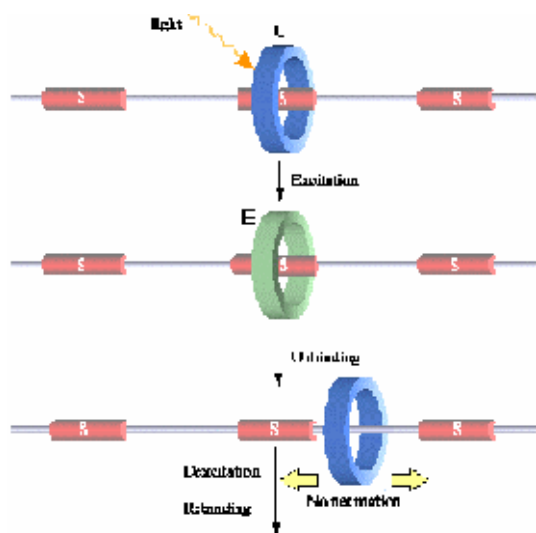
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**We suggest a design for a light-driven molecular motor, which is different from the existing designs. It is a rotaxane molecule, having identical 'stations' and an asymmetric 'shuttle'. We argue that the molecule would exhibit unidirectional rotational/translational motion continuously, upon shining with light of just one frequency. With this design, it should be possible to syn-**

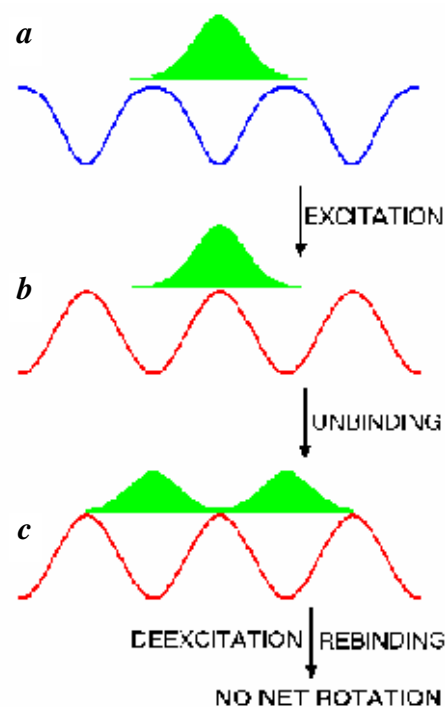
from papers on the working of Brownian motors<sup>17,18</sup>. However, as yet, there does not yet exist an efficient artificial molecular level Brownian motor. The only ones that exist are the natural ones. Our design is very simple and we argue that by just shining light of appropriate frequency, it is possible to generate net unidirectional motion (rotational or translational), a goal that has been found to be extremely difficult to achieve. As the energy comes from light, the response time of the motor can be easily made faster than would be the situation if it were chemically driven. In fact, our motor is simpler than the ones that exist in nature, whose workings are not well understood. With the expertise available in making [2]rotaxanes, it should be possible to synthesize a molecular motor based on the design, in the near future.

Our design is a [2]rotaxane, which uses the photochemical unbinding known in rotaxanes, shown in Figure 1. The design consists of a ring (the shuttle), which is threaded with an oligomer, which has identical stations (sites) where the shuttle could be bound. The oligomer could be a ring (so that one has a catenane) and then the shuttle would go around the ring, exhibiting rotational motion. Alternatively, the oligomer could be a very long chain molecule and the shuttle would then exhibit translational motion.

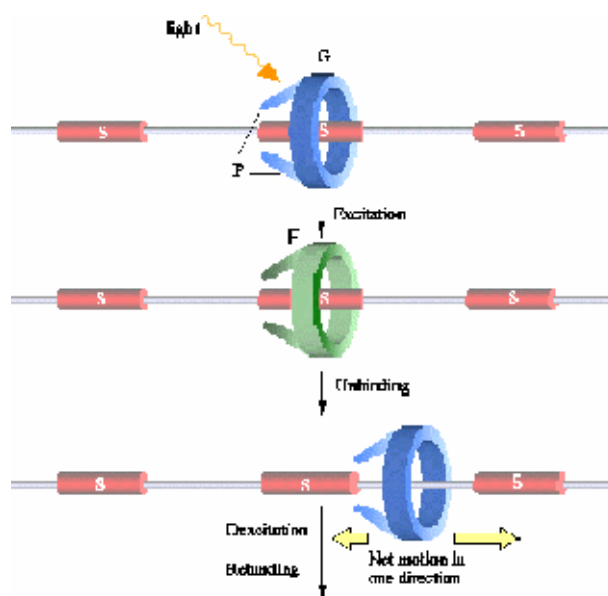
We imagine that the shuttle, when it is in the ground state (G) prefers to bind to the site, S. The state of the shuttle can be changed photochemically to a state E and in this state, it prefers to unbind from the site S (see ref. 19 for an example where this happens readily). So on photo-excitation, it would leave the site S and move to the region between the two sites. However, left to itself, the state E would decay back to G and the shuttle would get back to the site S. So, if the whole assembly is put in presence of light of appropriate frequency, the cycles of



