Light-driven molecular motors

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Light-Driven Molecular Motors

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Abstract. Molecular motors can be defined as molecules that are able to convert any type of energy input (a fuel) into controlled motion. These systems can be categorized into linear and rotary motors, depending on the motion induced. This brief account will discuss the state of affairs of the research on light-driven rotary molecular motors.

MOLECULAR ROTARY MOTION

Inspired by the unidirectional rotary motion found in F_1-ATPase[1], current pursuits towards nanomachines and synthetic molecular motors focus on systems that allow controlled molecular rotation and translation. Intramolecular rotary motion itself is trivial as, *e.g.* most single bonds in organic molecules freely rotate under ambient conditions. Already in the late sixties, Akkerman *et al.* [2] tried to exert control over the rotation of a carbon-carbon single bond, a concept that was later exploited by Mislow *et al.*[3]. In their molecular gear systems, two intramolecular rotations are coupled due to steric effects. However, no control over the direction is exerted and the motion is merely an oscillation as is the case for most reported examples of forced rotary motion, like *e.g.* in catenane systems[4], double-decker metal complexes[5] and molecular turnstiles[6]. An important design feature of unidirectionally rotating systems, which might find application in nanotechnological machinery, is the presence of an asymmetry in the molecular system. In an approach towards a chemically driven molecular motor, Kelly *et al.* demonstrated a unidirectional 120° rotation for a helical chiral molecule[7]. Recently, Leigh *et al.* developed a catenane system in which, due to four distinct sites on one ring, a unidirectional stepwise rotation (translation along a circular trajectory) around the other ring can be induced[8].

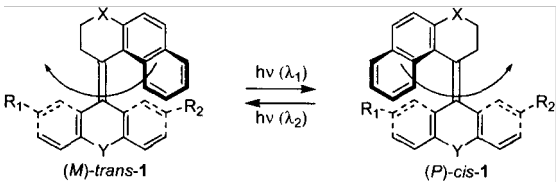

FIGURE 1. Unidirectional rotary motion in a chiroptical molecular switch **1**.

The first systems we designed that employed the controlled motion of a chiral molecule are molecular switches based on overcrowded alkenes[9]. These alkenes for steric reasons adopt a helical structure and the olefinic bond allows photochemical

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isomerization. For asymmetrically substituted compounds the state of the system, the (*cis* or *trans*) configuration and the helical (*M* or *P*) chirality, could be controlled by the wavelength of light employed (Figure 1). Selective chiroptical switching at the molecular level was demonstrated for a range of compounds, both in solution and in liquid crystal matrices. Next to the potential exploitation of these systems in optical data storage applications, it is demonstrated with these systems that controlled rotary motion around an olefinic bond, serving as an axis, is possible. Upon excitation, depending on the initial state of the system and the wavelength of the light employed, either a clockwise or a counterclockwise rotation of one half of the molecule relative to the other is induced. The step from partial to full repetitive unidirectional rotation (a prerequisite for the development of molecular motors) was realized by combining two photoisomerization steps with two irreversible thermal helix inversion steps.

LIGHT-DRIVEN UNIDIRECTIONAL ROTATION

First Light-Driven Molecular Motor

Biphenanthrylidene **2** is an overcrowded alkene where the intrinsic helical chirality is combined with two stereocenters of (*R*)-configuration (Figure 2)[10]. The combination of two chiral entities gives rise to four distinct stereoisomers, differing in photochemical properties and thermal stability. In the stable (*cis* or *trans*) configuration, the molecule adopts a (*P*)-helix and the methyl-substituents are allowed to adopt the sterically less hindered axial orientation.

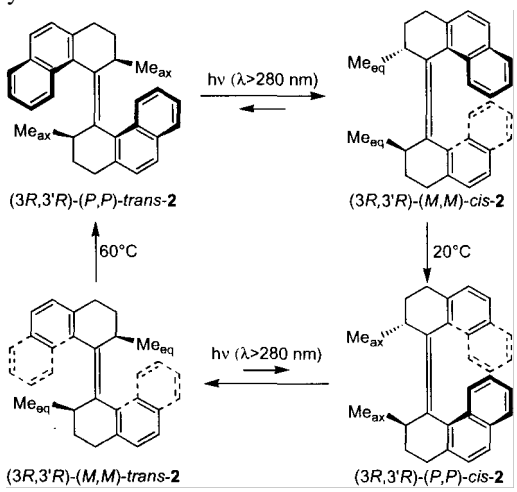

FIGURE 2. The first light-driven molecular motor **2**.

Irradiation of the molecules in their stable form results in an energetically uphill *cis-trans* isomerization, which reverts the helicity of the system and forces the methyl substituents into an unfavorable equatorial orientation. Upon heating, an irreversible energetically downhill helix inversion takes place, allowing the methyl groups to

adopt an axial orientation again. Combining the photochemical and thermal steps, by continuous irradiation at elevated temperature, a four step light-driven clockwise unidirectional rotation is induced of one half of the molecule relative to the other around a central axis. Although the irreversible helix inversion steps ensure unidirectional rotation, the photochemical *cis-trans* isomerizations are extremely selective. Already upon irradiation with polychromic light, high selectivities were found for both photoequilibria. Using monochromic light of different wavelengths, it was shown that the selectivity of the second photoequilibrium can fully be controlled and the system can function as a perfect chiroptical molecular switch[11].

