

Molecular motors under load: performing work with small-molecule machines

Biological molecular machines (BMMs) perform a variety of vital tasks in living organisms, such as driving the formation of energy carriers (ATP synthase), transporting cellular cargo (kinesin) or synthesizing proteins (ribosome). Taking BMMs as an example, a key challenge for artificial molecular machines (AMMs) is to perform work on a coupled system, *i.e.* converting the energy that is put into the system into other forms of energy, by avoiding heat dissipation as efficiently as possible.^[1]

Photochemical rotary motors are crucial components in AMMs, as they can be utilized as energy converters able to transduce light into continuous and unidirectional rotation. Nowadays, one of the key question is how to couple molecular motors to an external load, so that their directed motion can be harnessed to execute complex tasks. One possible way to achieve this target is by constraining their motion, *i.e.* applying a mechanical load, so that parts of the motor movement are converted into, e.g. coupled motion or chemical strain of a secondary molecular entity. In recent studies we show how strain affects the rotation of a molecular motor and that constrained motion can be used to shift a coupled chemical equilibrium energetically uphill.^[2,3] By linking the two contra rotating parts of a molecular motor with an alkyl tether and systematically increasing its size, we found that ring strain has a significant impact on the thermal and photochemical steps in a 360° rotational cycle. From these findings we could derive design principles that allowed us to engineer a nanoratchet which can drive the formation of an energetically disfavored species in a coupled imine equilibrium. By bridging two imine macrocycles with a molecular motor the machine forms crossings and consequently adopts several distinct wound states by either a thermal (temporary bond-dissociation) or photochemical (unidirectional rotation) pathway (Figure 1). While the former will relax the machine towards the global energetic minimum, the latter increases the number of crossings in the system above the equilibrium value.

We anticipate that our findings will serve as a blueprint and open up design space for the development of more complex AMMs that can, for instance, store light in form of chemical energy or perform sophisticated synthetic tasks on the molecular scale.

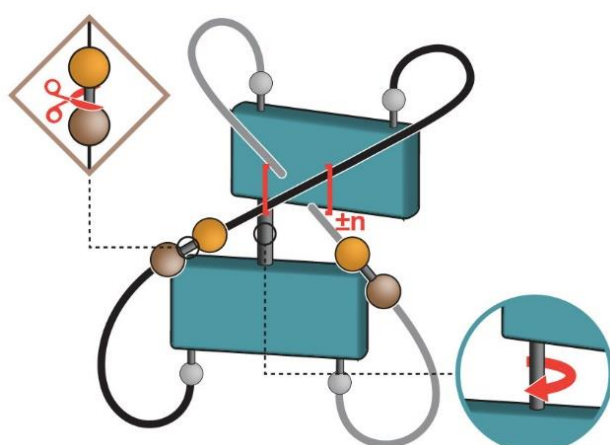


Figure 1: Schematic representation of a nanoratchet. Crossings can be induced by temporary bond cleavage (brown) or unidirectional rotation (blue).

[1] I. Aprahamian, *ACS Cent. Sci.* **2020**, *6*, 347–358.

[2] M. Kathan, S. Crespi, N. O. Thiel, et al., *Nat. Nanotechnol.* **2022**, *17*, 159–165.

[3] M. Kathan, S. Crespi, A. Troncossi, C. N. Stindt, R. Toyoda, B. L. Feringa, *Angew. Chem. Int. Ed.* **2022**, <https://doi.org/10.1002/ange.202205801> (accepted article).