**Figure 1.** Schematic picture of unbinding of a symmetric [2]rotaxane, where there is no net (directional) rotational motion.



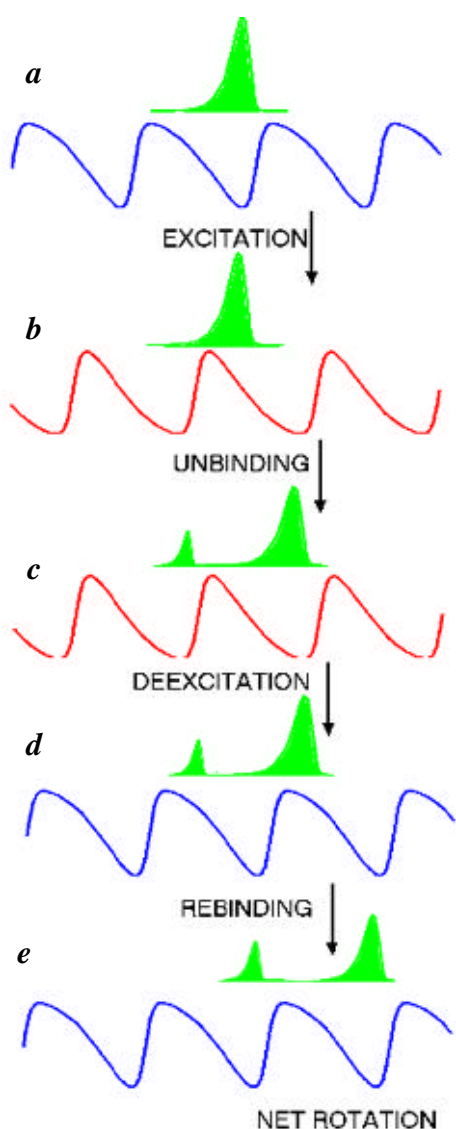
**Figure 2.** The symmetric case. *a*, Variation of the potential energy of the shuttle-oligomer system, as the position of the shuttle is varied along the oligomer. It also shows the probability distribution (shaded) for the position of the shuttle on a site to which it is initially bound. *b*, Effect of exciting the shuttle. As a result of the excitation, the potential energy curve is changed drastically and the initial probability distribution, which was sitting in a minimum of the ground state potential energy curve now sits on top of a barrier. It can now go forward or backward with equal likelihood, as a result of which it splits up into two parts as shown in *c*. This is the unbinding step. Then, the shuttle would get de-excited and rebind to a site. When the rebinding happens, it can bind to the original site, as well as the one preceding it, or to the one that follows it. The probabilities of the latter two are equal and hence there is no net rotation.



**Figure 3.** Schematic picture of a [2]rotaxane, where there is a net motion in one direction.

excitation, unbinding, de-excitation and rebinding would go on (see Figure 2)<sup>17,18</sup>.

With a symmetric shuttle, the motion can be either in the forward or backward direction with equal likelihood and hence there would not be any net unidirectional motion. If one can prevent it from occurring with equal likelihood, then there will be a net motion in one direction. This however is easy to achieve – all that is required is to have a shuttle that is asymmetric. For example, if the shuttle has pawls (P) as in Figure 3 on one side, then its motion towards the left will be less likely than that to-