A next step toward application of this molecular motor would be to perform actual work, using the unidirectional rotation to drive another process. For this purpose, the molecule was doped into a liquid crystalline matrix[12]. Here, the molecular chirality is amplified to macroscopic chirality that can visually be detected. Doping of an aligned liquid crystal film with pure (*P,P*)-*trans*-**2** resulted in a violet color, which upon irradiation gradually changed to red. This is the first demonstration of (albeit primitive) work performed by a molecular motor, where in this particular case molecular rotation drives a pitch elongation of the liquid crystalline host assembly.

Second-Generation Molecular Motor

The major drawback of the original system is the requirement of elevated temperatures to achieve continuous rotation. In order to tune the properties and lower the barriers for helix inversion (the rate determining step for unidirectional rotation), a second-generation motor was developed. The molecular skeleton combines one *rotor* half of the original motor with a *stator* half of the molecular switches (**3**, Figure 3).

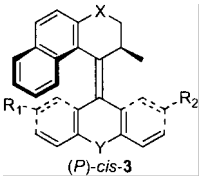

FIGURE 3. The second-generation light-driven molecular motor **3**.

The prototype second-generation motor (X,Y=S; R_1=OMe; R_2=H) was shown to function in essentially the same way as the original system, combining two energetically uphill photoisomerization steps with two thermal helix inversion steps to allow, in a four step process, unidirectional rotation of the rotor part of the molecule with respect to the stator part[13]. The key feature here is that the unidirectional rotation is fully controlled by a single stereogenic center. The design should allow lowering of the energy barrier for the thermal steps by decreasing the steric hindrance for helix inversion. This can be achieved by changing the bridging atoms (X,Y) whereas the spectral properties can be tuned by changing the substitution pattern, mainly in the lower half of the molecule (*e.g.* R_1,R_2). Furthermore, the distinct upper and lower half might allow anchoring of the sterically overcrowded alkene to surfaces, an important step toward future application.

It was demonstrated for a large range of molecules that indeed tuning of the thermal barriers and as a consequence the speed of rotation is possible[14]. Whereas the original second-generation motor had a half-life for helix inversion of 215 h at room temperature, for the fastest analogue (X=CH_2; Y=O; R_1,R_2=H) this value is only 40 min. The introduction of donor and acceptor substituents in the lower half (R_1=NMe_2; R_2=NO_2) resulted in a bathochromic shift of the absorption bands, allowing unidirectional rotation driven by visible light[15]. These examples demonstrate the versatility of the design and current efforts towards more elaborate systems focus on geared molecular motor systems and mounting these molecular motors onto surfaces.

Exploring the Boundaries

Although the fastest second-generation motor readily functions at room temperature, half-lives are still too long for any practical application, for which Brownian motions have to be overcome. In our pursuit for faster motors we explored the boundaries of our motor design in three ways. First, the methyl substituent adjacent to the central olefinic bond, which causes steric hindrance in the helix inversion steps to some extent, was shifted one position away from the axis (**4**, Figure 4)[16]. In this homologous overcrowded system, the thermal helix inversion steps were proven to be reversible due to a decreased energy difference between stable and unstable isomers. The rotary motion is no longer unidirectional under the conditions employed, although there still is a preferred direction of rotation. Remarkably, the barrier for thermal helix inversion was slightly increased. Rather than speeding up the motor system, the rotary motion was slowed down.

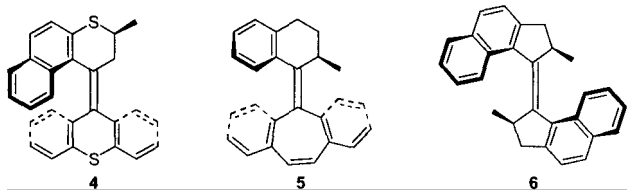

FIGURE 4. Exploring the boundaries of a molecular motor design.

In a second attempt to lower the barriers for thermal helix inversion, the upper half of the molecule was changed from a dihydrophenanthrene to a dihydronaphthalene unit (**5**, Figure 4)[17]. Although this system functions as a unidirectional motor, also here, the barrier for thermal helix inversion was increased with respect to the second-generation counterpart. Both examples show that the unidirectional rotary process relies on a delicate balance of ground state and excited state parameters. In a successful approach toward faster molecular motors, the initial design was reexamined. Although all parts of the molecular system add up to the steric hindrance in the thermal helix inversion steps, an important factor is the conformation of the two rings directly adjacent to the rotation axis. These six-membered rings impose substantial repulsion in the molecule. When the ring size is decreased, as is the case in five-membered rings, this repulsion should be lowered. A pertinent question is whether such a five-membered ring compound (**6**, Figure 4), where the difference

between axial and equatorial orientation of the methyl substituents are less pronounced, is still capable of performing a light-driven unidirectional rotation[18]. Analogous to the six-membered ring systems, this molecular motor performs a four-step light-driven unidirectional rotation with the distinct advantage that it occurs readily at room temperature. This last system offers tremendous possibilities for the design of faster systems but the key step to be taken in the research on molecular motors is the incorporation of this molecular component into more complex supramolecular systems and demonstrate the ability of the presented photoactive alkenes to perform useful work as part of nanomachines.

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