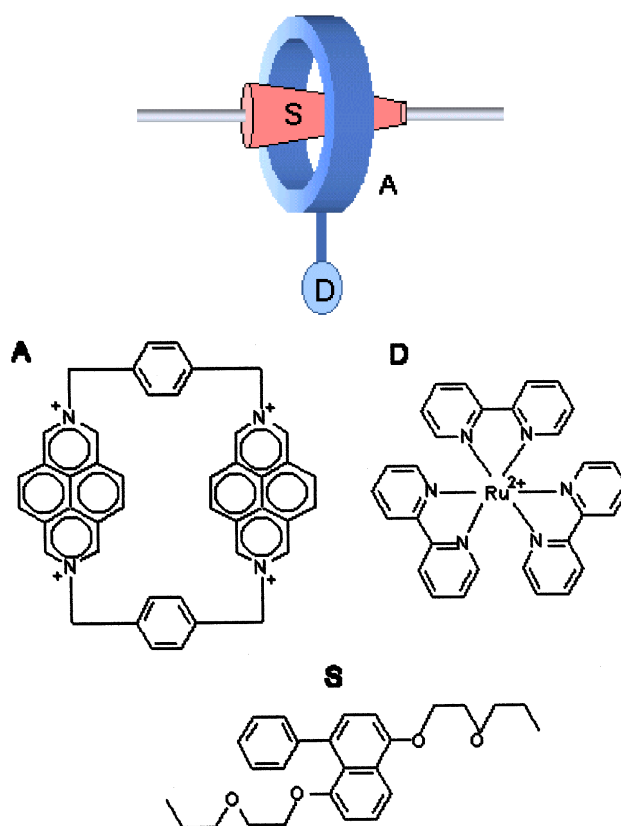


**Figure 4.** The unsymmetric case. *a*, Variation of the potential energy of the shuttle-oligomer system, as the position of the shuttle is varied along the oligomer. The probability distribution is seen to be asymmetric, due to the asymmetry of the shuttle. *b*, Effect of exciting the shuttle. Unbinding occurs in the forward/backward directions with unequal probabilities as shown in (*c*). The shuttle would get de-excited and rebind to a site, as shown in (*d*) and (*e*). The net result is more probability that the shuttle moves forward, rather than backward, resulting in net rotation.

wards the right. This will cause a net unidirectional motion towards the right. It may be asked whether such unidirectional motion is really possible, in view of the fact that a molecular ratchet, kept at constant temperature, does not show any net rotational motion, as that would violate the second law of thermodynamics<sup>20-23</sup>. The answer to this question is that, it is possible in this case, as the system is driven by an external stimuli and hence unidirectional motion does not violate the second law of thermodynamics. In Figure 4, we show pictorially the detailed mechanism. It is not necessary to have an extra group acting as a pawl, if the shuttle itself is a molecule like calixarene, as in ref. 24. Alternatively, one can have a symmetric shuttle and have asymmetry built into the stations, as in the example given in Figure 5.

We give in Figure 5 a system in which the suggested mechanism is likely to work. Photoexcitation of the electron donor D would cause electron transfer to the shuttle A, which is assumed to be an electron acceptor. The A<sup>-</sup> so formed has no affinity towards the station S and hence would unbind from it. Typical examples of D, A and S are suggested in Figure 5.

Typically, the unbinding would need a time of the order<sup>25</sup> of 10<sup>-6</sup> s. Asymmetry of S would cause the unbinding to be more in one direction than in the other. The



**Figure 5.** The case where unbinding is due to electron transfer. Note that the station S is asymmetric. Typical examples for A, D and S are shown.

major problem would be that back electron transfer is usually fast<sup>25</sup> ( $\sim 10^{-9}$  s). One would then have to tune the donor acceptor system in such a manner that the back electron transfer takes place in a time longer than  $\sim 10^{-5}$  s. This may be achieved by varying the free energy change for the back electron transfer to be in the Marcus inverted regime and by varying the solvent polarity. The time could be made longer also by increasing the physical separation between the donor and the acceptor.

Finally, we note: (1) the net rotational motion would occur in presence of steady light and that the net motion would stop when the light is switched off. (2) Our motor combines the ideas of devices that have already been used in the literature rotaxanes[2] with idea of a ratchet<sup>21-23</sup>. (3) In the earlier motors that have been suggested, it is the site (station) that is excited/reacted, while for our motor, it is the shuttle that is changed externally. (4) Further, all the earlier suggestions have stations that are different while in our model, all the sites are the same and therefore synthesizing the motor should be easier. (5) In our opinion, the suggested change in design, though simple, is the easiest way to get an efficient working molecular motor. (6) The synthesis of the motor poses a challenge, but it should be possible in the near future, given the abilities that organic chemists have attained in synthesizing elegant structures.

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